Heyrovský-Ikovič-Nernst Lecture 2022
Přírodovědecká fakulta Univerzity Karlovy
Katedra analytické chemie
6.12.2022

ulm university universität ulm

Unraveling interfacial processes by scanning (electrochemical) probe microscopy

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uni-ulm.de/iabc
IABC

Facts about Ulm (University)

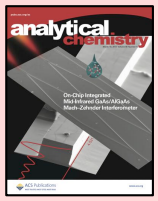
>10,200 students +++ (T.H.E.) globally among the best 10% of universities (2022)

- Natural Sciences
- Mathematics & Economics
- Engineering, Computer Science and Psychology
- Medicine

Overview IABC

Spectroscopy

- Thin-film waveguides
- Hollow waveguides
- Integrated photonics
- IR-lab-on-chip
- AFS, AAS, TXRF, ICP-OES

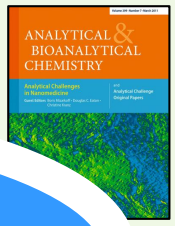


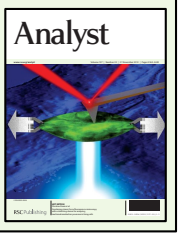
COMBINING TECHNIQUES

- AFM
- AFM/FM
- SECM/FM
- AFM-SECM
- AFM-IR-ATR
- AFM-EC-IR-ATR

Electrochemistry

- SECM
- Electrochemical sensors
- Spectroelectrochemistry
- Boron-doped diamond

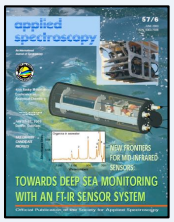


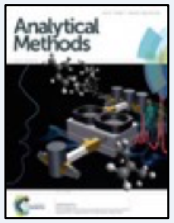


Insitute of Analytical and Bioanalytical Chemistry

ANALYZERS

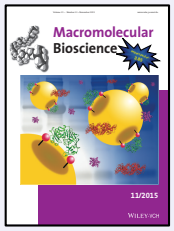
- Mycotoxin analyzer
- Dissolved CO_2/CH_4
- Breath analyzer
- Deep sea spectrometers

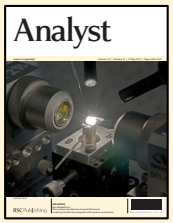


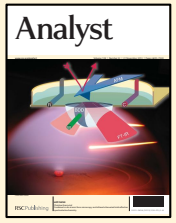


MATERIALS

- Biomimetic recognition
- Molecular imprints
- Nanoparticles & nanostars
- SPE & enrichment







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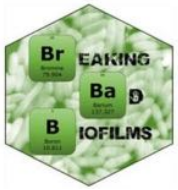
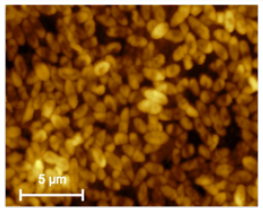
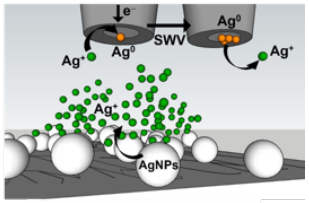
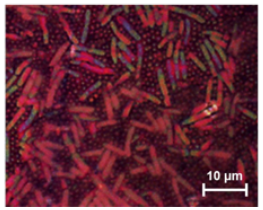
Current projects

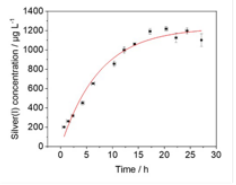
Break Biofilms







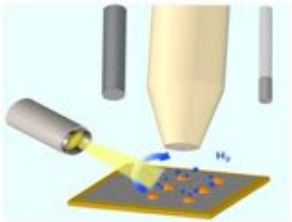


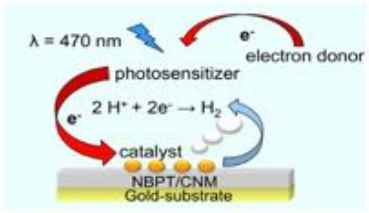


CataLight

SFB/Transregio

DFG Deutsche Forschungsgemeinschaft



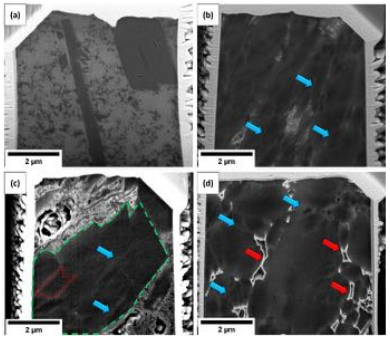


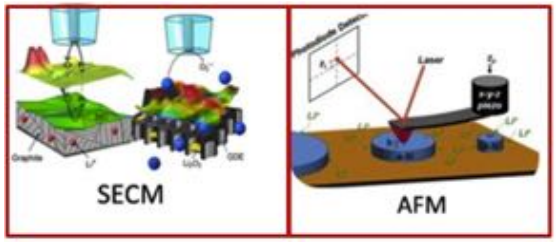
POLiS Post Lithium Storage Cluster of Excellence

DFG Deutsche Forschungsgemeinschaft

Degradation studies of polymeric electrode materials

FIB/SEM tomography

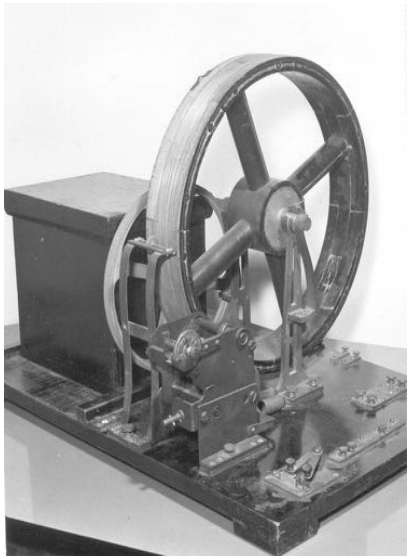




Solid/electrolyte interphase (SEI) formation

Electronanalytical Chemistry: Before and Today

Electroanalytical techniques always played and play a significant role in Analytical Chemistry



1959: Nobel Prize in Chemistry was awarded to J. Heyrovsky for "*his discovery and development of the polarographic methods of analysis*" .

Hervosky published his first results in the journal Chemické Listy (Heyrovský, J. *Chem. Listy* 16, 256, **1922**)

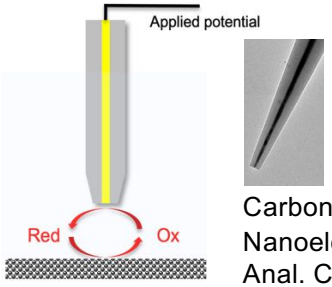
high selectivity

high sensitivity

spatial resolution

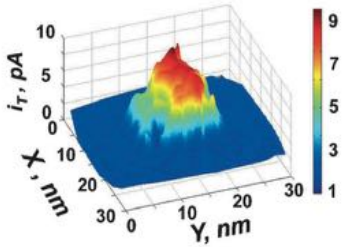
temporal resolution

Scanning electrochemical Microscopy, SECM



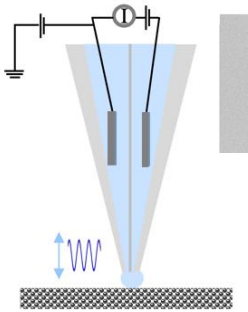
Carbon-Nanoelectrode Anal. Chem **2019**

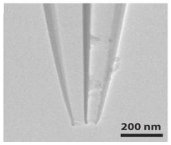
A.J. Bard et al., Science **1991**

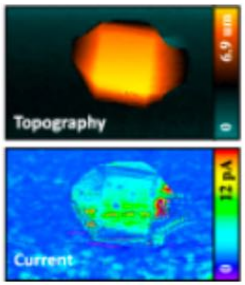


T. Sun et al., Angew. Chem. Int. Ed. **2014**

Scanning electrochemical cell microscopy, SECCM

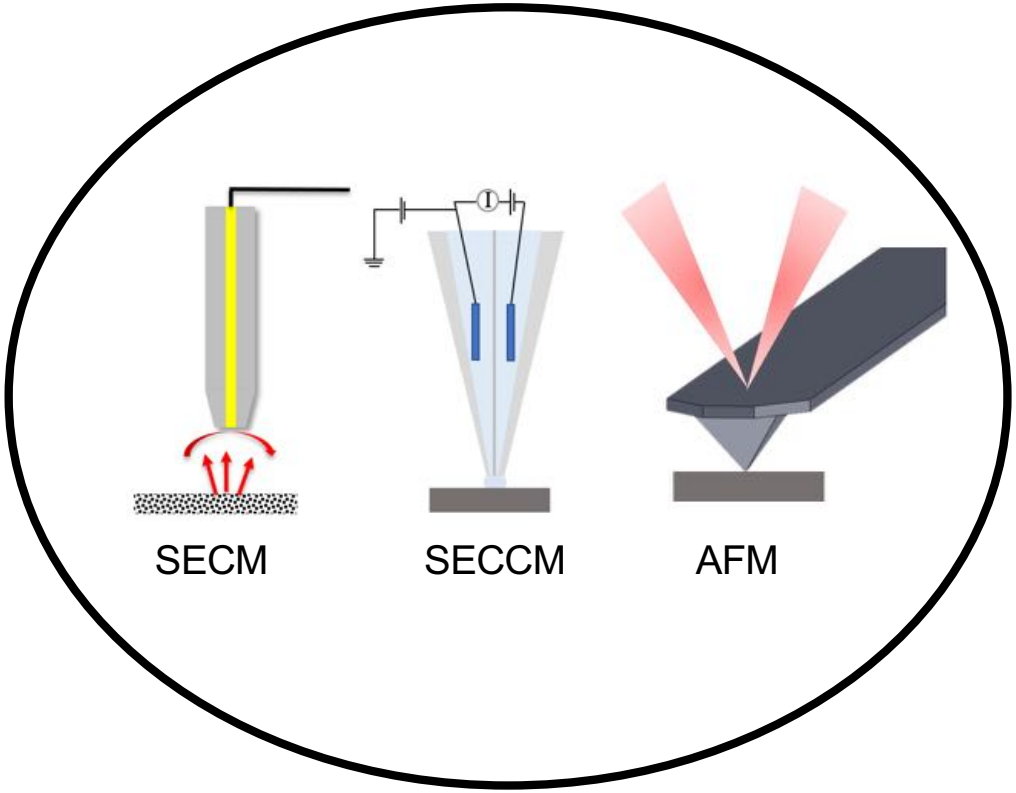






Single-Crystal Boron-Doped Diamond Particle

T. Ando et al., Anal. Chem **2021**



Miniaturized electrodes

- Enhanced mass transfer
- Reduced ohmic (IR)-drop and reduced capacitive current
- Spatially resolved detection of electroactive molecules
- Measurements in small volumes

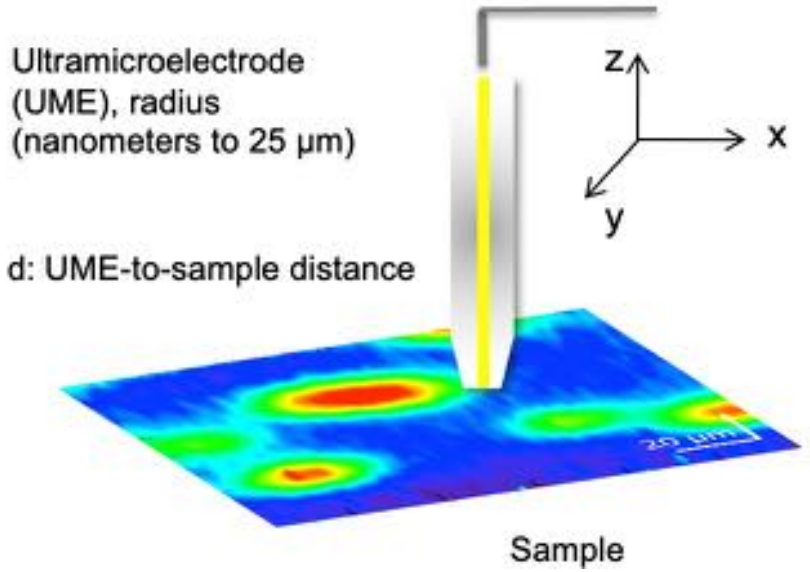
Bard, *Anal. Chem.* **1962**
Wightman, *Anal. Chem.* **1980**
Bond et al., *J. Electroanal. Chem*. **1984**
Amatore, Fosset, *Anal. Chem.* **1996**

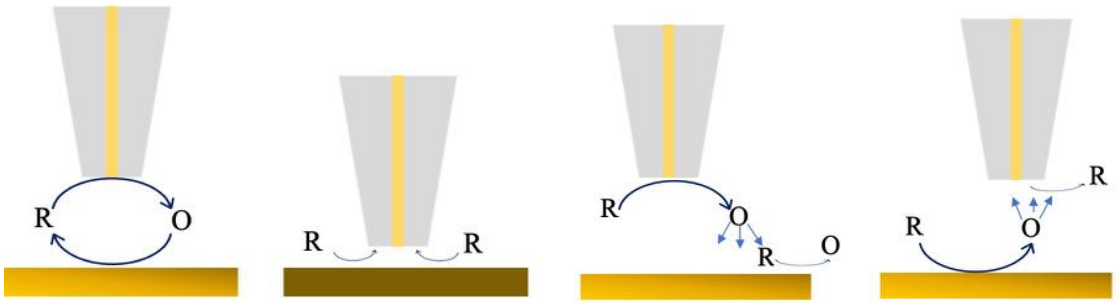
Microelectrodes for measuring local oxygen tension in animal tissue

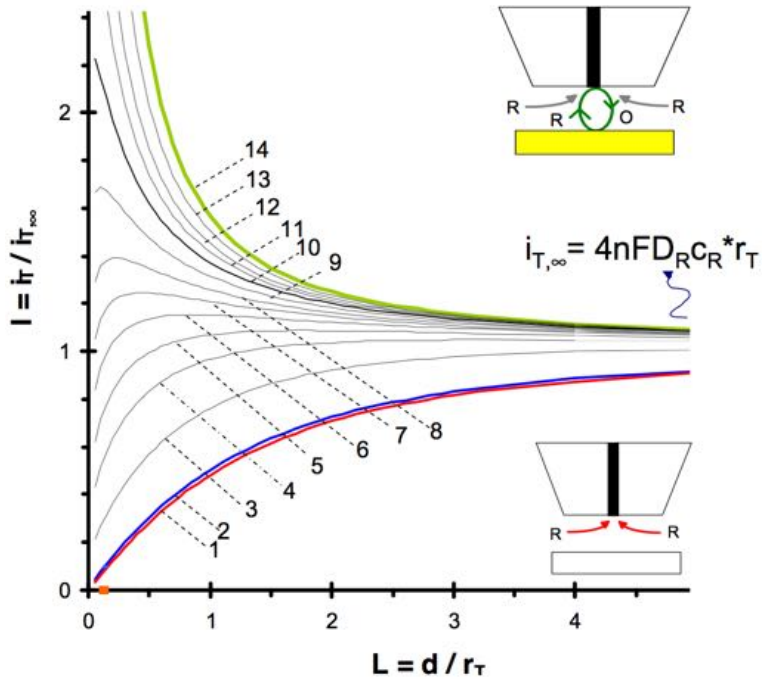
Davies et al., Rev. Sci. Instrum., **1942**

Scanning electrochemical microscopy, SECM

Feedback Mode **Generation/Collection Mode**



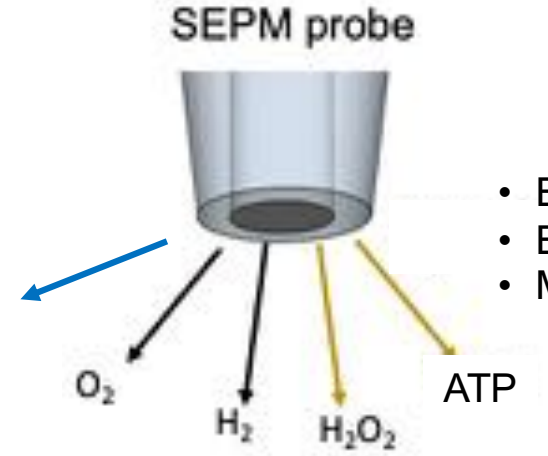




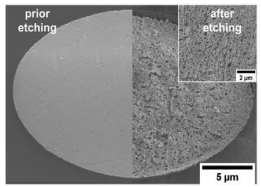
- Voltammetry
- Potentiometry
- Surface modification
- Screening experiments

Curves for different κ values: (1): hindered diffusion; (2): Cornut fit; (3): 0.1; (4): 0.2……(13): 10; (14): diff. controlled positive feedback (G. Wittstock Summer School on SECM (EPFL 2011).

Microelectrodes

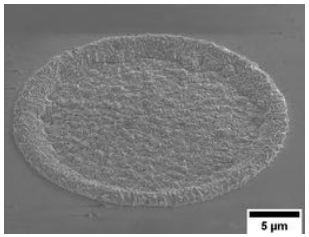


- Enzyme layer
- Electrocatalytic layer
- Mercury thin film

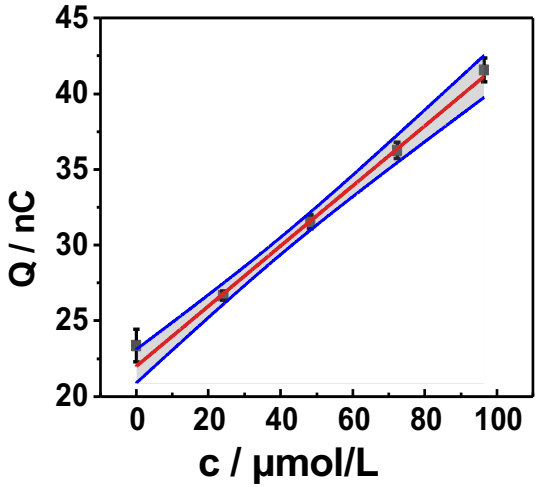


Deposition of Pd-film

from K_2PdCl_4 solution



Calibration curve for H_2

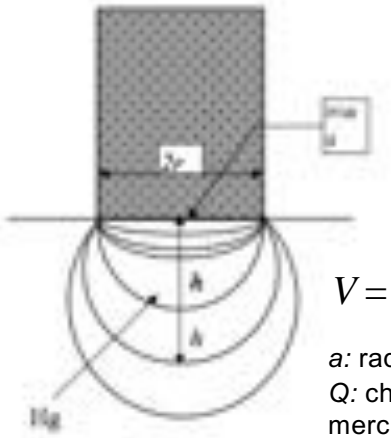


J. Kund et al., ChemElectroChem, **2022**

- Antimicrobial coatings: silver(i) ion release
- Photocatalysis: *in situ* measurements of water splitting (H_2; O_2)
- *In situ* measurements of signaling molecules (cell measurements)
- Read out for gel electrophoresis

Mercury thin film electrodes

Potentiostatic deposition at -0.1 V vs. SCE from 0.01M $Hg_2(NO_3)_2$ solution (pH 1).



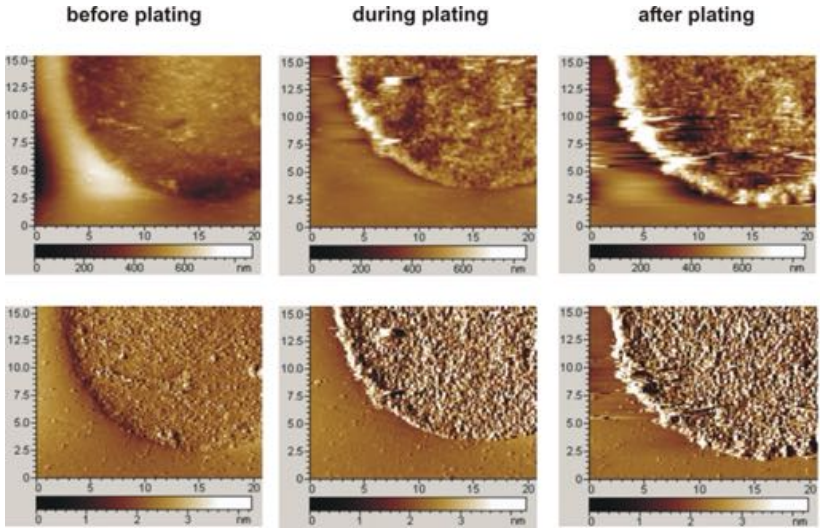
$$V = QM/F\rho_0 = \pi h(3a^2 + h^2)/6$$

a: radius of UME, *h:* height of the Hg deposit, *Q:* charge, *M* and ρ: atomic mass and density of mercury ; F: Faraday constant

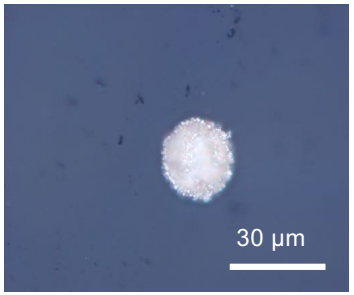
- Large cathodic potential window
- Stripping voltammetry for sensitive metal ion detection
- SECM probe for imaging metal dissolution

P. J. Brendel, Luther, G. W., III. *Environ. Sci. Technol.* **1995**
S. Daniele et al., *Electroanalysis* **2003**
I. Ciani et al., *Electrochem. Commun*. **2003**
M.A. Apuche-Avilis et al., *Anal. Chem.* **2008**
J. Mauzeroll et al., *Anal. Chem.* **2003**

In situ AFM imaging

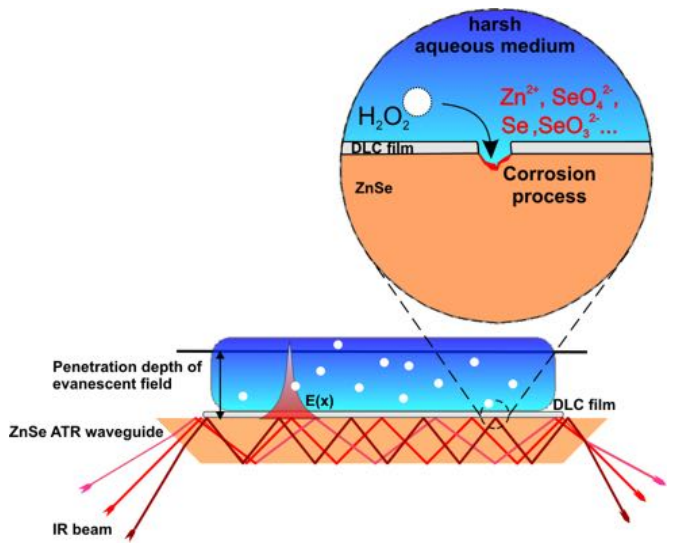


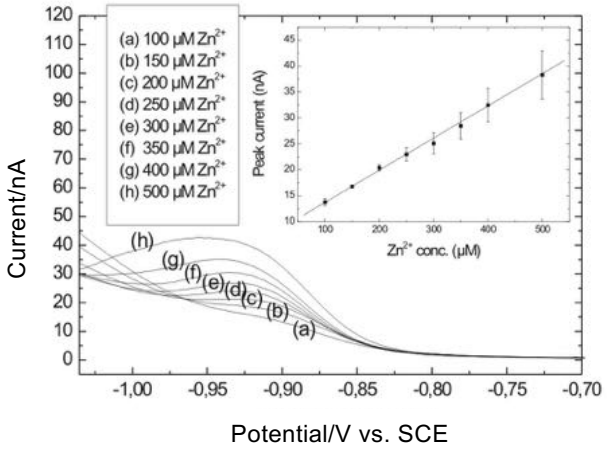
Optical image



Mapping ZnSe MIR waveguide corrosion

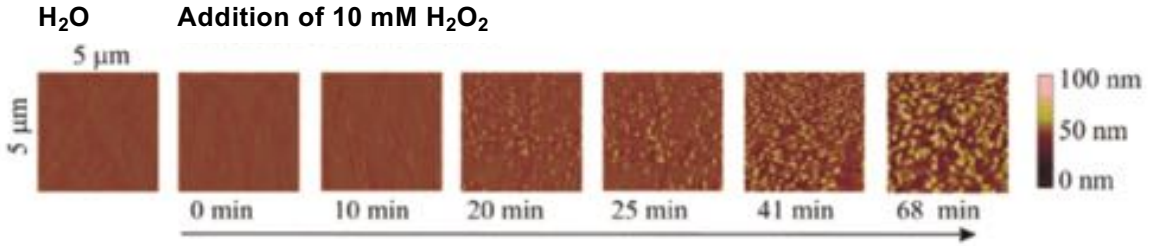
DLC films as corrosion protection for MIR



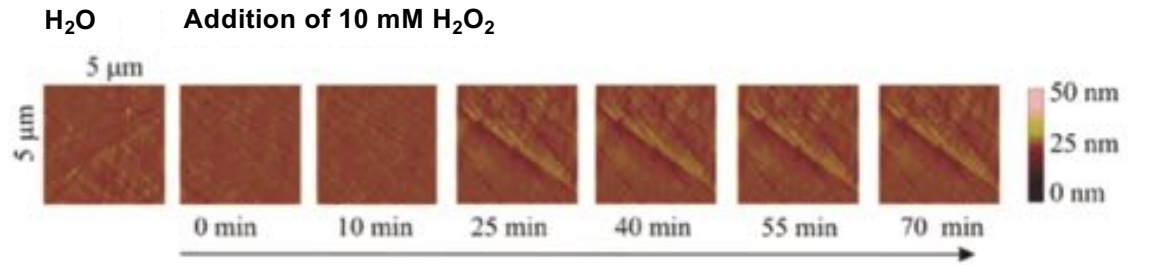


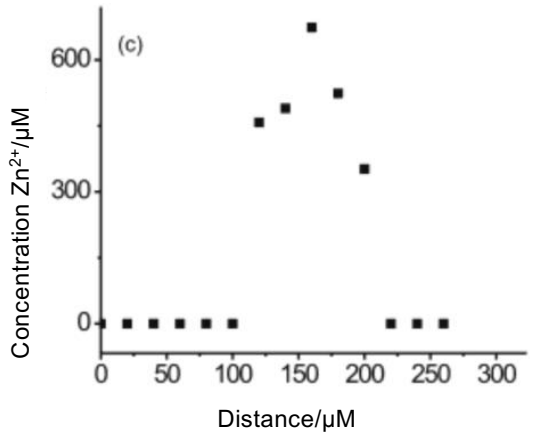
SWV (-1.6 V to -0.2 V; scan rate: 5 mV/s; frequency: 40 Hz; amplitude 25 mV) in acetate buffered solution (pH =3); calibration graph (error bars reflect 3 repetitive measurements)

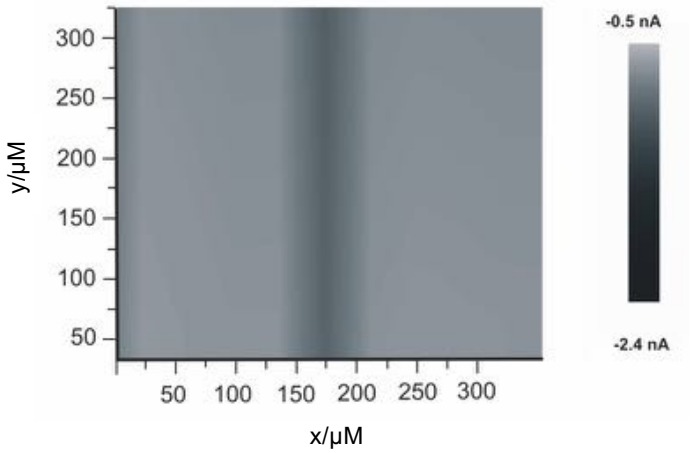
Bare ZnSe crystal



DLC-coated ZnSe crystal







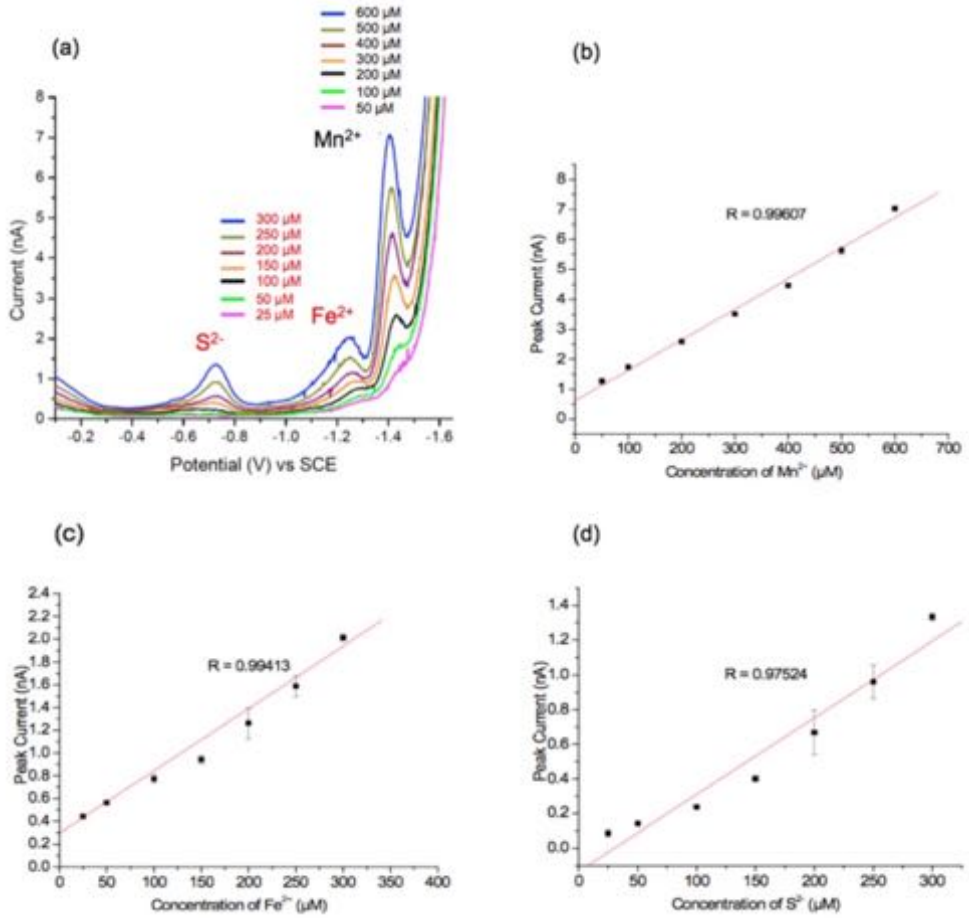
M. Janotta et al, *Langmuir 20*, 6834, **2004**

SECM as readout for gel electrophoresis

Microbial metal respiration

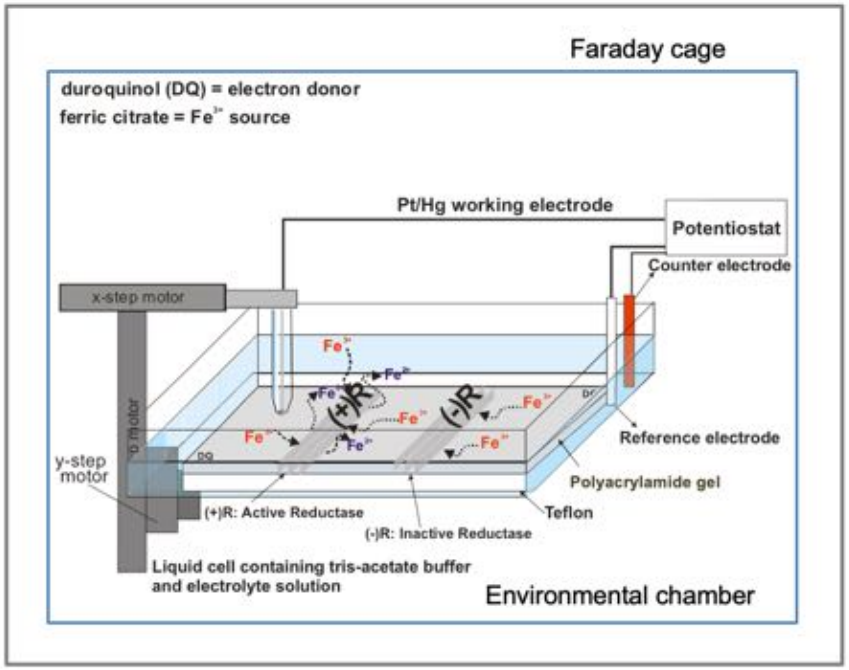
Anaerobic bacteria: Shewanella *oneidensis*
Fe(III) and Mn(IV)–reducing proteins isolated from the outer membrane

Square-wave anodic stripping voltammetry (SWASV)



SWV in degassed tris-acetate buffer (pH 7.5) (n = 3, error bars at lower concentrations are smaller than the symbol size.

Set-up

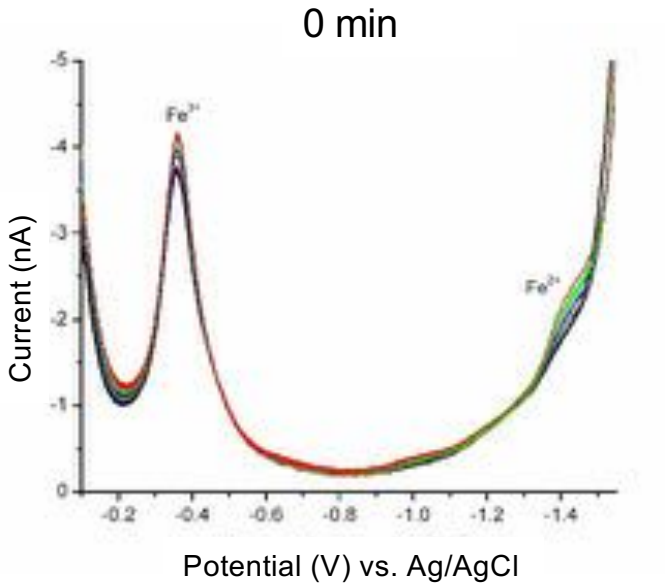


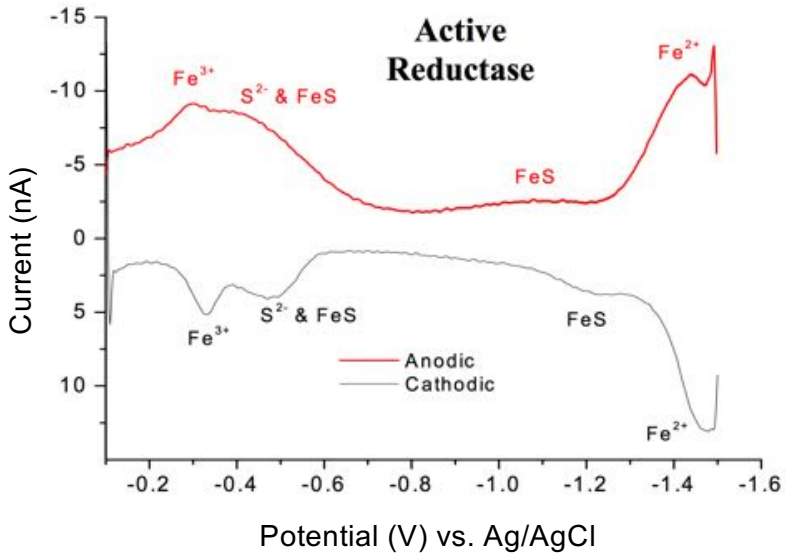
- No staining required

D. Rudolph et al, *Electroanalysis 28*, 2459, **2016**

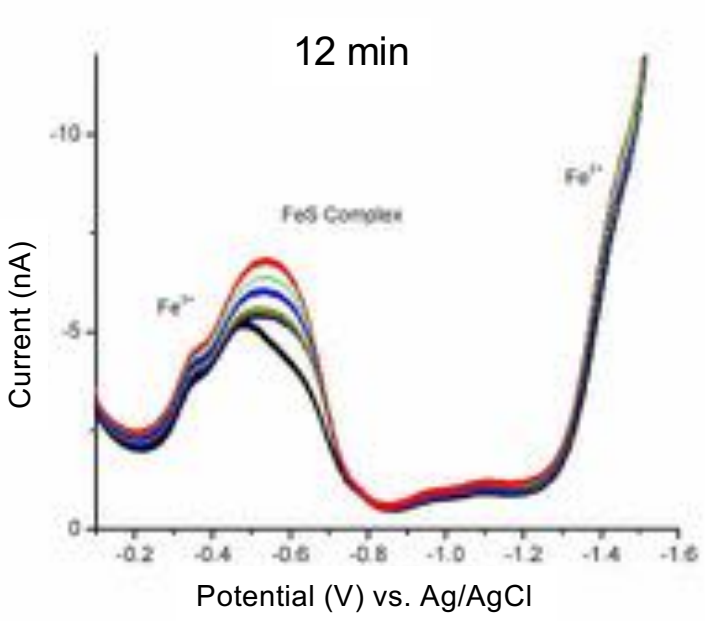
SECM as readout for gel electrophoresis

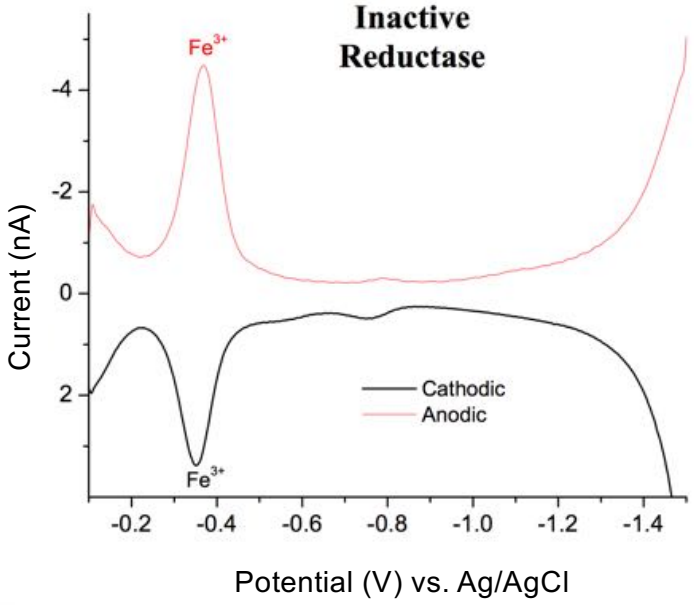
Activity of the protein complex is directly reflected in a decrease of Fe(III) and an increase in Fe(II)





Lower levels of Fe^{2+} and sulfur were determined above zones containing **inactive** proteins.





D. Rudolph et al, *Electroanalysis 28*, 2459, **2016**

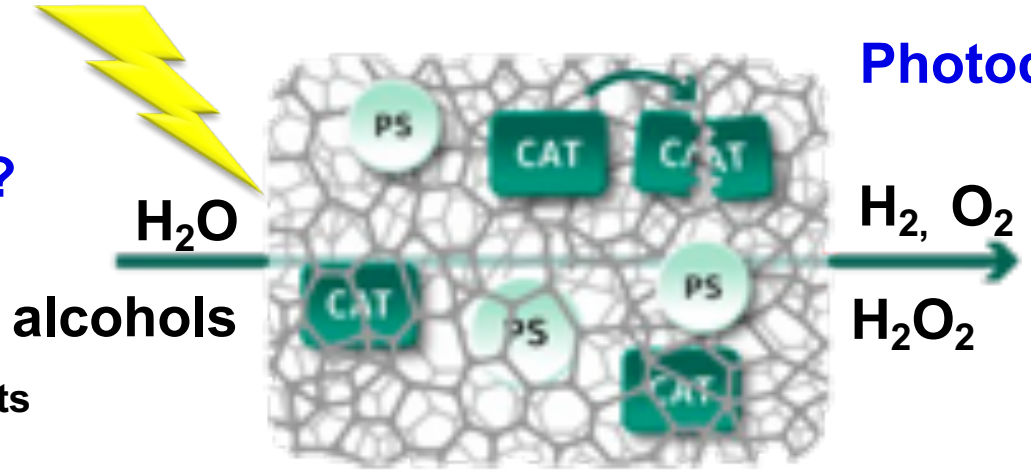
Light-driven catalysis in hierarchically structured materials

Integration of molecular components into soft matter materials for light-driven catalysis

- water oxidation catalysts
- **catalysts for hydrogen evolution reaction**

Heterogeneity?

Photocatalytic activity?



Degradation?

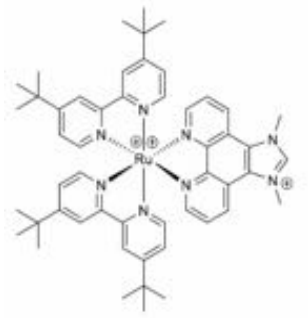
Water oxidation catalysts

polyoxometalates

$[Co_4(H_2O)_2(PW_9O_{34})_2]_{10-}$

Photosensitizer

$[Ru(tbbpy)_2(mmip)]Cl_3$



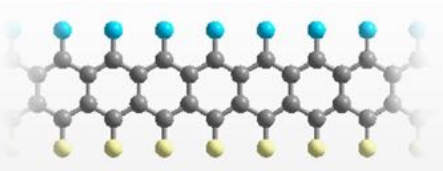
(tbbpy= 4,4'-di-*tert*-butyl-2,2'-bipyridine; mmip = 1,3-dimethyl-1*H*-imidazol[4,5*f*][1,10]phenanthrolinium

Membranes

Hydrogen evolution catalysts

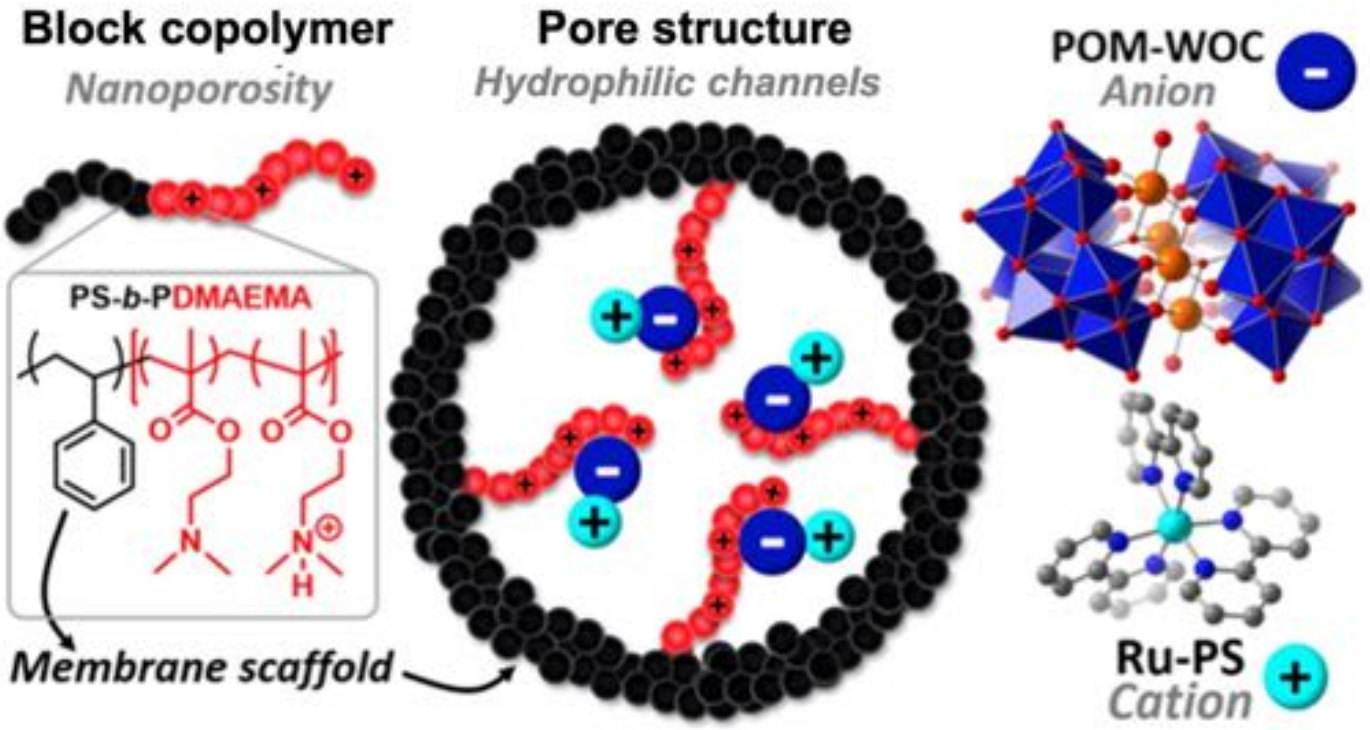
double and single complex cobaloxime salts

Nanoporous block copolymers



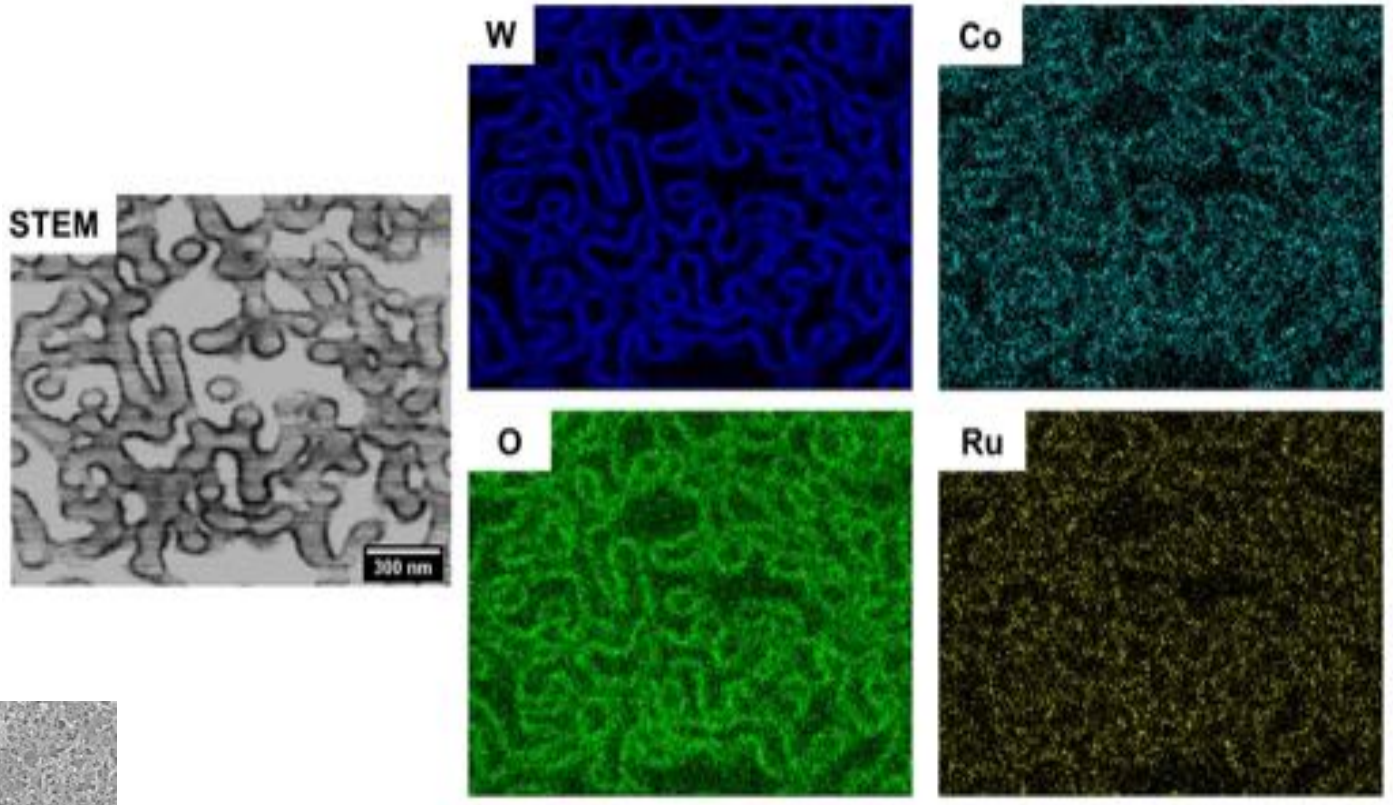
Carbon nanomembrane (CNM)

- Nanoporous block copolymer (PS_{304}-*b*-$PDMAEMA_{71}$)
- Electrostatic immobilization with WOC ($[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$) and PS ($[Ru(bpy)_3]^{2+}$)

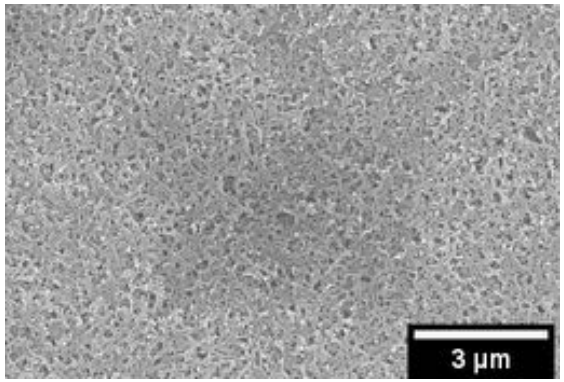


J. Kund et al., *ChemRxiv* **2021**

STEM/EDX mapping of the elemental distribution

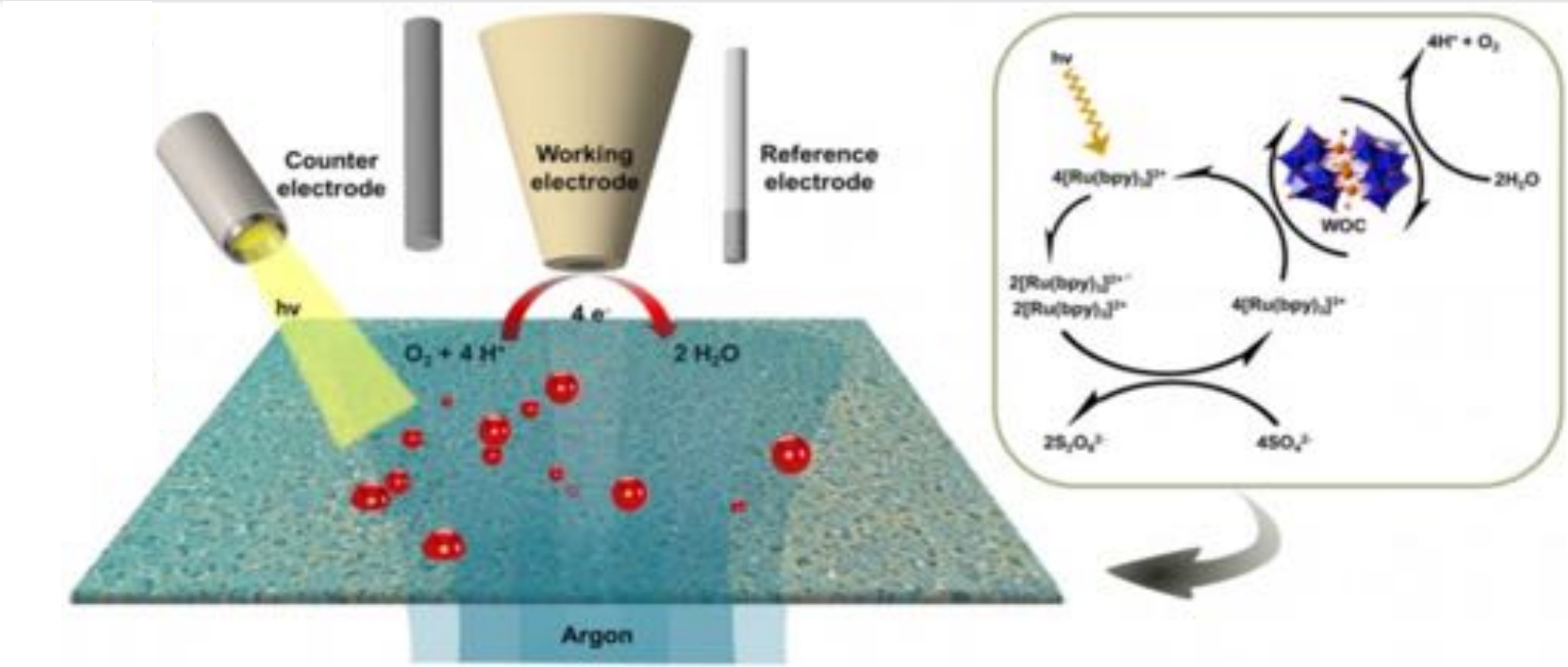


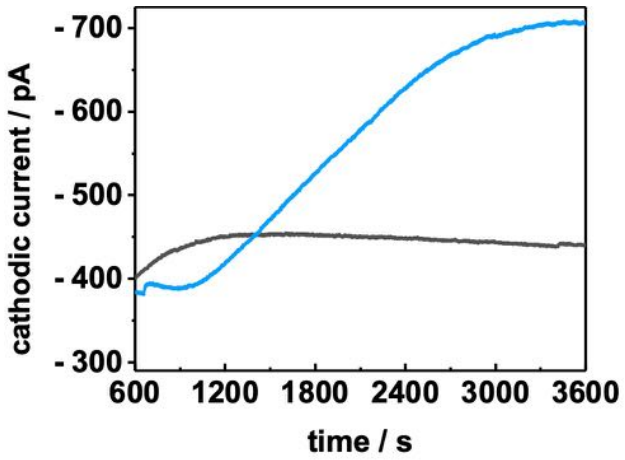
STEM/EDX mapping of the elemental distribution of tungsten (W), cobalt (Co), oxygen (O), and ruthenium (Ru).



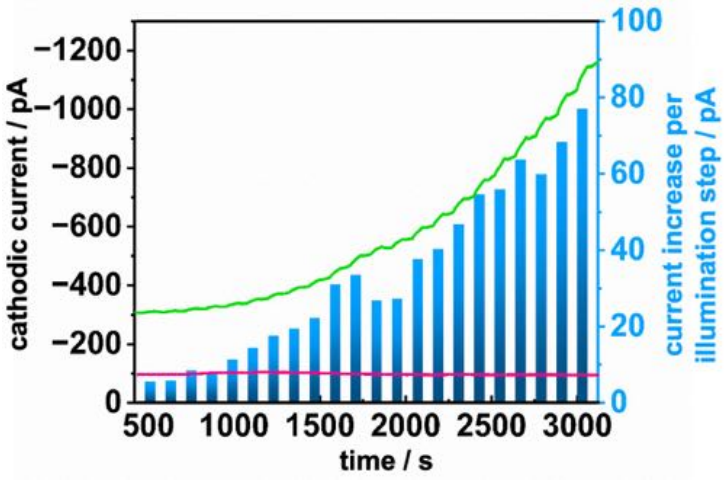
SEM image

In situ O_2 measurements



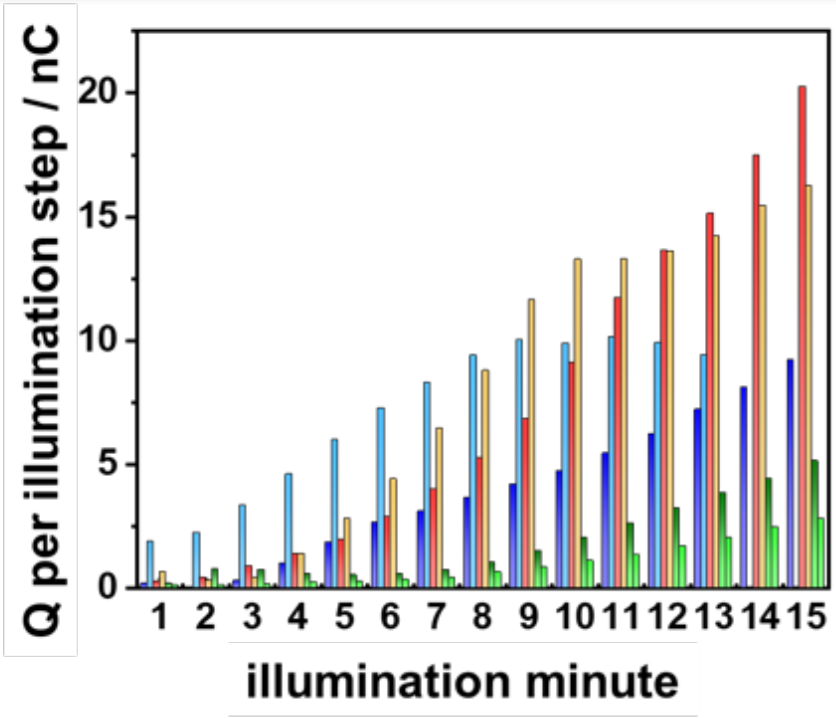


Current response during a) continuously illumination (blue, illumination was started after 660 s) and under dark conditions (grey)

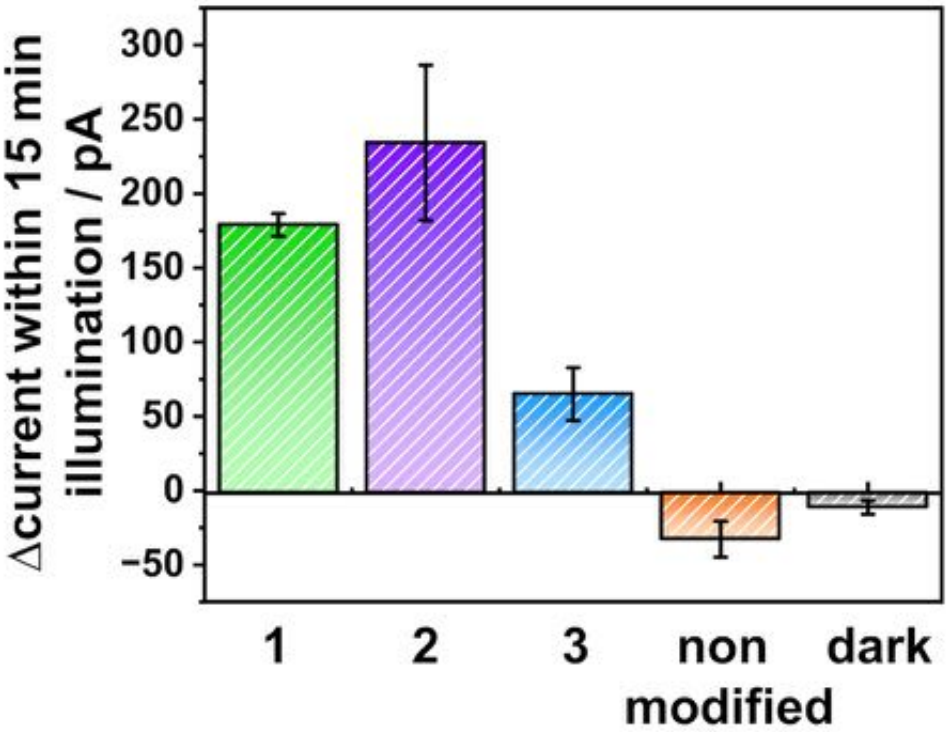


Current response during illumination (pink, illumination was started after 500 s) and under dark conditions (orange)

In situ O_2 measurements



6 individual WOCbranes from two immobilization batches



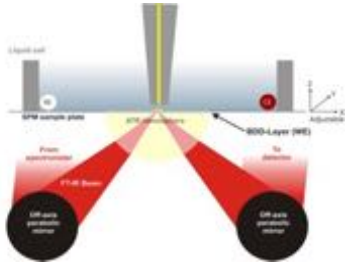
non-mod. membrane (n = 4), WOCbranes batch 1 (green, n =2); batch 2 (purple, n = 4)

J. Kund et al., *ChemRxiv* **2021**

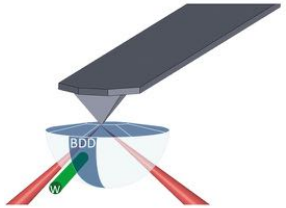
Hybrid scanning probe microscopy methods

- **Coupling spectroscopy with AFM or SECM**

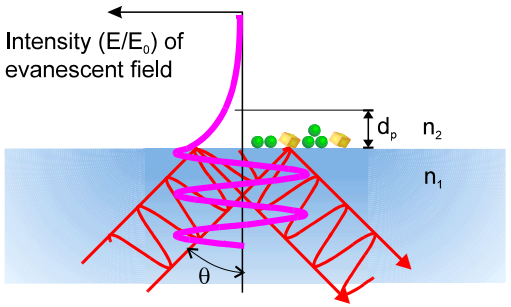
  - mid-IR



L. Wang et al., *Anal. Chem*. **2008**



D. Neubauer et al. *Analyst* **2013**

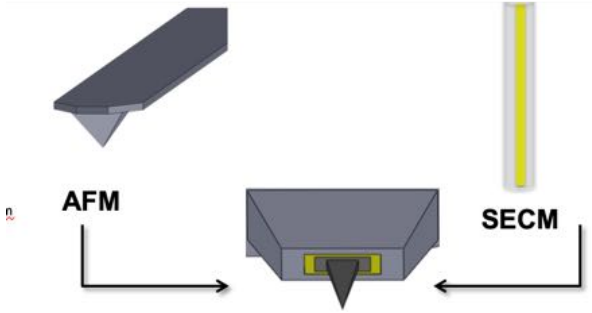


$$d_p = \frac{\lambda}{2\pi\sqrt{n_1^2 \sin^2\theta - n_2^2}}$$

ATR crystals

ZnSe
ZnS
Ge
Diamond
Boron-doped diamond

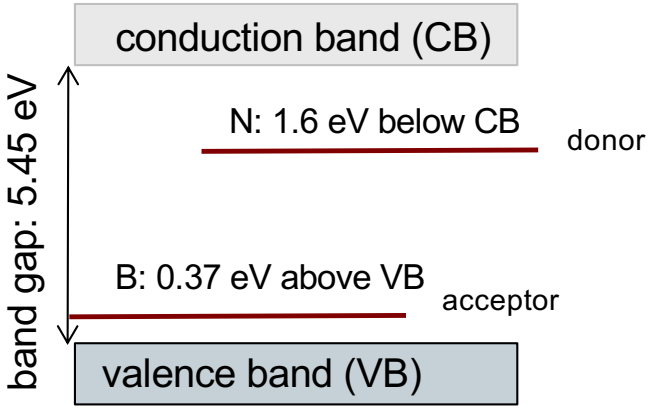
- **AFM-SECM**



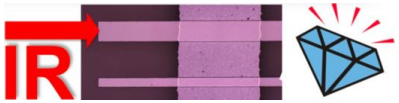
Boron-doped diamond (BDD)

Characteristics

- Large potential window
- **Wide spectroscopic window** (near UV 0.25 – far IR 100 µm)
- Less electrode fouling
- Enhanced chemical and mechanical stability
- Reduced background currents

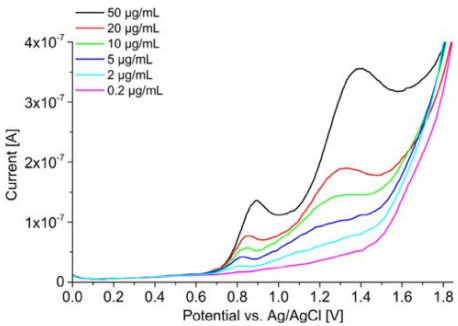


Thin-film diamond IR-ATR waveguides



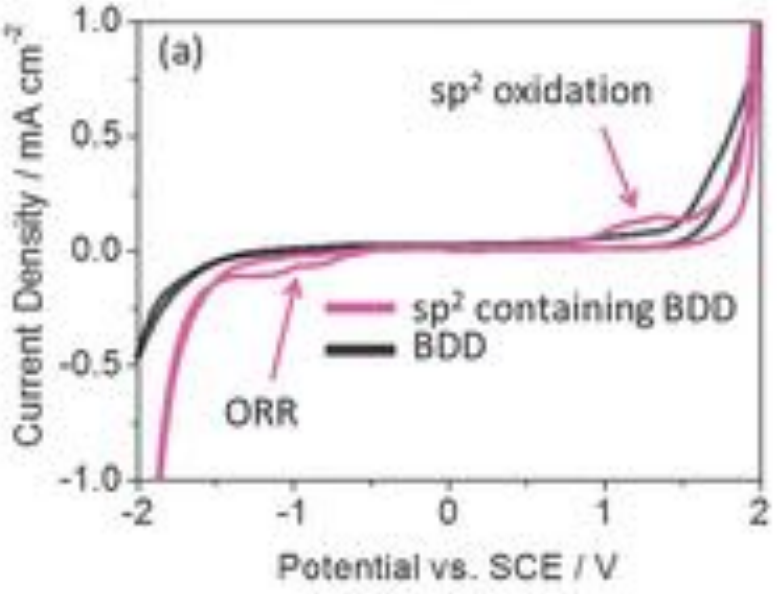
Wang et al., *Anal. Chem.* **2014**
Haas et al., *ACS Omega* **2018**
Haas et al., *Analyst* **2018**
Teuber et al., *under revision*, **2022**

Reduced electrode fouling



Detection of gentamicin sulfate at BDD electrodes

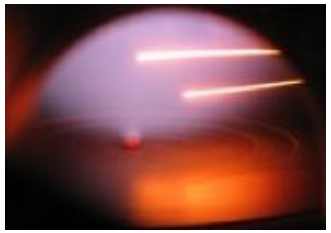
Abt et al., *Electroanalysis* **2016**



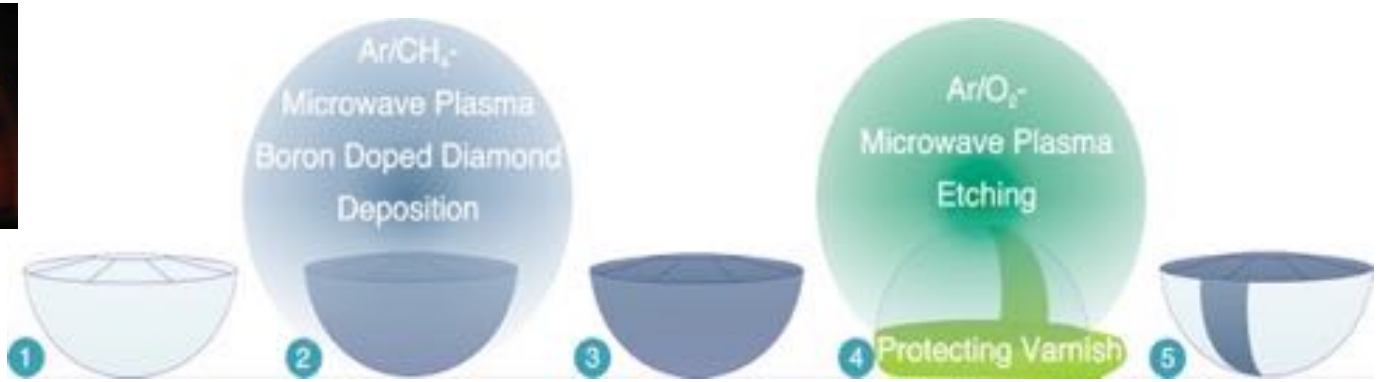
J. V. MacPherson Phys. Chem. Chem. Phys. **2015**

BDD-coated single bounce diamond ATR-crystal

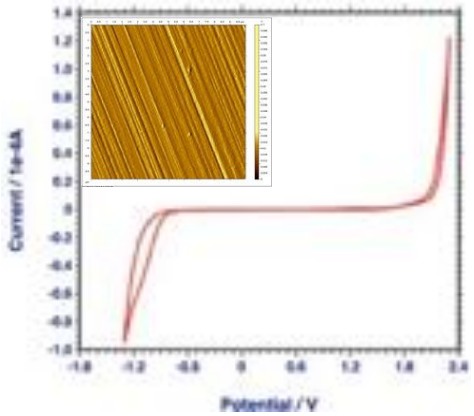
BDD coating and plasma etching



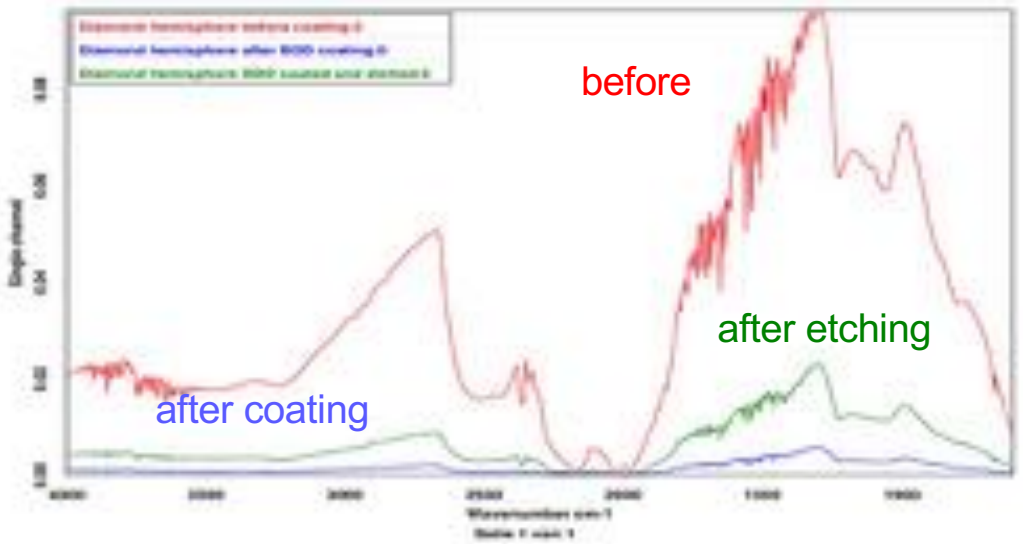
~100 nm BDD
B/N ~5*10^{20} cm^{-3}

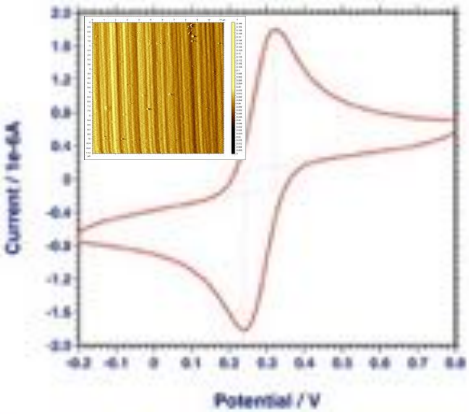


Single beam spectrum



Potential window





Electrochemical behavior
in ferrocyanide solution

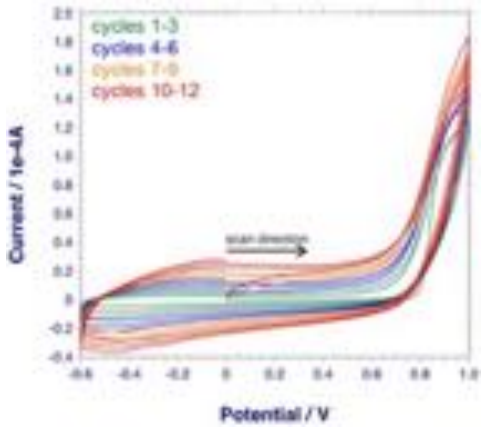
Homoepiaxial growth of BDD (BDD matches exactly the diamond lattice)

D. Neubauer et al., *Analyst* 138, 6746, **2013**

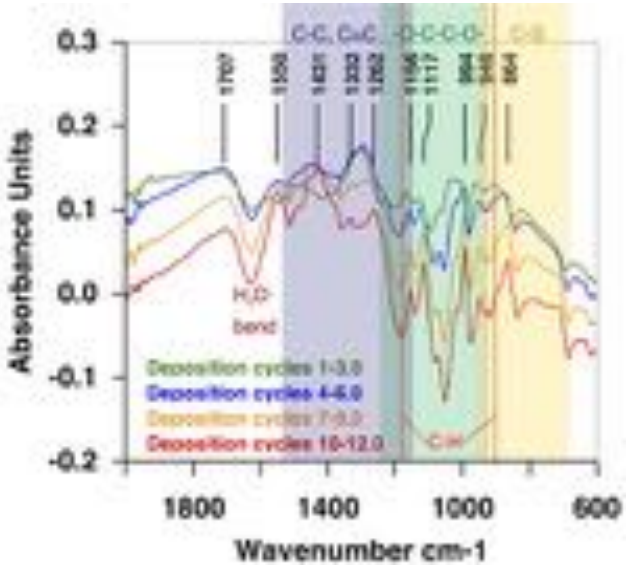
Combined AFM-EC-IR-ATR

Electropolymerization of 3,4-ethylenedioxythiophene

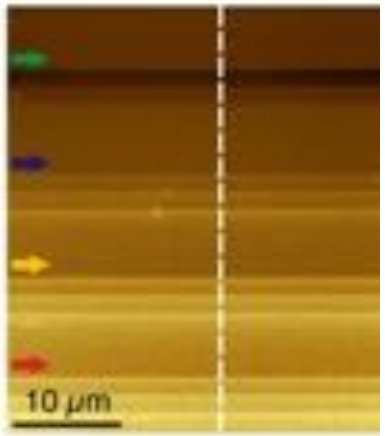
EC: PEDOT formation

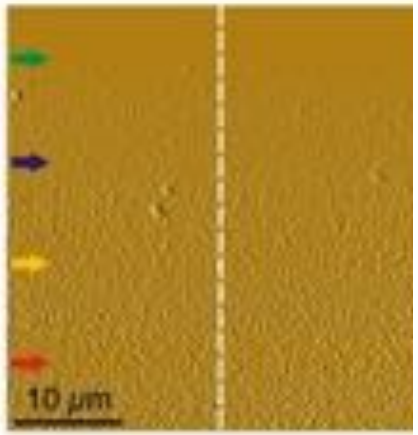


IR: molecular information



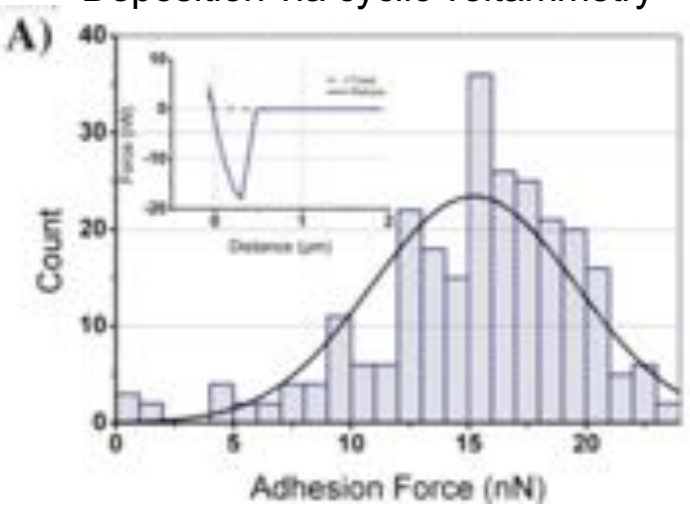
AFM: change in morpholgy



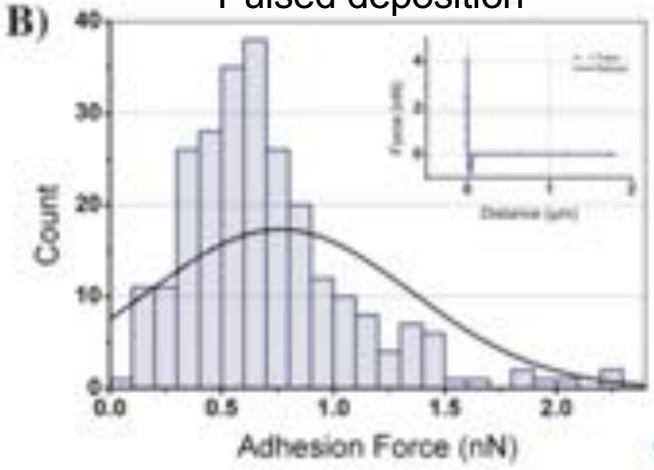


Force spectroscopy

Deposition via cyclic voltammetry



Pulsed deposition



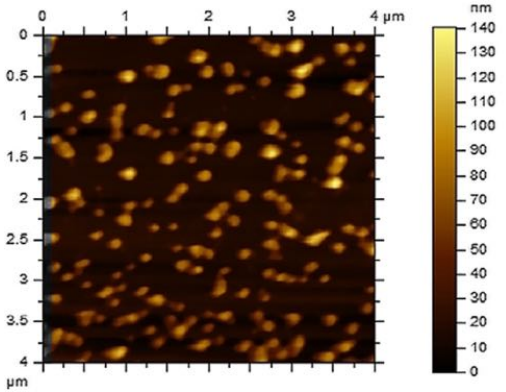
Adhesion force of 16x16 measured force curves (N = 256) Insets show representative force curves

D. Neubauer et al., *Analyst* 138, 6746, **2013**

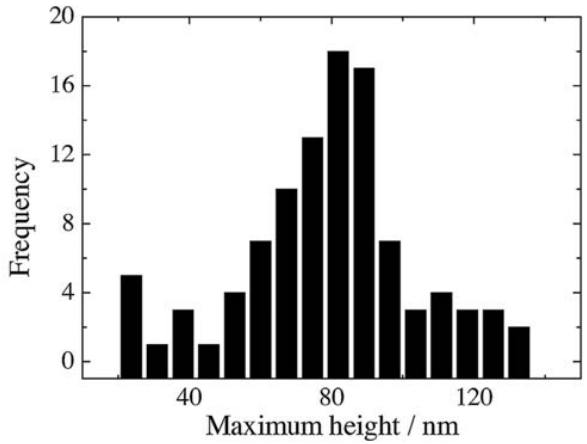
Surface enhanced IR absorption (SEIRA)

Electrochemically induced modification of BDD with AuNPs

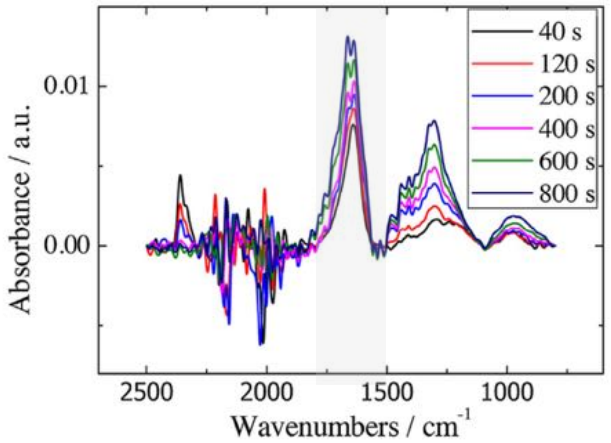
- IR absorption of adsorbed analytes is known to be **enhanced** by the presence of **AuNPs**



AFM image



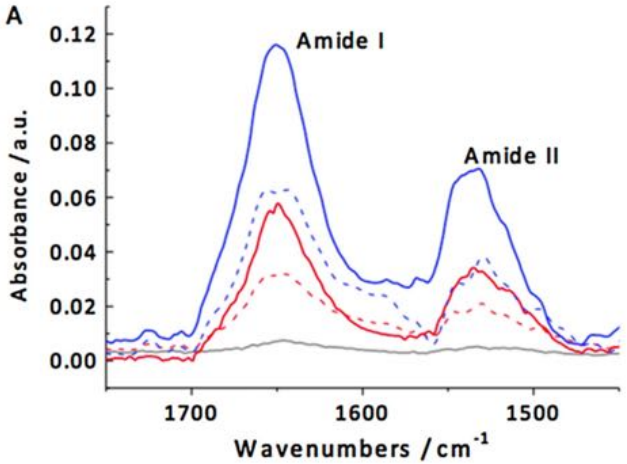
Size distribution of AuNPs

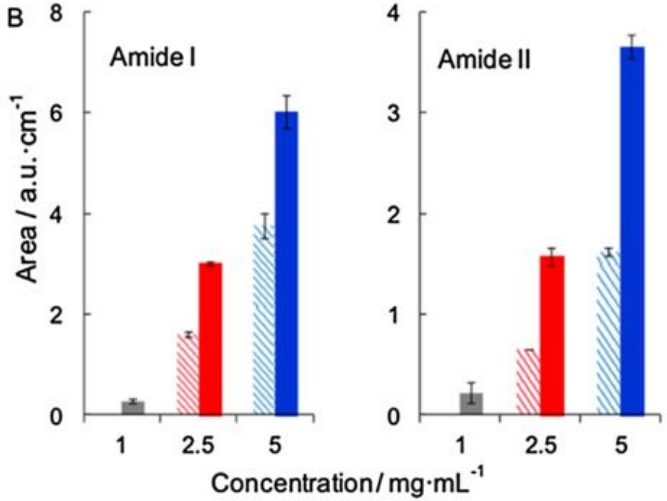


Background subtracted IR-ATR spectra recorded during the synthesis of AuNPs; 1640 cm^{-1} water bending

J. Izquierdo et al., Physica Status Solidi A 213, 2056, **2016**

Spectroelectrochemical investigation of **globular and fibril BSA films**



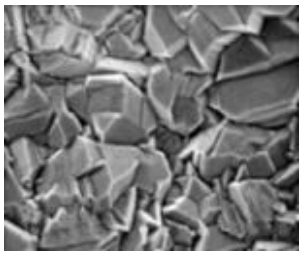


IR absorption signals and (B) average integral values (N=4),corresponding to the amide I and II bands films formed from1.0 (grey),2.5 (red) and 5.0 (blue) mg mL1 BSA solution. Dashed lines in (A) and dashed filling in (B): the non-modified BDD crystal, solid lines in (A) and solid filling in (B): BDD/APTES/AuNPs surface.

A. Lopez-Lorente et al., *Vib. Spectrosc*. 91, 147, **2017**

Diamonds are a ~~girl~~'s best friend …

(spectro)electrochemist's



http://www.clipartbest.com/clipart-di87M48ie

analytical chemistry

Article

pubs.acs.org/ac

Diamonds Are a Spectroscopist's Best Friend: Thin-Film Diamond Mid-Infrared Waveguides for Advanced Chemical Sensors/Biosensors

Xiaofeng Wang,[†] Mikael Karlsson,[‡] Pontus Forsberg,[‡] Markus Sieger,[†] Fredrik Nikolajeff,[‡] Lars Österlund,[*,‡,§] and Boris Mizaikoff[*,†]

[†]Institute of Analytical and Bioanalytical Chemistry, University of Ulm, Albert-Einstein-Allee 11, 89075 Ulm, Germany

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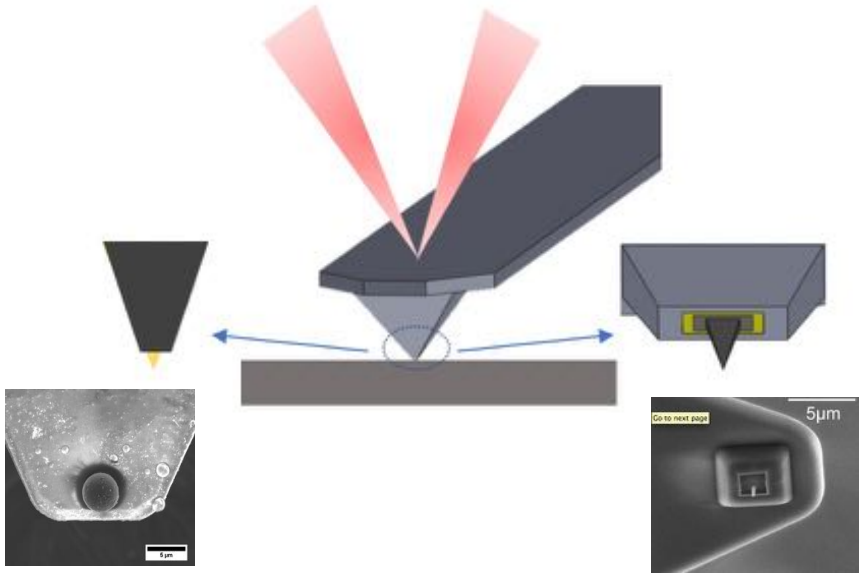
[§]Molecular Fingerprint Sweden AB, Ekslätravägen 130, SE-756 55 Uppsala, Sweden

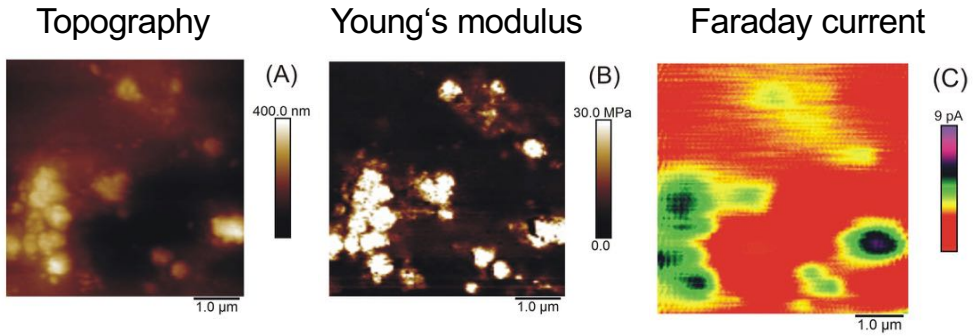
Hybrid AFM-SECM



P. Unwin, J. Macpherson Anal. Chem. **2000**
C. Kranz et al., Anal. Chem. **2001**
J. Abbou et al., Anal. Chem. **2002**

- ✓ offers combined mapping of nanoechanical and (electro)chemical properties
- ✓ at least for the AFM part ISO norms are available
- ✓ issues with artifacts are well described for AFM
- ✓ spatial resolution in SECM significantly increased
- ✓ ONE probe with two functionalities

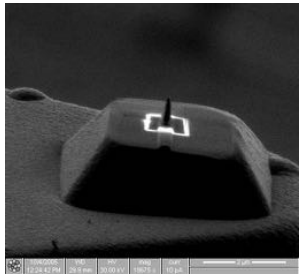
Soft conductive PDMS electrodes



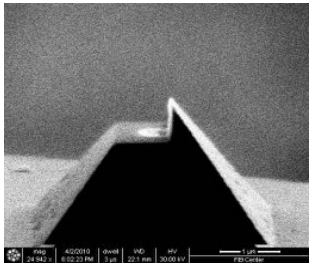
S. K. Guin et al., *Chem. Asian J.* **2017**

AFM-SECM probe design

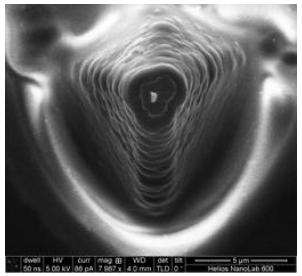
- **Microfabricated AFM probes with integrated electrode**
- **Silicon nitride cantilevers with force constants in the range of 0.8- 2 N/m**
- **Recessed electrode → modification with sensing layers**
- **No lift mode needed**



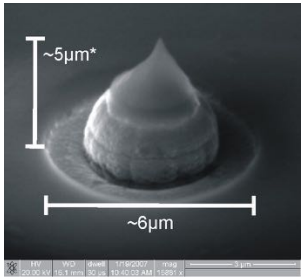
Frame electrode



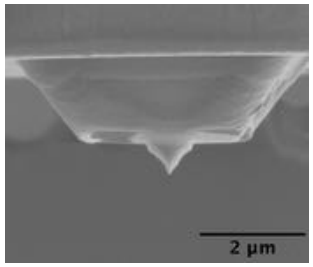
Nanodisc electrode



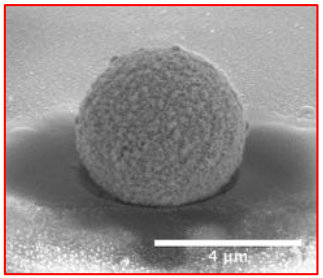
BDD ring electrode



Ring electrode



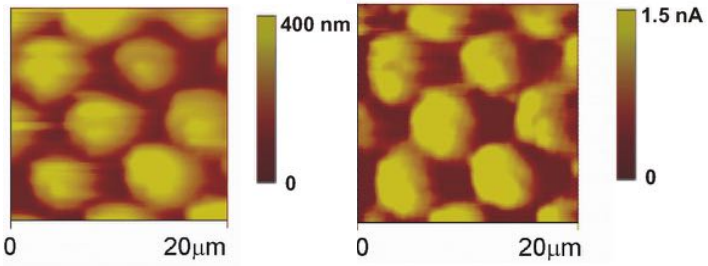
Conical electrode



Colloidal electrode

Enzyme activity

Topography SECM

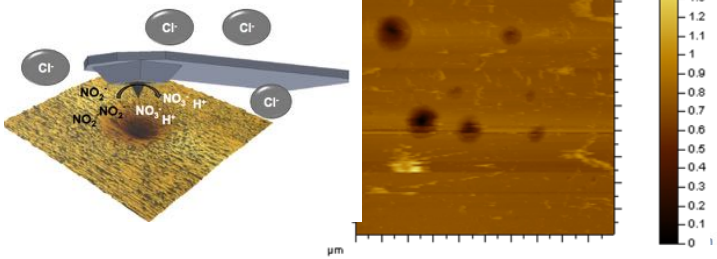


GOD containing polymer spots

A. Kueng et al., *Angew. Chem. Int. Ed*. **2003**;

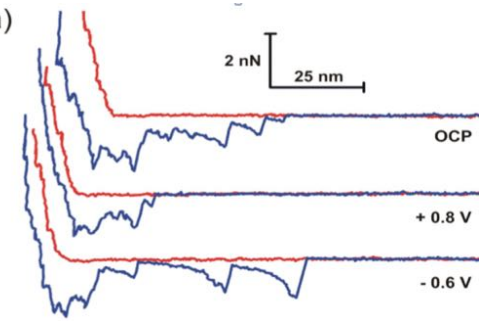
Corrosion studies

Simultaneously induced corrosion and imaging



J. Izquierdo, et al, *ChemElectroChem* **2015**;

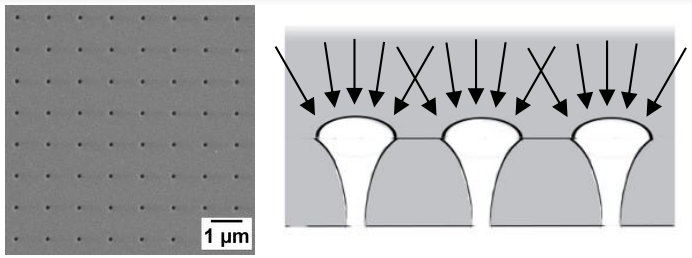
Force spectroscopy under potential control



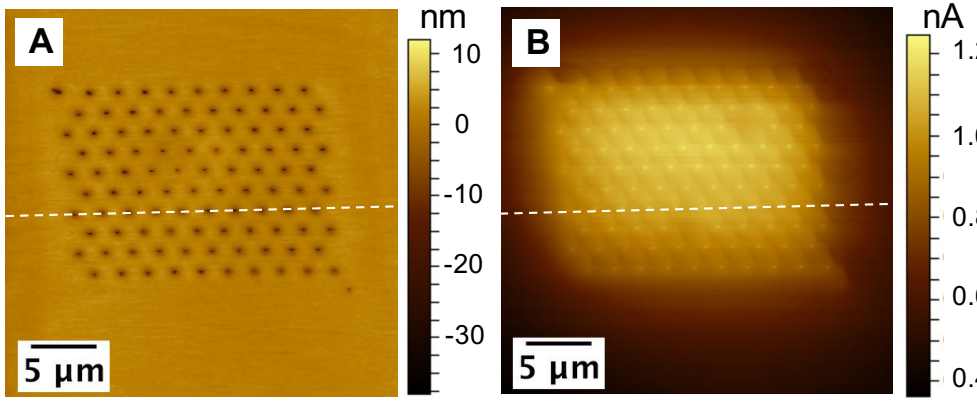
P. Knittel et al., N*anoscale* **2016**

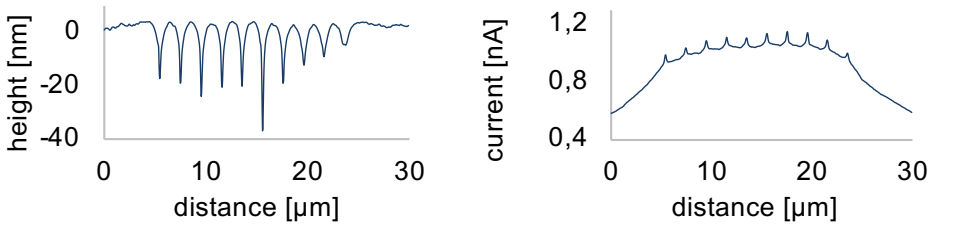
Nanopore diffusion

Overlapping diffusion profiles

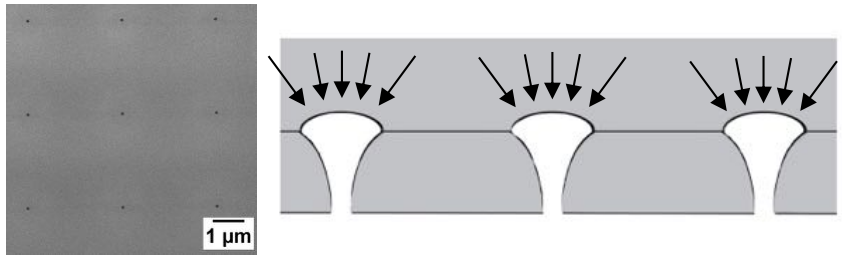


Ratio: $r_{distance}/r_{Pore\ radius}$ = 21

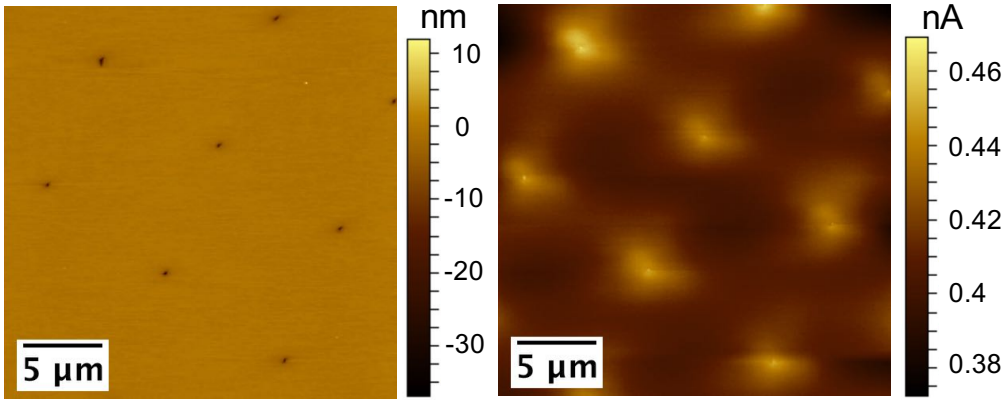


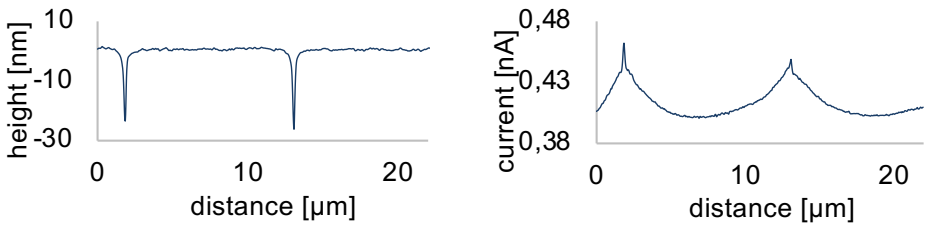


Individual diffusion profiles



Ratio: $r_{distance}/r_{Pore\ radius}$ = 91





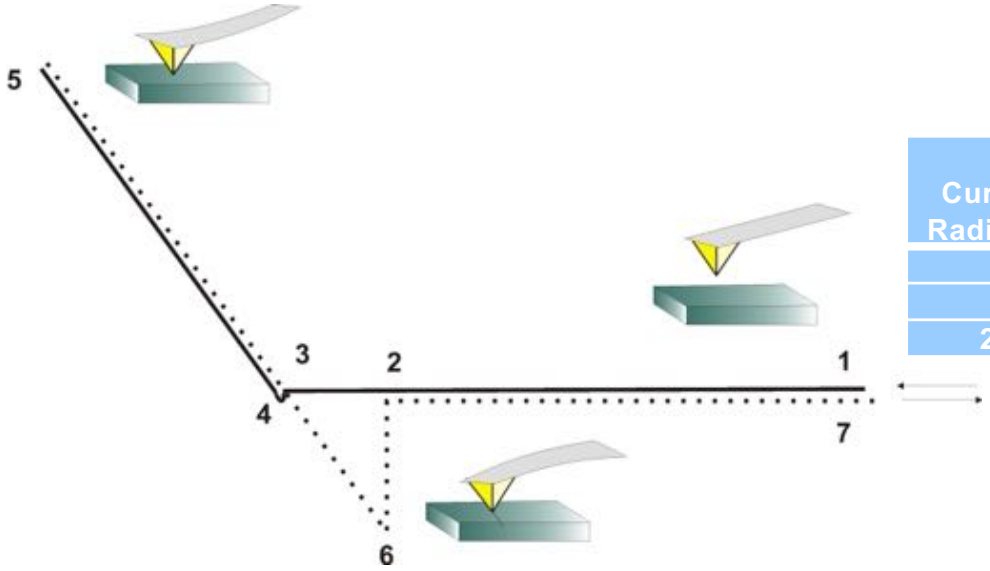
Collaboration: Damien Arrigan, Curtin University Perth

Y. Liu et al., *Anal. Chem. 88,* 6689, **2016**

Colloidal AFM probes

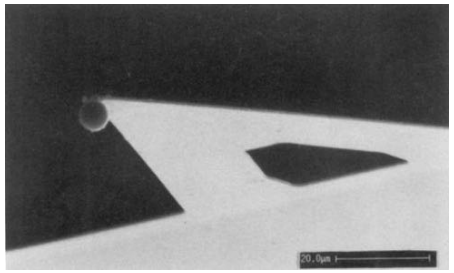
Force spectroscopy

Soft samples



$$p = \frac{F}{2\pi r^2}$$

Tip Curvature Radius / nm	Contact Area / nm²	Pressure / kPa for Applied Force		
		0.1 nN	2 nN	5 nN
2	25,13	3978,874	79577,472	198943,679
20	2513,27	39,789	795,775	1989,437
2500	39269908,17	0,003	0,051	0,127



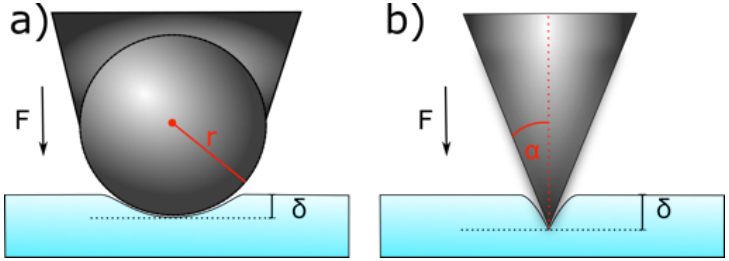
Derjaguin-Muller-Toporov (DMT) model

$$F - F_{adh} = \frac{4}{3} E^* \sqrt{r \cdot \delta^3}$$

$$E^* = \left[\frac{1-\upsilon_s^2}{E_s} + \frac{1-\upsilon_{tip}^2}{E_{tip}} \right]^{-1}$$

Hertz model

Sneddon model

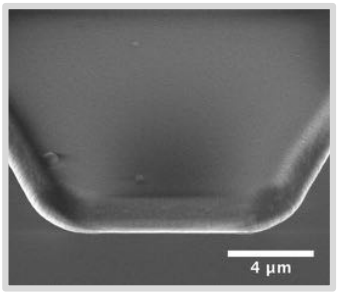


F_{adh} is the recorded adhesion force, E^* the reduced **Young's modulus** as, r the tip curvature radius, υ_s and υ_{tip} are the Poisson ratio of the sample and the tip, and δ the indentation

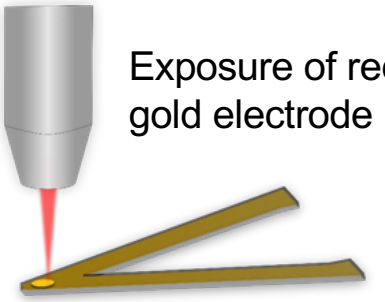
Derjaguin et al., *J. Colloid Interf. Sci.* **1975**

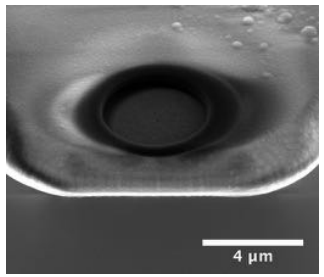
Conductive colloidal AFM probe

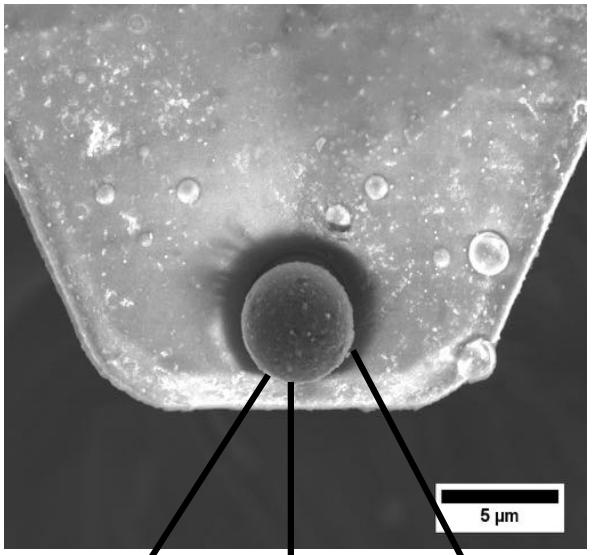
Tip-less Au-coated and insulated SiN cantilever



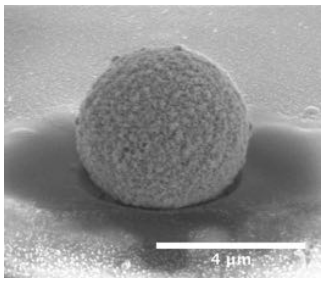
Exposure of recessed gold electrode

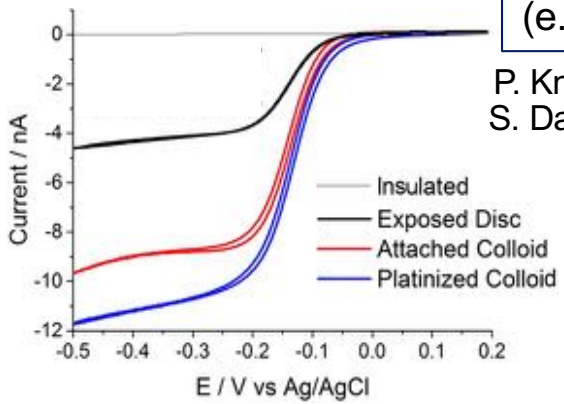






Attachment of Au-colloid via a UV-curable glue





Colloidal polymer coated AFM-SECM probe (e.g., PEDOT, **PDA**)

P. Knittel et al., *Nanoscale* **2016**
S. Daboss et al., *Anal.Chem.* **2020**

Colloidal **Prussian blue** coated AFM-SECM probe

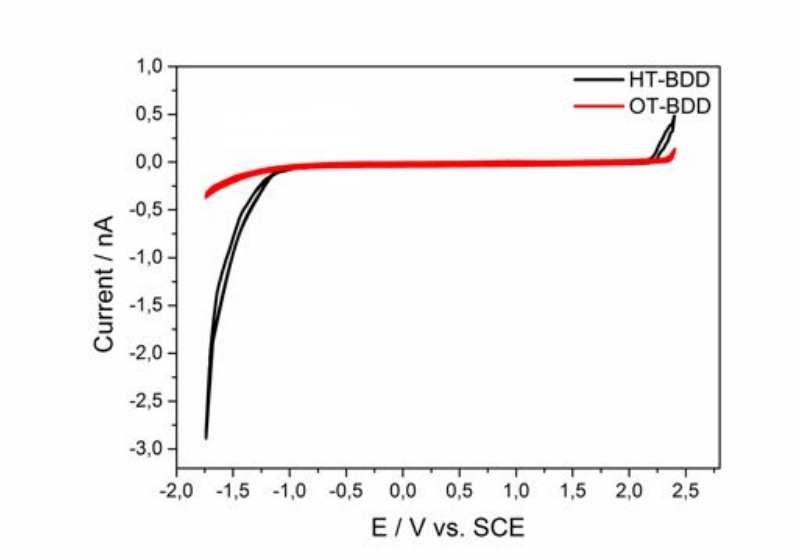
Colloidal **Pt black** coated AFM-SECM probe

Colloidal boron-doped diamond AFM-SECM probe

S. Daboss et al., *Small* **2019**

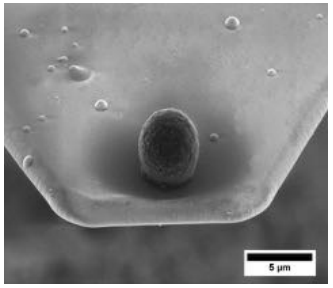
Colloidal boron-doped AFM-SECM probes

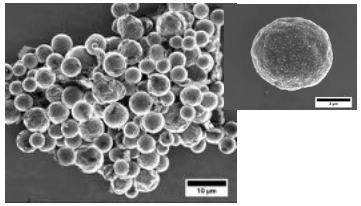
- Low force constants (silicon nitride cantilever)
- Control of surface termination
- Physical and chemical inert probe
- Large potential window

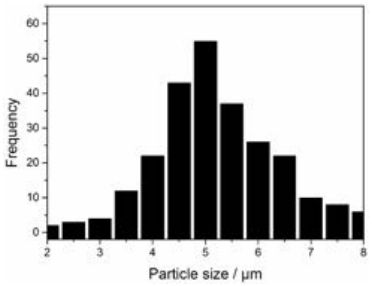


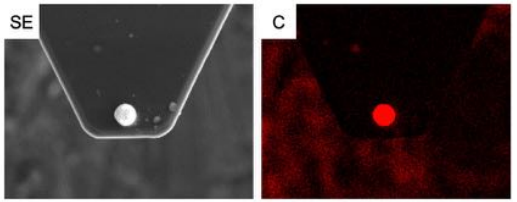
H-terminated (black) and O-terminated (red) BDD-AFM-SECM probe (0.5 M H_2SO_4, scan rate 100 mV/s).

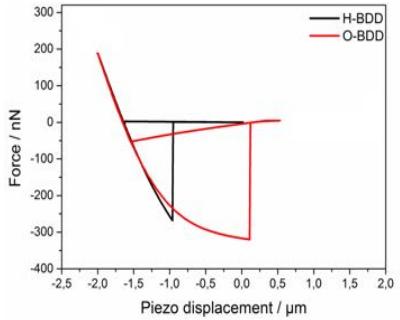
***k* = 0.85 ± 0.04 N·m^{-1} (n =5)**

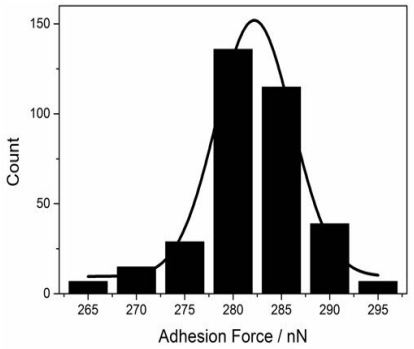


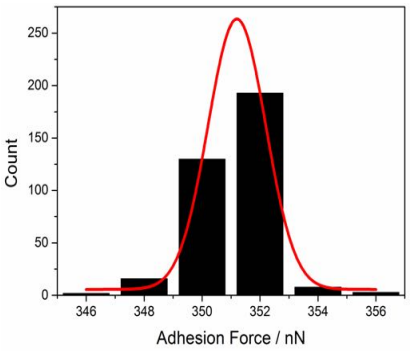












S. Davos et al., *Small* 15,1902099, **2019**

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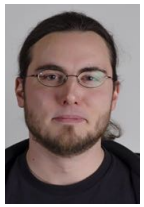
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19th International Conference on Electroanalysis

ESEAC 2024

Organizers: Fred Lisdat (Technical University of Applied Sciences Wildau)
Christine Kranz (Ulm University)

19th International Conference on Electroanalysis

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Organizers: Fred Lisdat, Christine Kranz

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- Sensor and biosensor developments and applications
- Fundamental studies on electrochemical conversions
- Photoelectrochemical systems
- Electrochemical impedance spectroscopy
- Hybrid methods for studying electrochemical systems
- Electroanalytic studies on (bio)corrosion
- In vivo electroanalysis
- Electroanalysis from the nano- to the macroscale