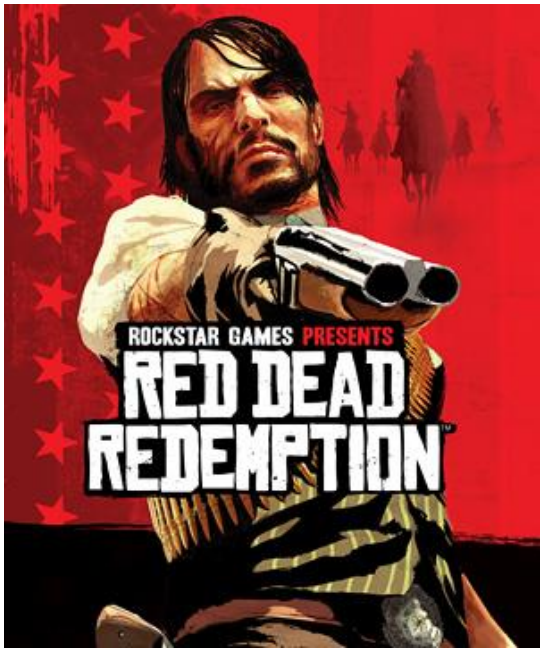
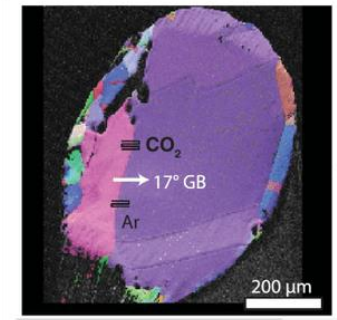
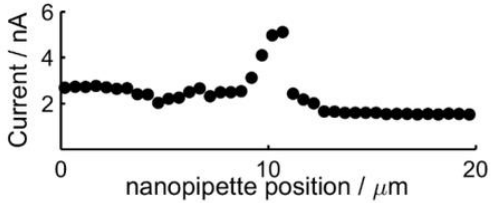
The Wild West of Nanoelectrochemistry







Dr. Kim McKelvey

25th Nov 2020

Background

Computational Modelling

(Applied Mathematics and Scientific Programming)

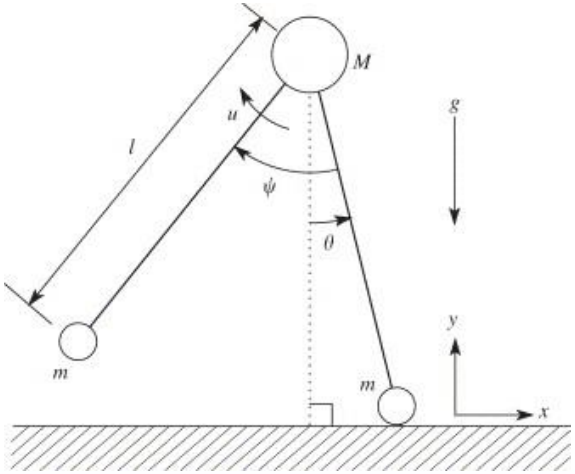
UNIVERSITY of OTAGO

SAPERE AUDE

Te Whare Wānanga o Otāgo

NEW ZEALAND

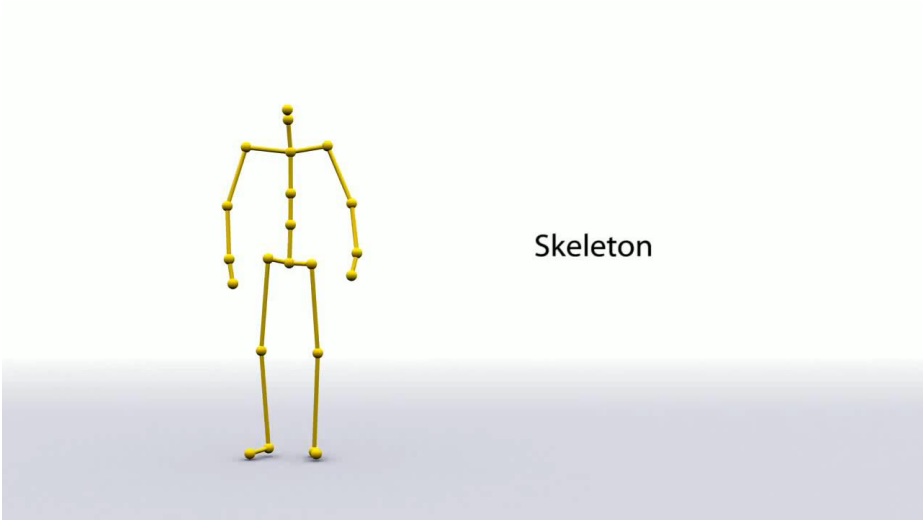
Simplest Walking Model



Background:

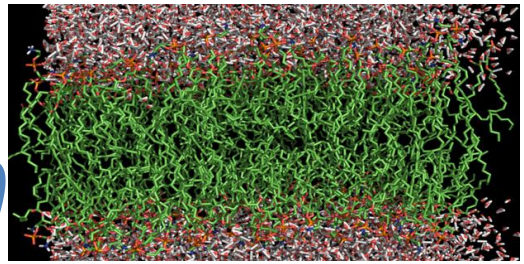
Character Simulation and AI in Computer Games

naturalmotion

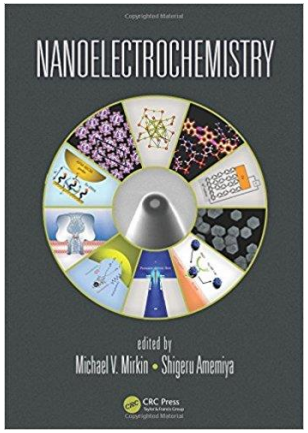


Computer Games Physics

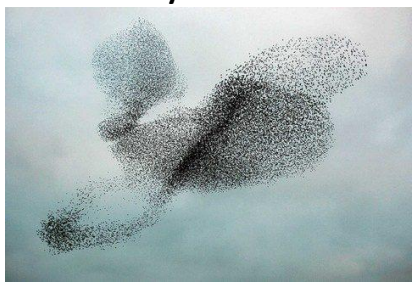
Biophysics and Membrane Dynamics



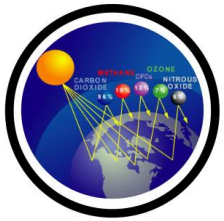
Nanoscale Electrochemistry



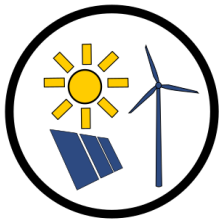
Emergent Behavior in Physical Systems



THE UNIVERSITY OF WARWICK



Climate Change

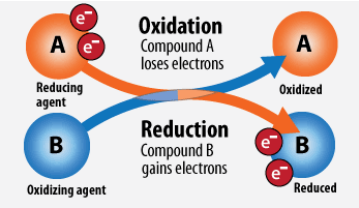


Renewable Electricity

Energy storage and conversion

Electrochemical Reactions

Interconvert electrical energy and chemical energy

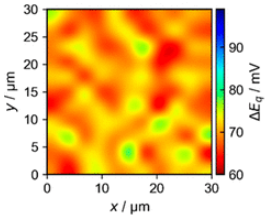


Batteries **Fuels cells** **Electrolysis cells**

Nanoelectrochemistry

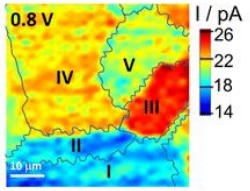
Heterogeneity of electrode surfaces

Carbon electrode



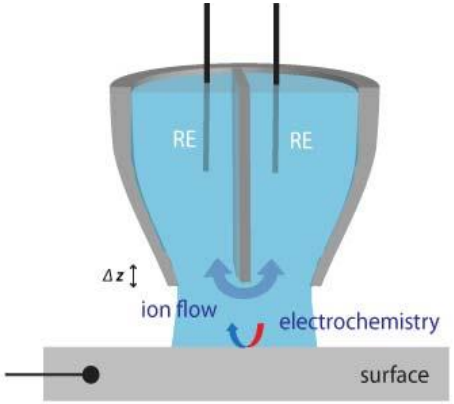
ACS Sens. 2019, 4, 8, 2173–2180

Pt electrode

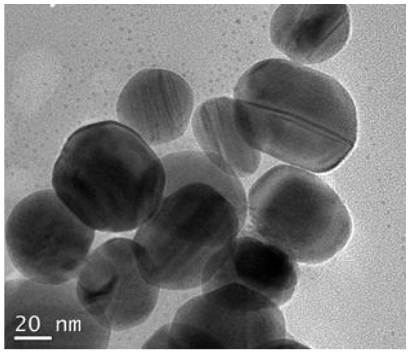


J. Am. Chem. Soc. 2013, 135, 10,

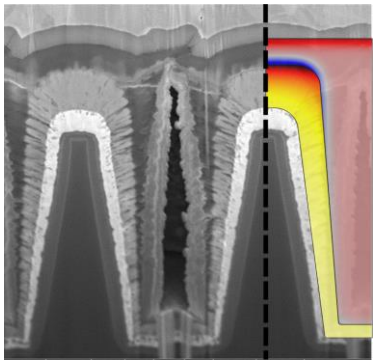
Nanoelectrochemistry



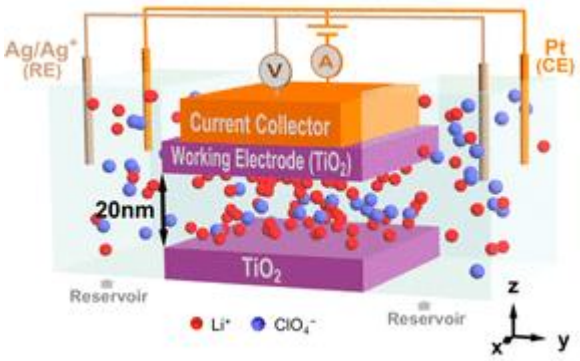
Electrochemical Scanning Probe Microscopy



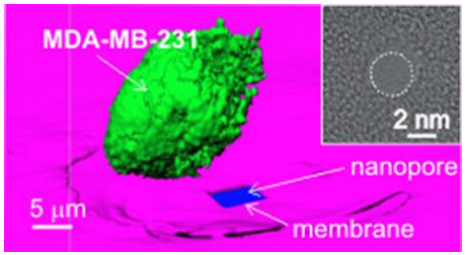
Single Nanoparticles



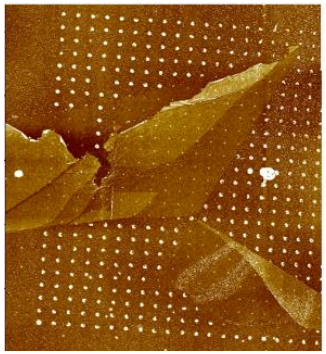
3D Nanostructure in Batteries



Effect of Nanoconfinement

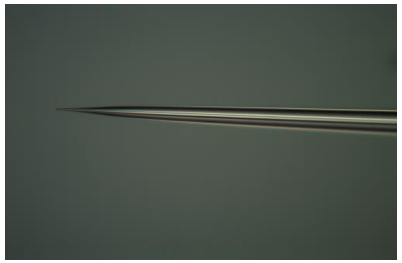


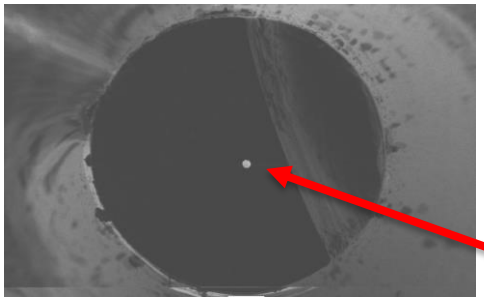
Detecting cancer in single living cells



2D Materials

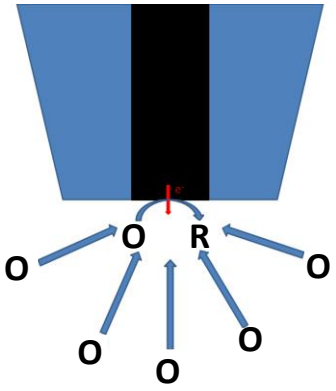
Electrochemical Scanning Probe Microscopy

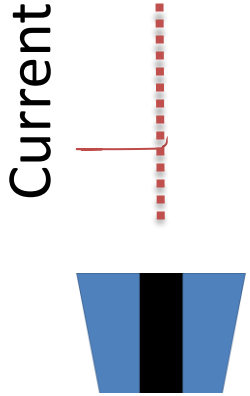


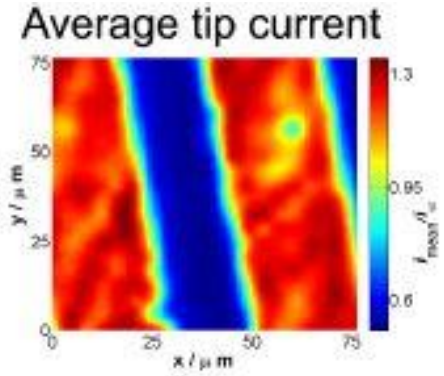


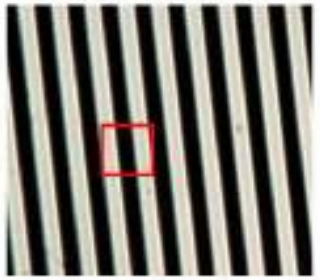
Electrode

Microelectrode/Nanoelectrode
(Ultramicroelectrode)

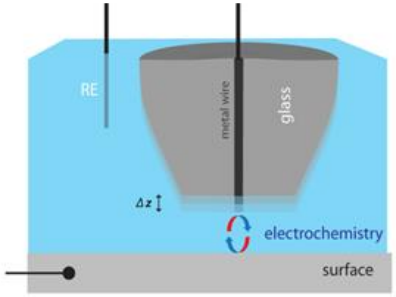




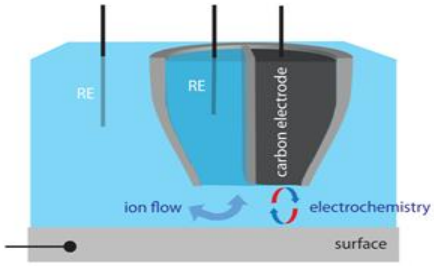




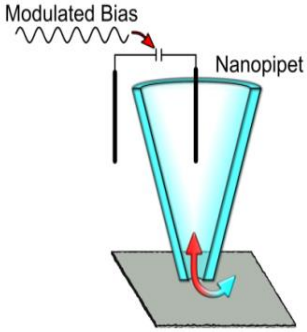
Intermittent Contact SECM



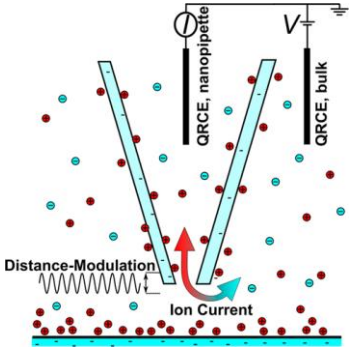
SICM-SECM



Bias Modulation SICM

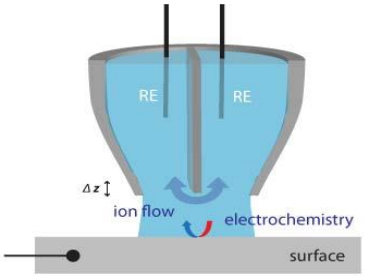


Surface Charge Mapping with SICM

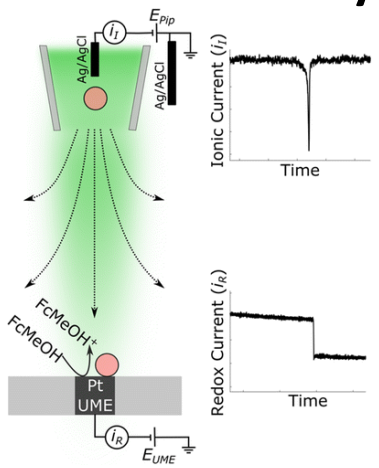


SECCM

'Scanning Droplet'

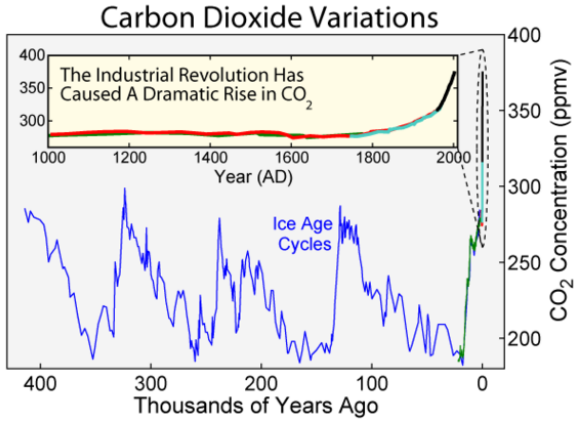


Single Nanoparticle Electrochemistry

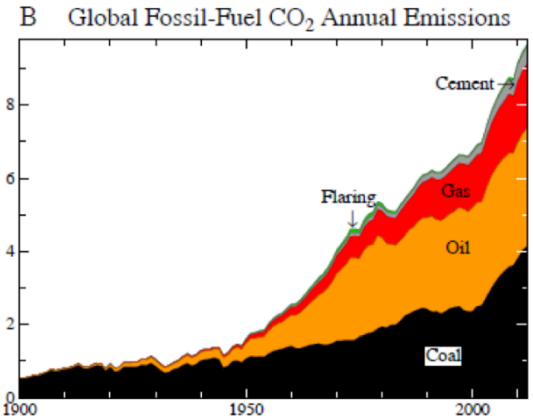


SECM = **S**canning **E**lectro**c**hemical **M**icroscopy
SICM = **S**canning **I**on **C**onductance **M**icroscopy

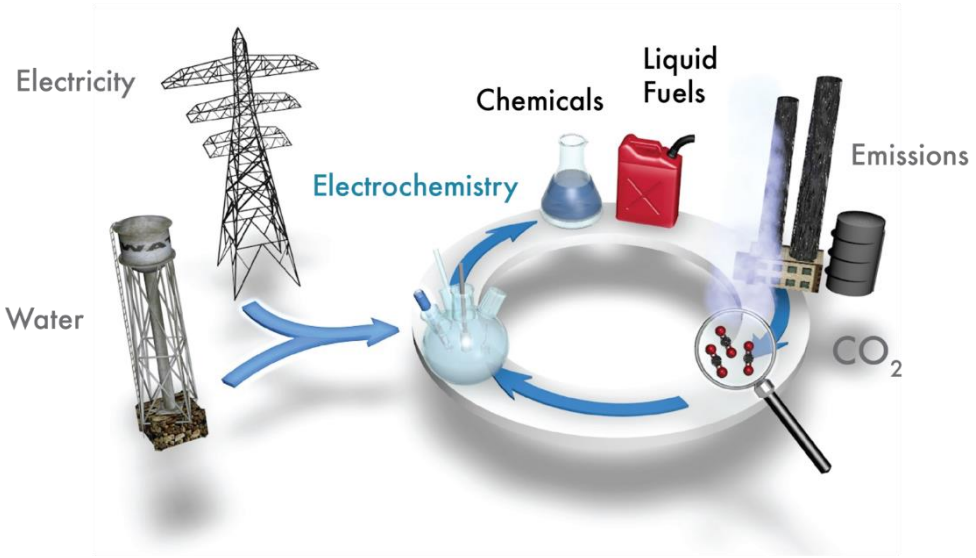
CO_2 Capture and Utilization



PLoS One **2013**, *8* (12), e81648.



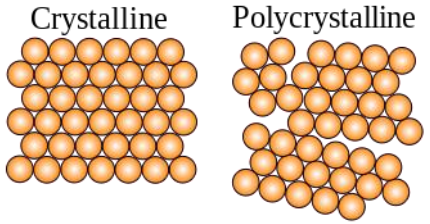
Green Chem. **2015**, *17* (4), 2304–2324.

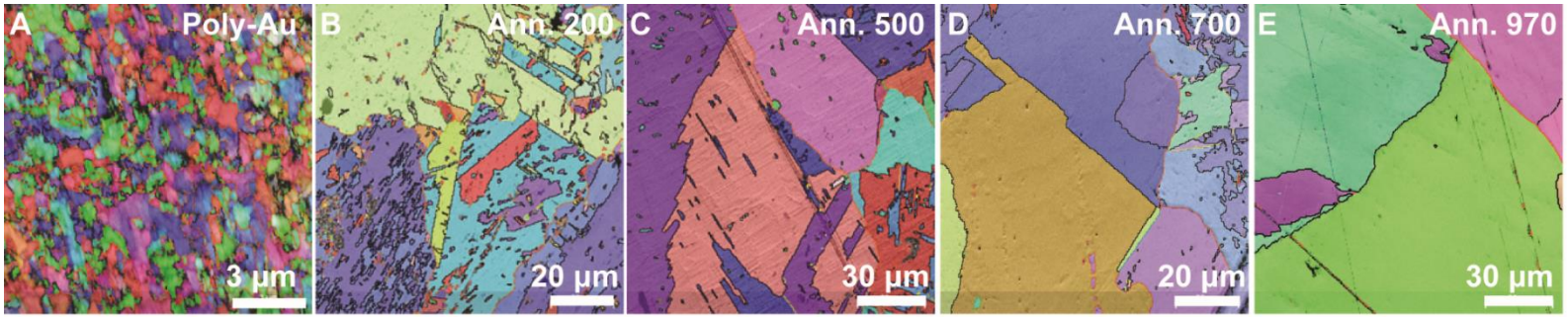


Credit: Opus 12

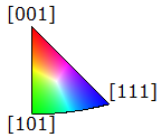
CO_2 reduction in water on polycrystalline Au foil.

Rain Mariano, Matt Kanan
Kanan Lab, Stanford University

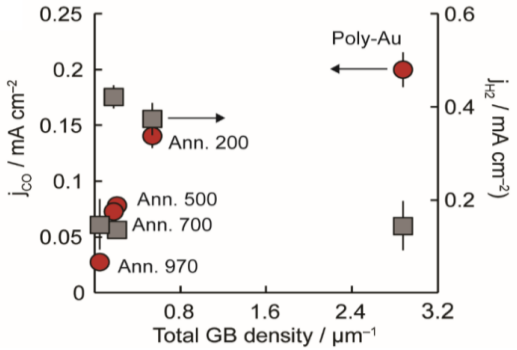




SEM-based Electron Backscatter Diffraction



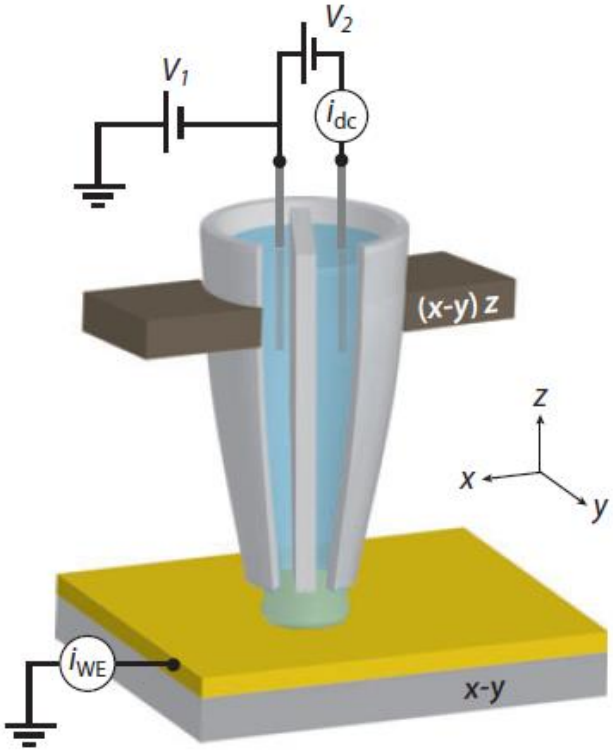
Products (gas chromatography): CO *or* H_2
Electrode held at -0.4 V vs. RHE
1 atm of CO_2

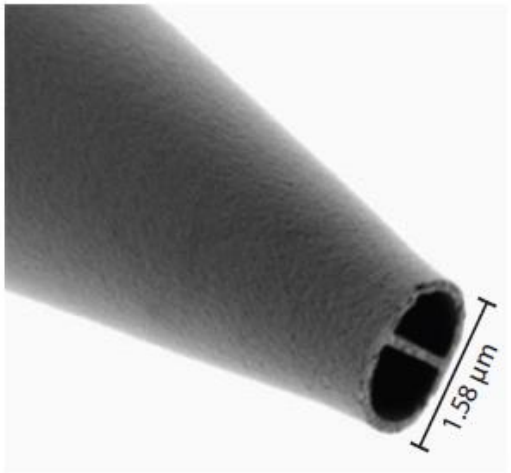


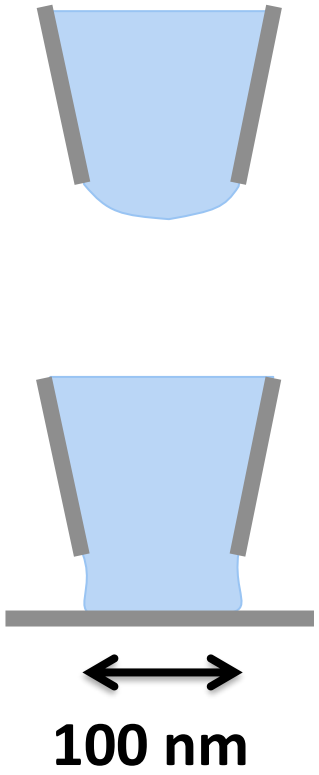
Selective increase in CO_2 electroreduction activity at grain-boundary surface terminations. Mariano, R. G.; McKelvey, K.; White, H. S.; Kanan, M. W. *Science* **2017**, *358* (6367), 1187–1192.

Scanning **E**lectro**c**hemical **C**ell **M**icroscopy (**SECCM**)
'Scanning Droplet'

Restrict electrochemical measurement to a small point of a large sample





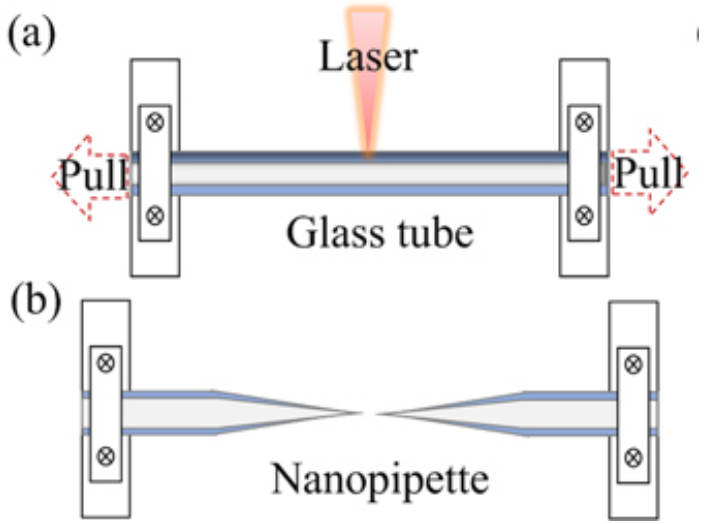


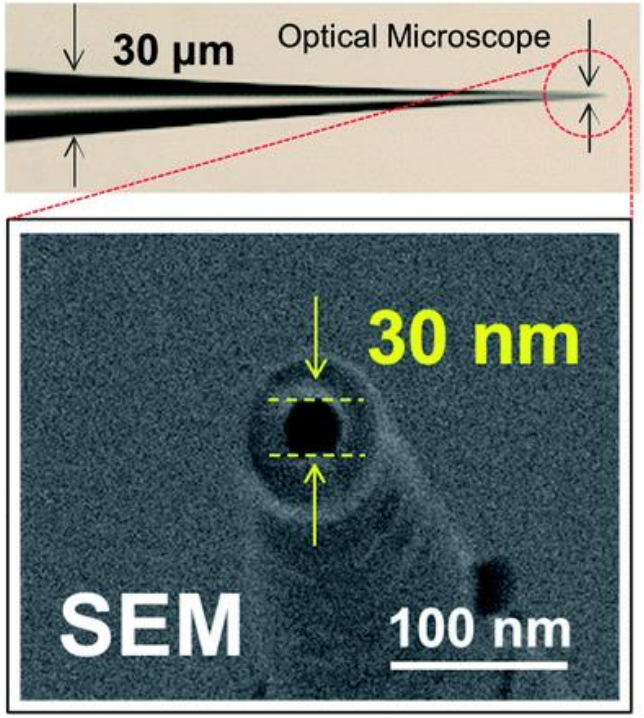
Ann. Rev. Anal. Chem. **2013**, 6, 329-51.

11

SECCM Key Attributes:

Simple quick probe fabrication





-> 4 seconds to fabricate 2 nanoscale probes

Shen, Y.; Zhang, Z.; Fukuda, T. *Nanotechnology* **2015**, *26* (15), 155702.

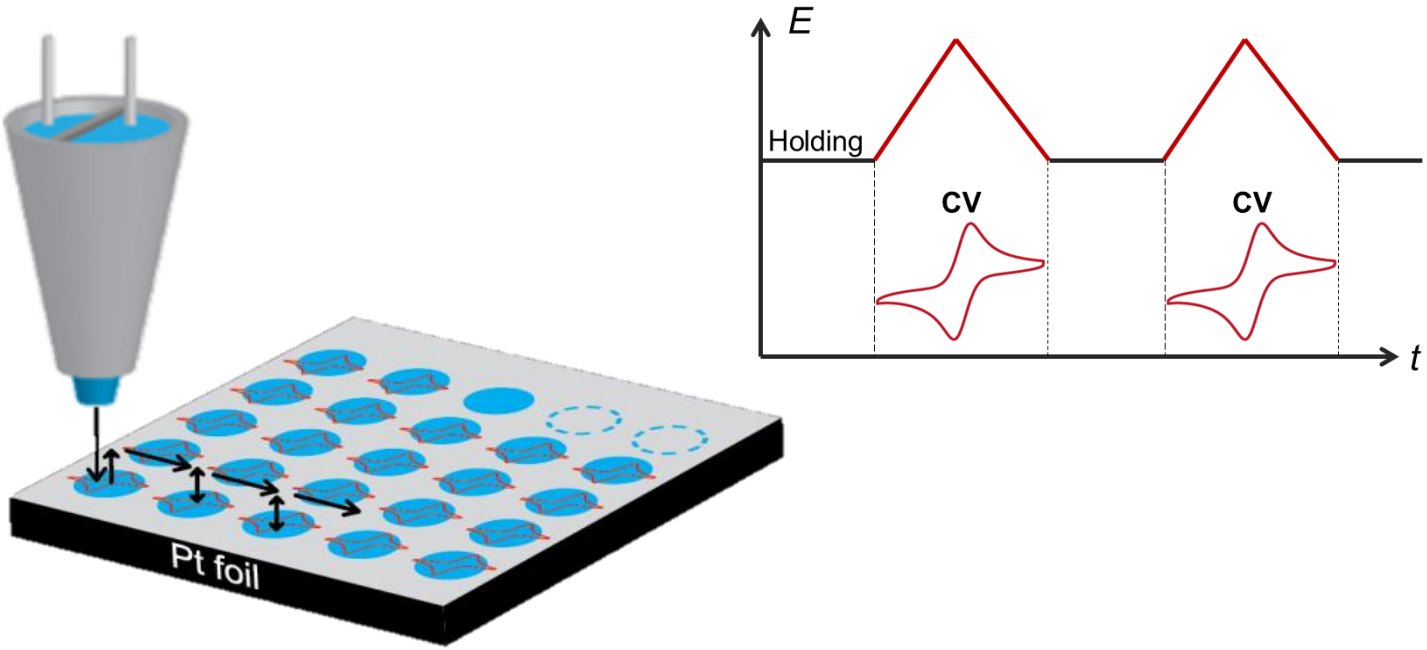
An, S.; Stambaugh, C.; Kim, G.; Lee, M.; Kim, Y.; Lee, K.; Jhe, W. *Nanoscale* **2012**, *4* (20), 6493–6500.

SECCM Key Attributes:

Electrochemical spectroscopy mapping

(Cyclic voltammetry, amperometry, potentiometry, arbitrary waveforms)

Hopping CV Scan

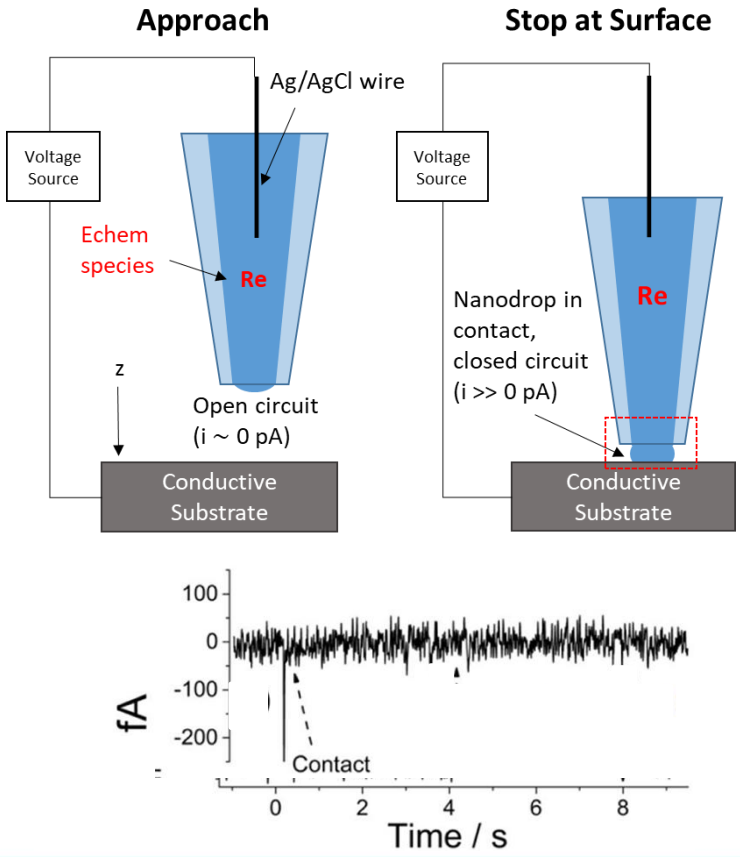


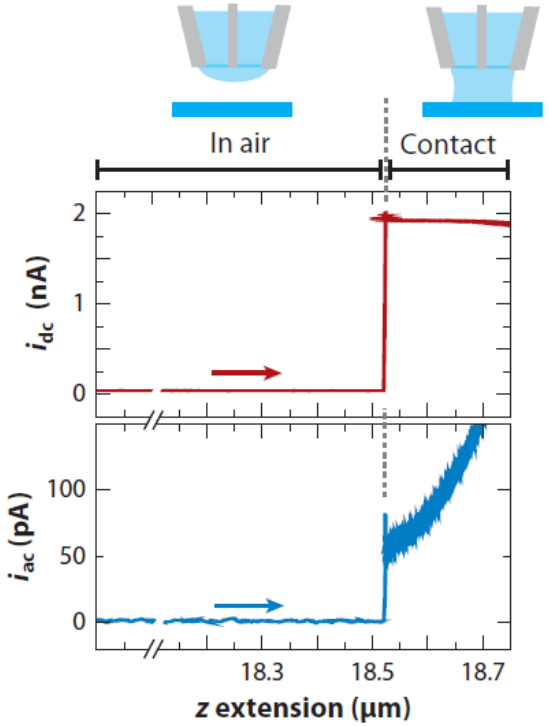
Anal. Chem. **2015**, *87*, 5782.

SECCM Key Attributes

Resolution

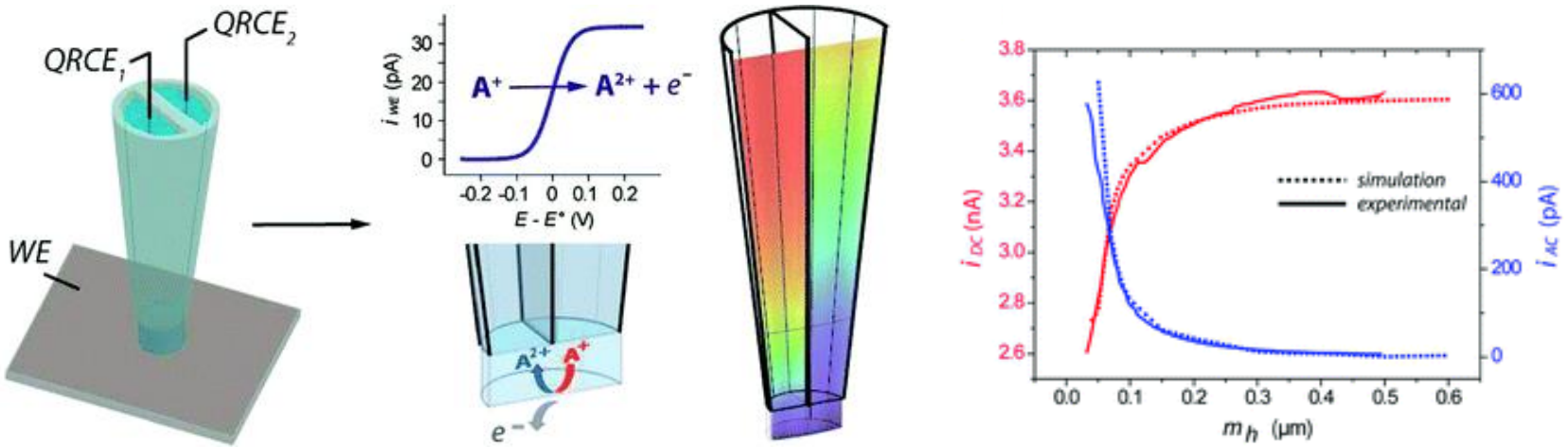
Feedback response (positive, negative, increasing, decreasing, or **transient**)





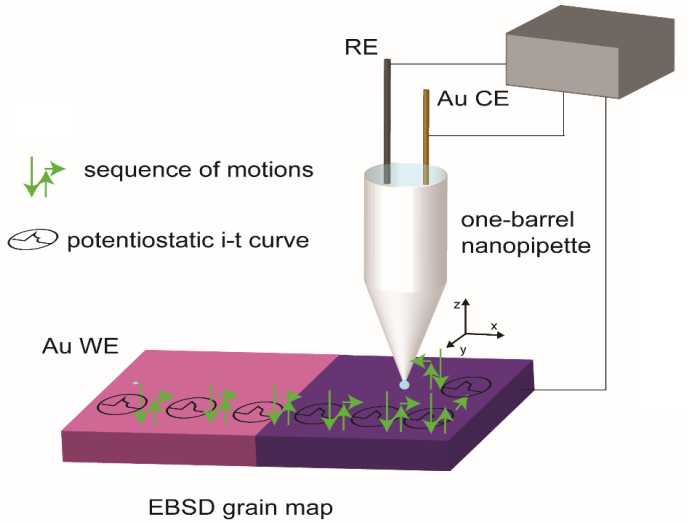
SECCM Key Attributes

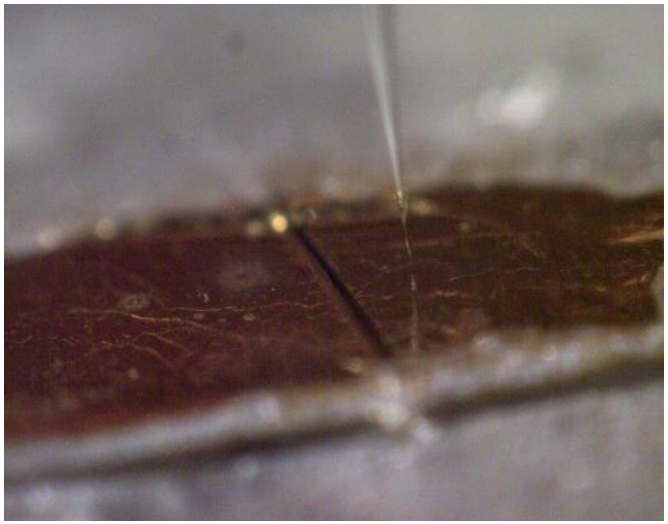
Quantitative:

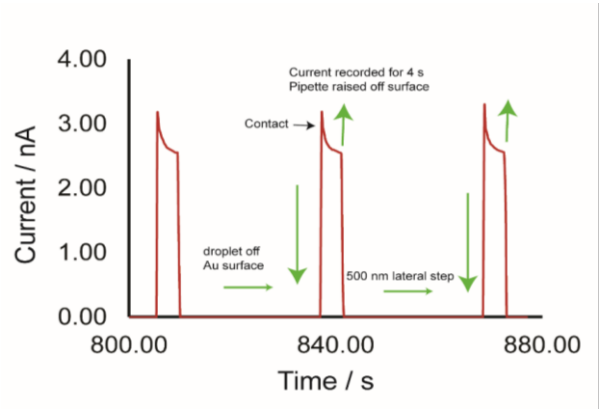


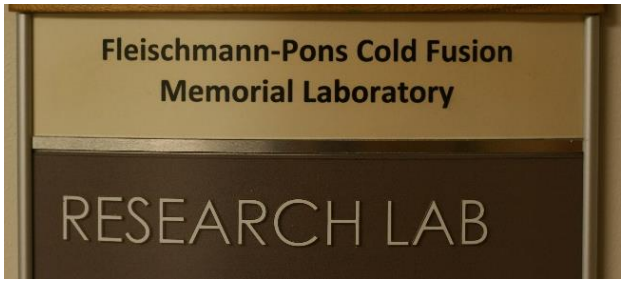
Anal. Chem., **2012**, 84(52), 2483–2491.

SECCM to map CO_2 reduction activity

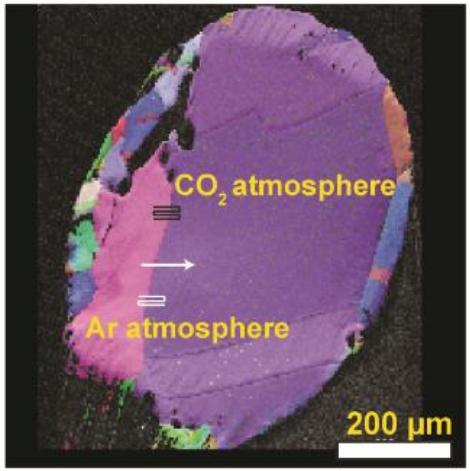


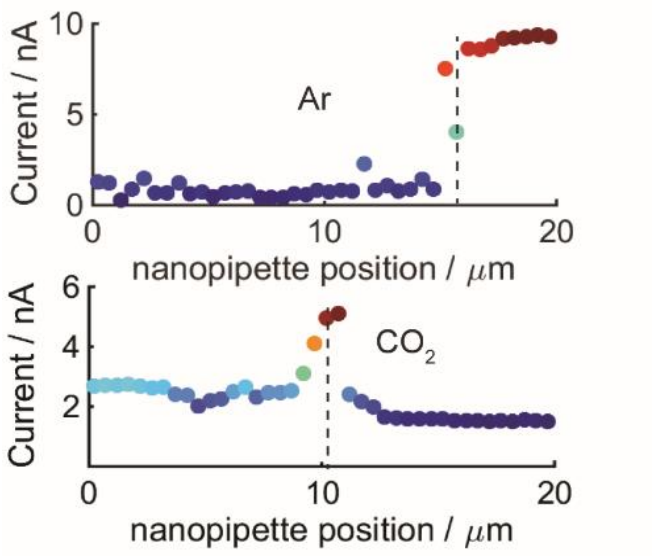






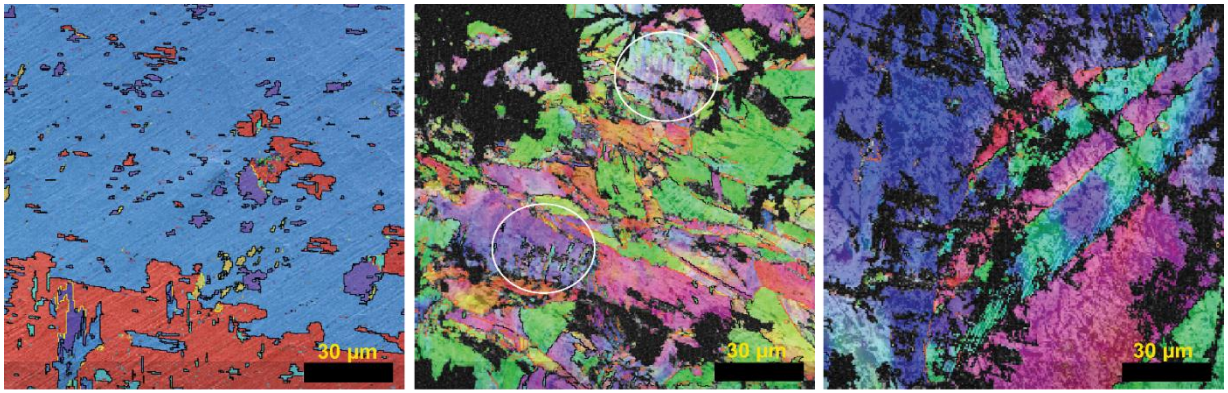
CO_2 and H^+ reduction activity

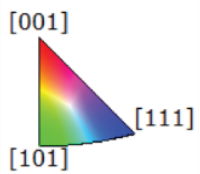


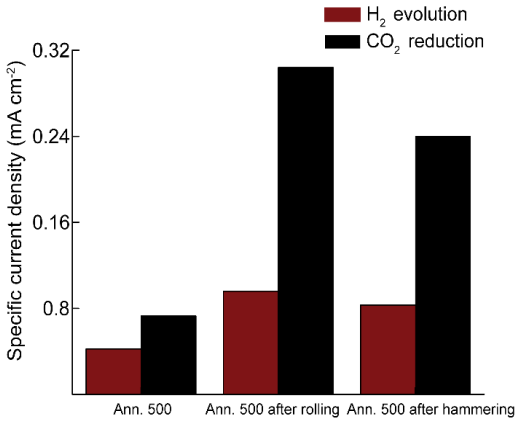


Want to improve CO_2 reduction activity on Au?

-> increase grain boundary density



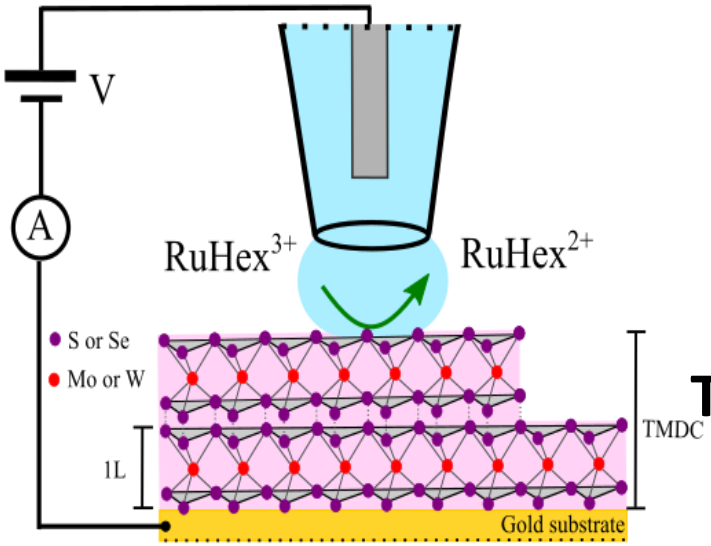


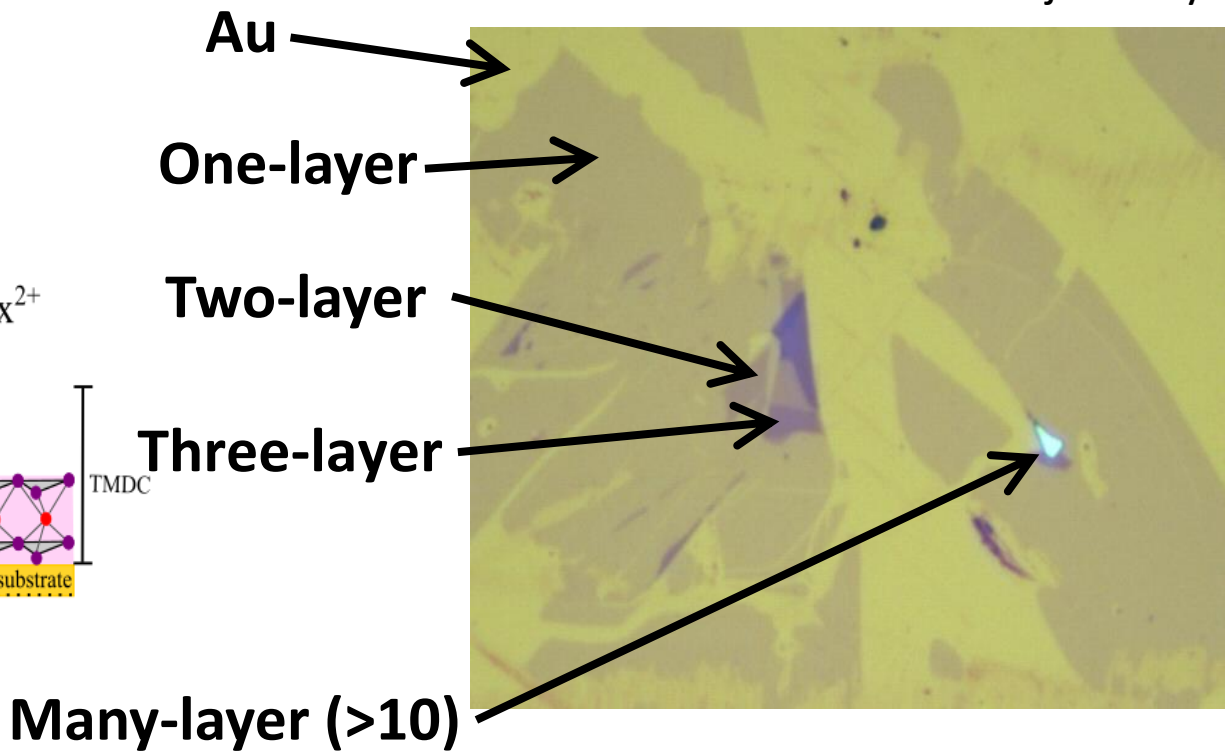


Effect of 2D transition metal dichalcogenides layer thickness

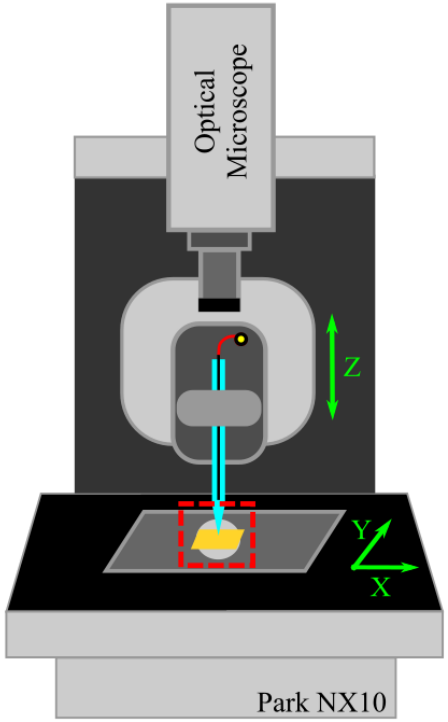
TMDCs: MoS_2, $MoSe_2$, WS_2, WSe_2,

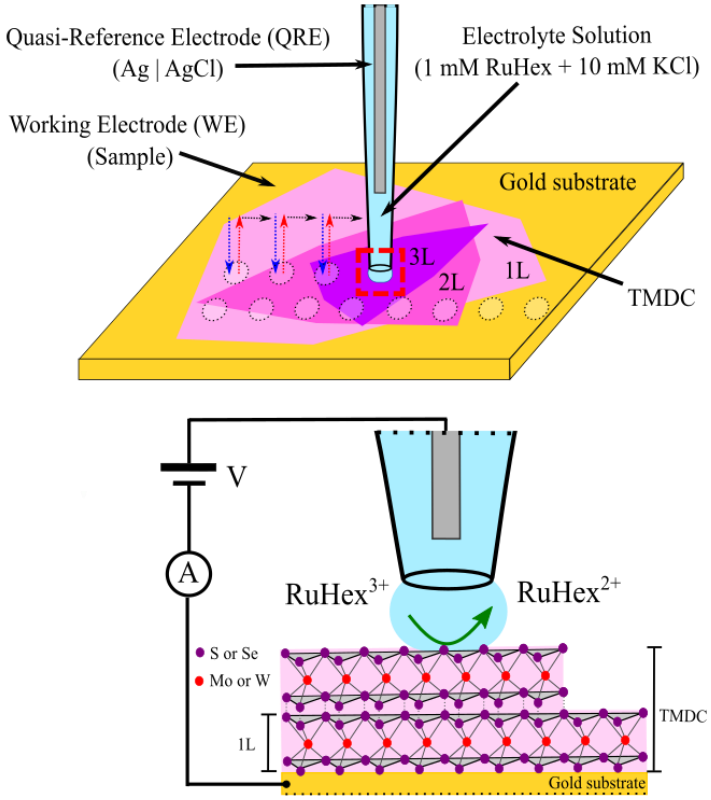
Collaborator: Dr. Matěj Velický

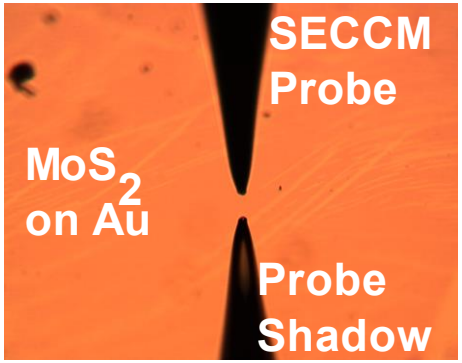




SECCM configuration



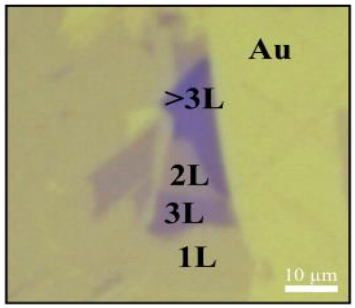


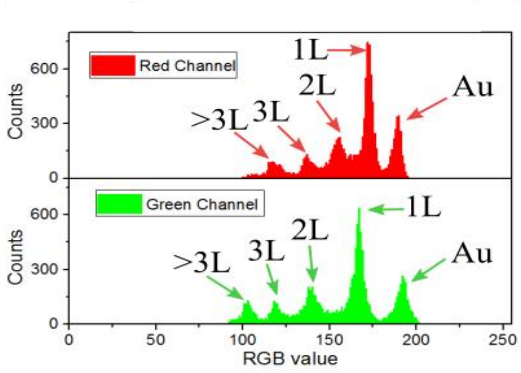


Hopping mode LSV scans (@1 V/s) with a 200 nm nanopipette

Correlating electrochemical response with material structure

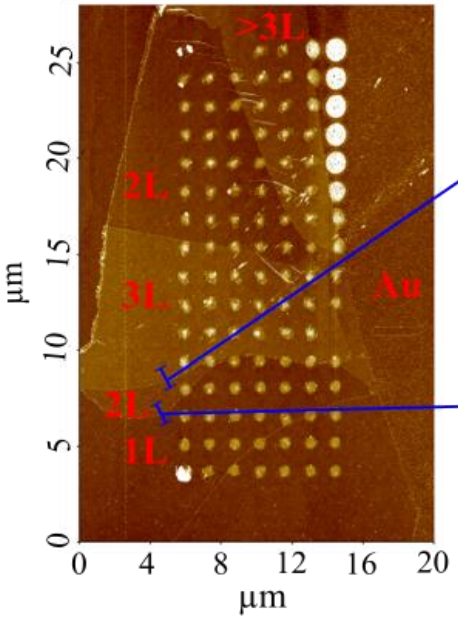
Optical Microscopy

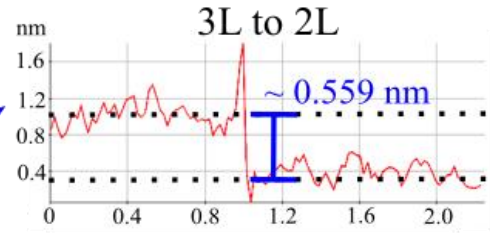


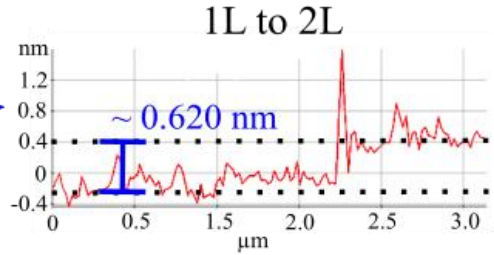


Sample: WSe_2

Atomic Force Microscopy (AFM)







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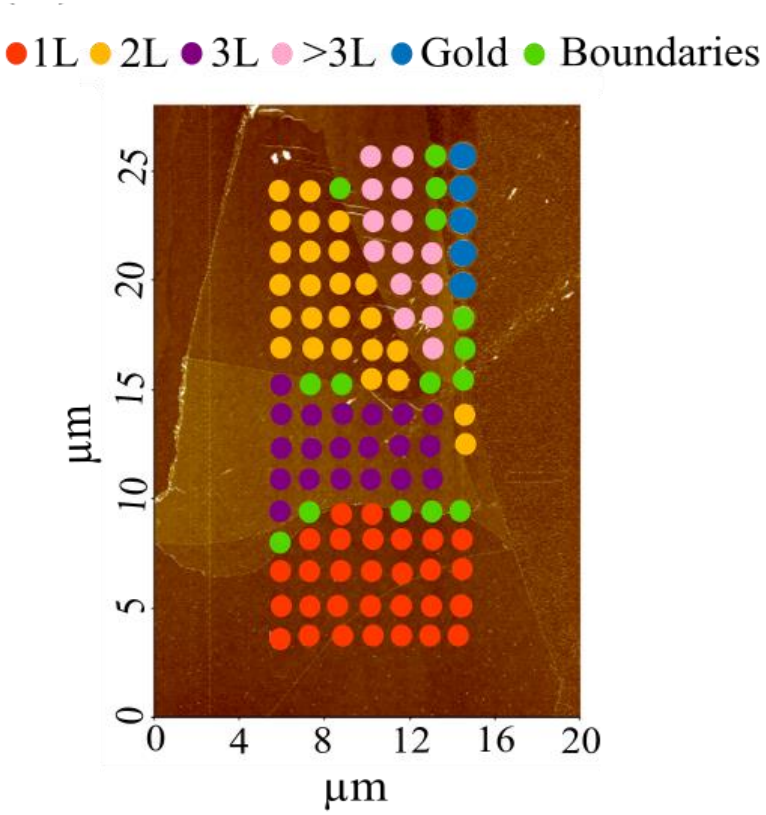
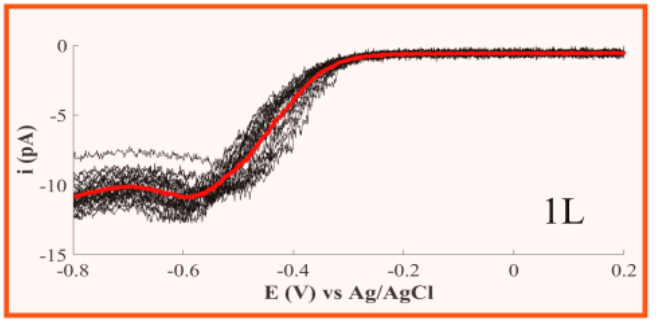


One Layer



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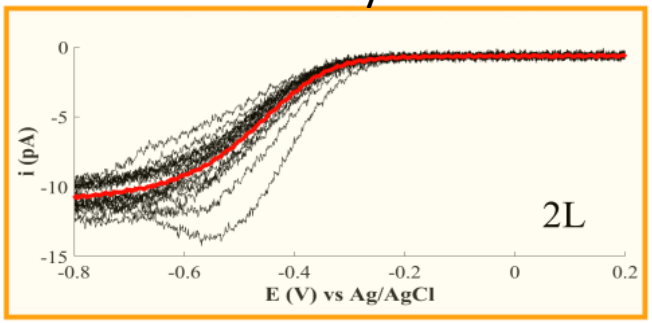

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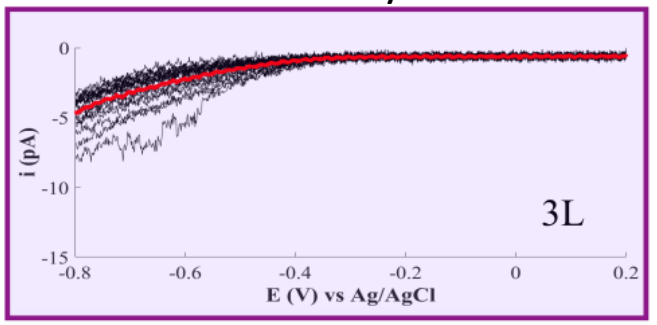
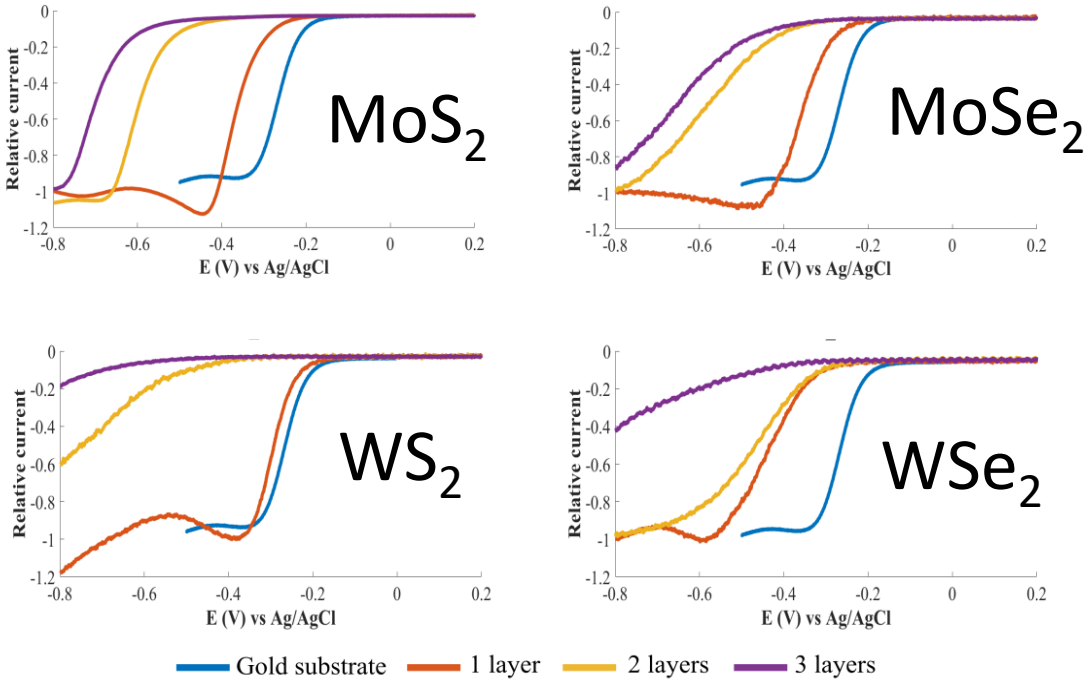
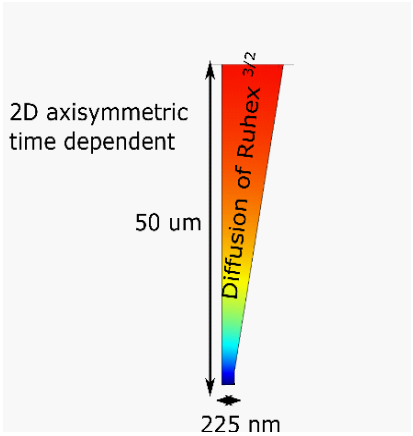


Manuscript in preparation

Kinetics of RuHex reduction



Finite element simulations



Marcus-Hush-Chidsey kinetics

$$j = k_{red} c_{RuHex^{3+}} - k_{ox} c_{RuHex^{2+}}$$

$$k_{red} = k_0 e^{-\frac{\theta}{2}} \frac{I(\Lambda,\theta)}{I(\Lambda,0)}$$

$$k_{ox} = k_0 e^{\frac{\theta}{2}} \frac{I(\Lambda,\theta)}{I(\Lambda,0)}$$

$$I(\Lambda,\theta) = \int_{-\infty}^{\infty} \frac{e^{\frac{-(\varepsilon-\theta)^2}{4\Lambda}}}{2\cosh(\varepsilon/2)} d\varepsilon$$

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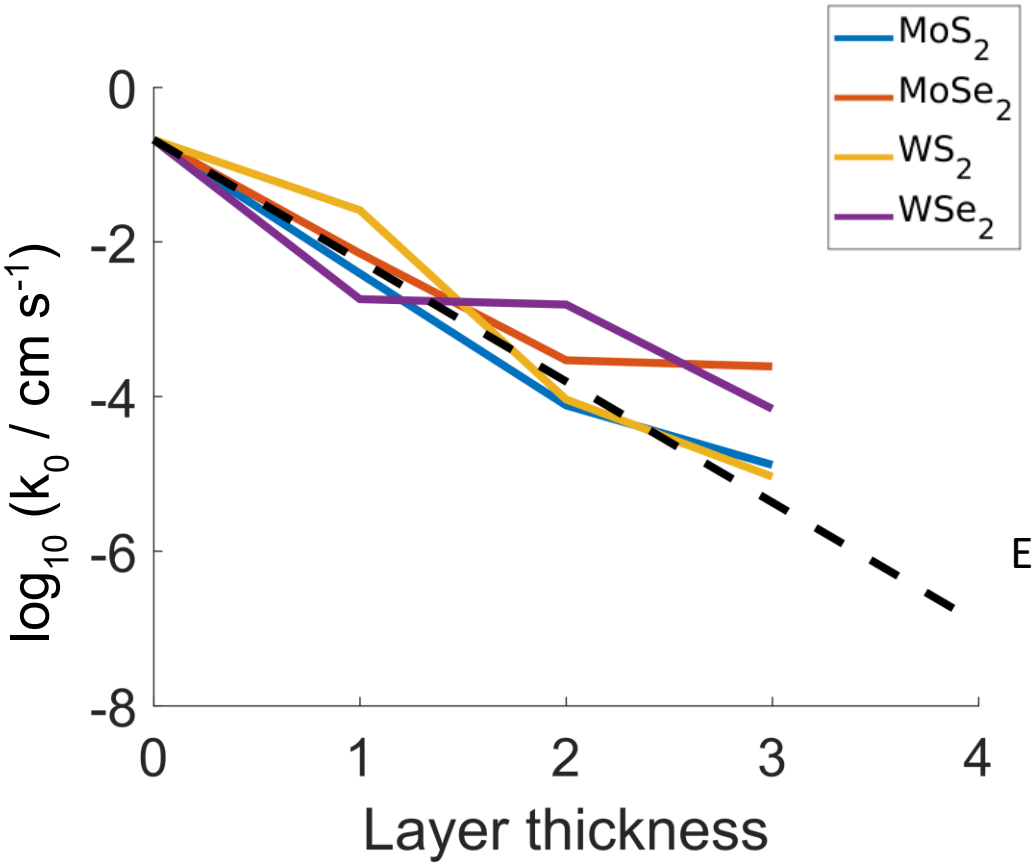

Electron transfer via tunnelling

$$k_{et} = k_0 e^{-\beta x}$$

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McKelveyLab

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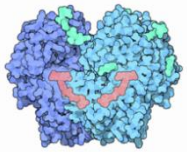
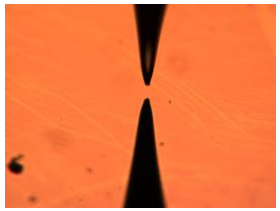
Electrochemical Sensors

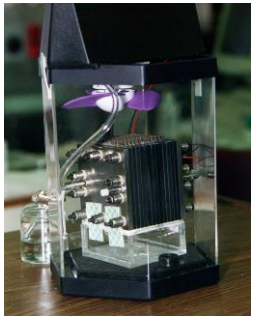
Redox-Active Enzymes



2D Materials

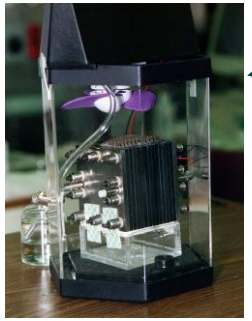


Fuel Cells

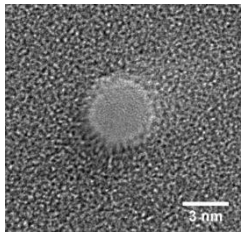


Nanostructure in Energy Storage and Conversion Devices

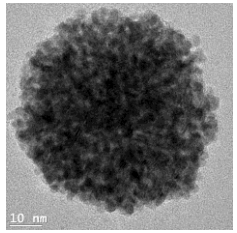
Electrocatalysis



Nanopores



Nanoparticles



Batteries

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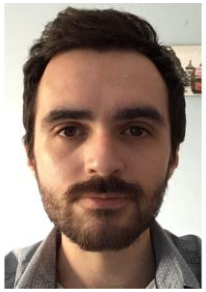
Acknowledgements

McKelveyLab

http://www.mckelveylab.com/



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