High Efficiency Coupling of Chemical Sensing to Chemical Treatment in Low-Dimensional Nanofluidic Structures

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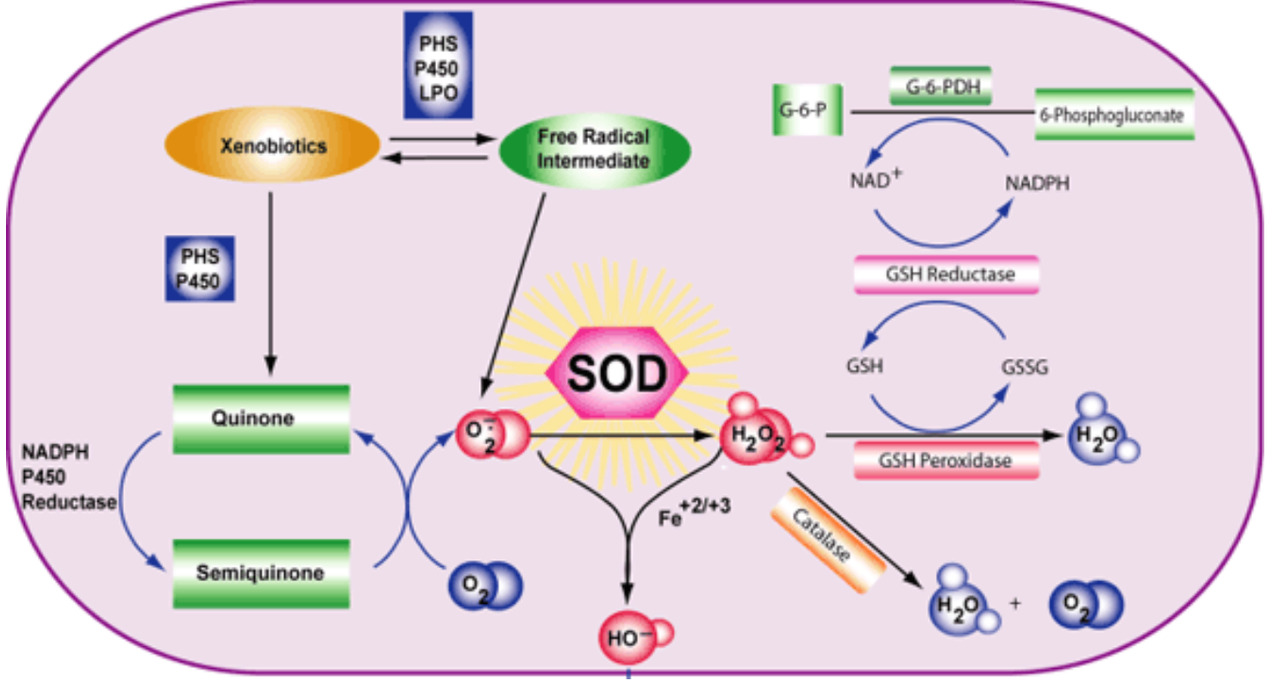
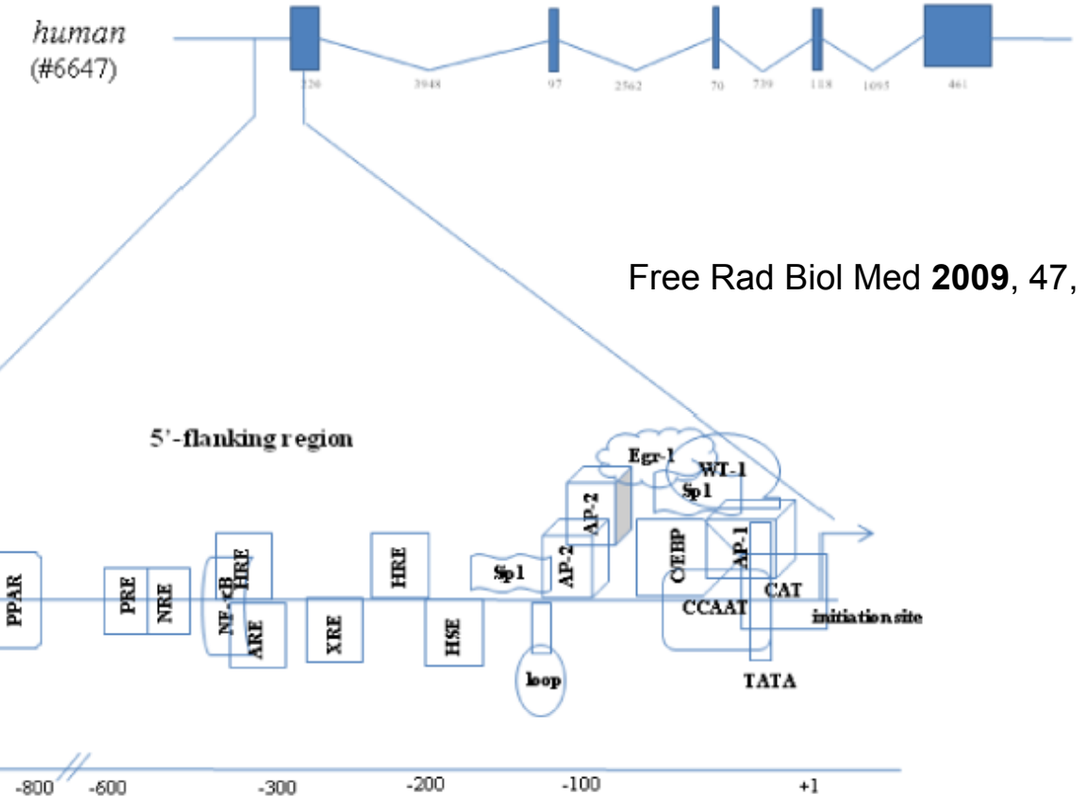
Using Chemical Signals

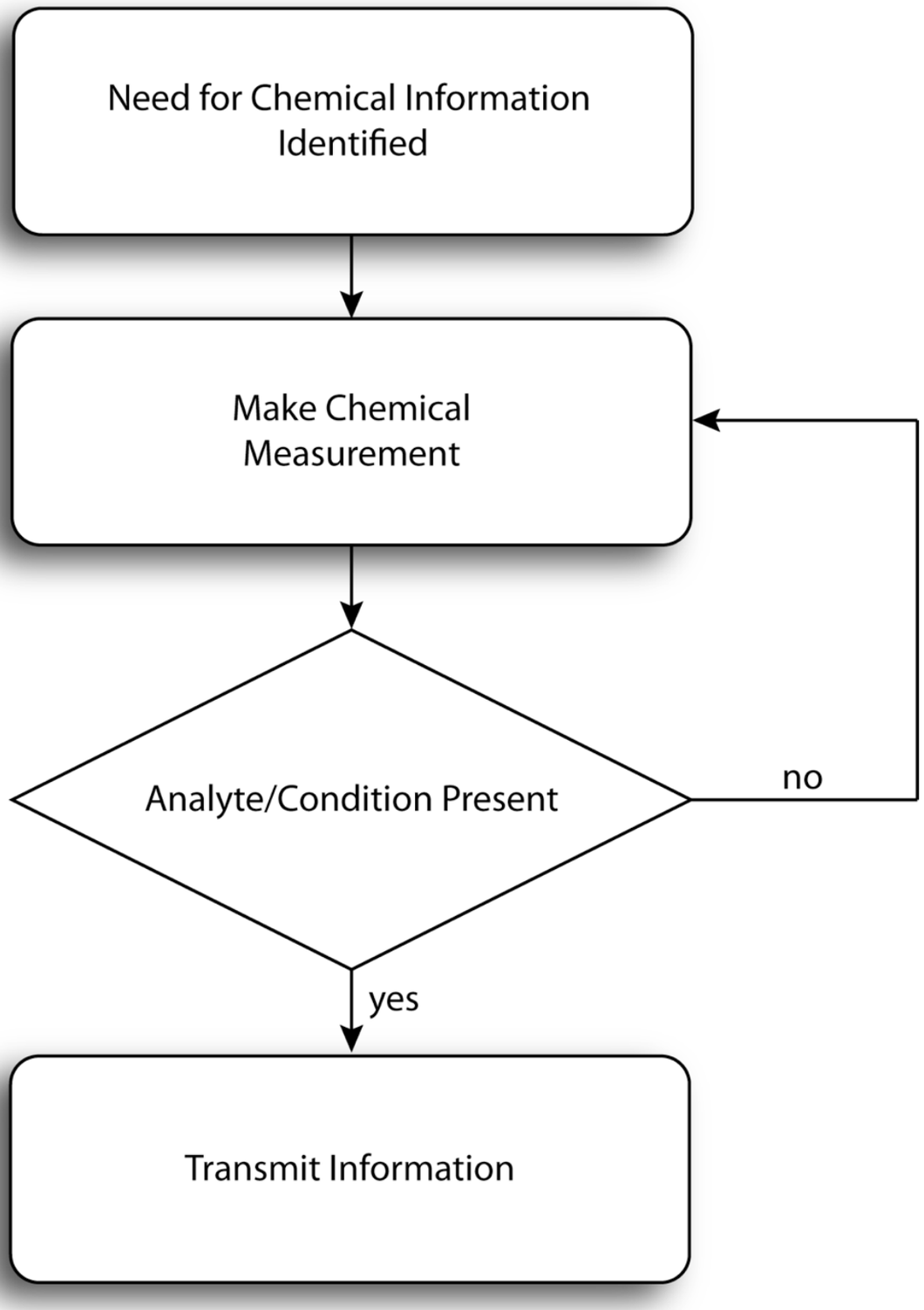
Using Chemical Signals

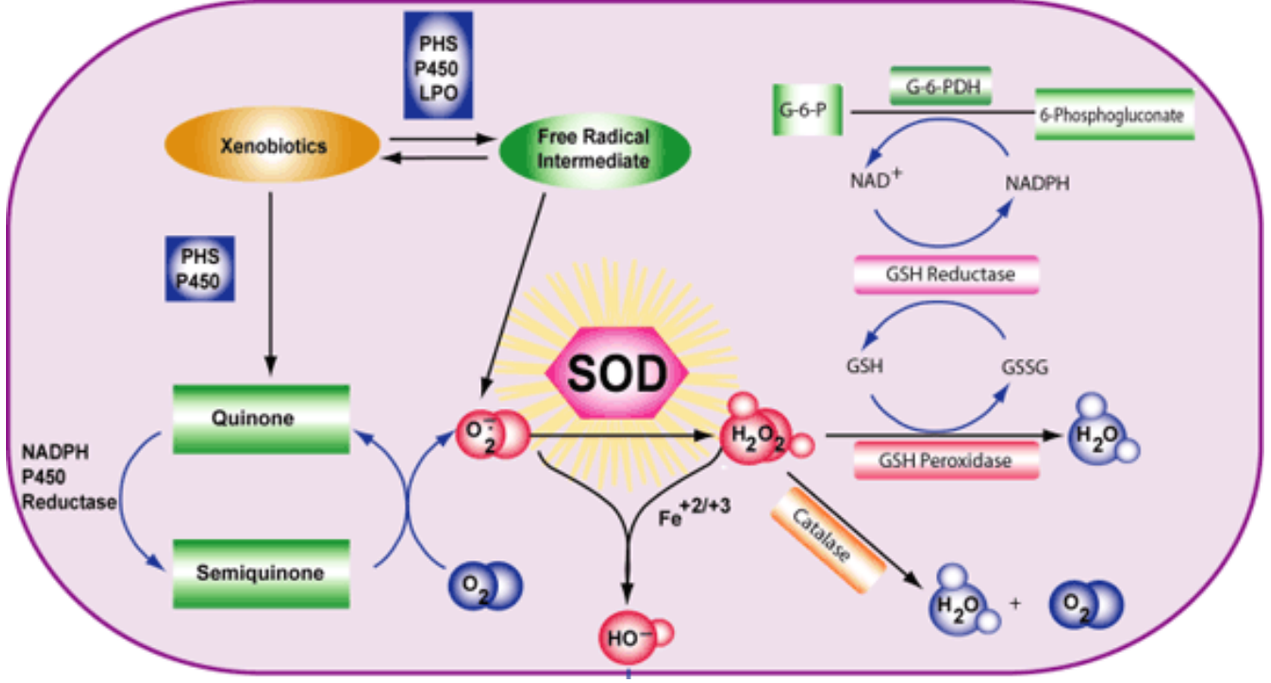


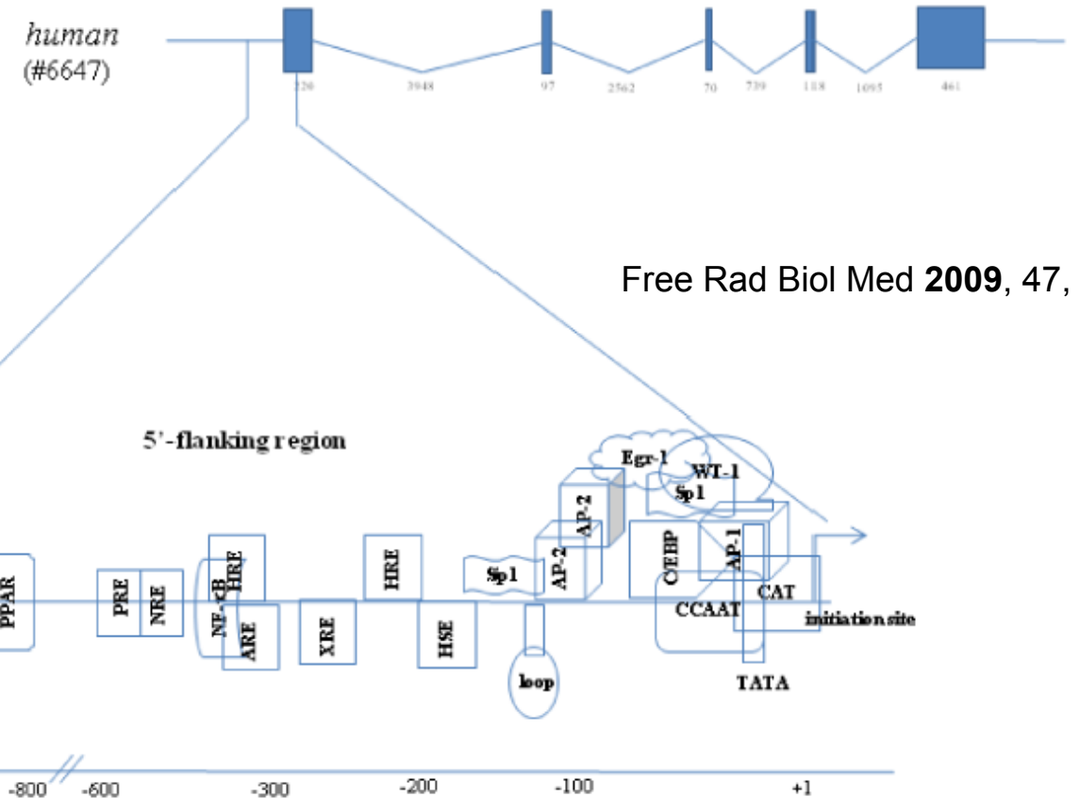


Free Rad Biol Med **2009**, 47, 344.

Using Chemical Signals







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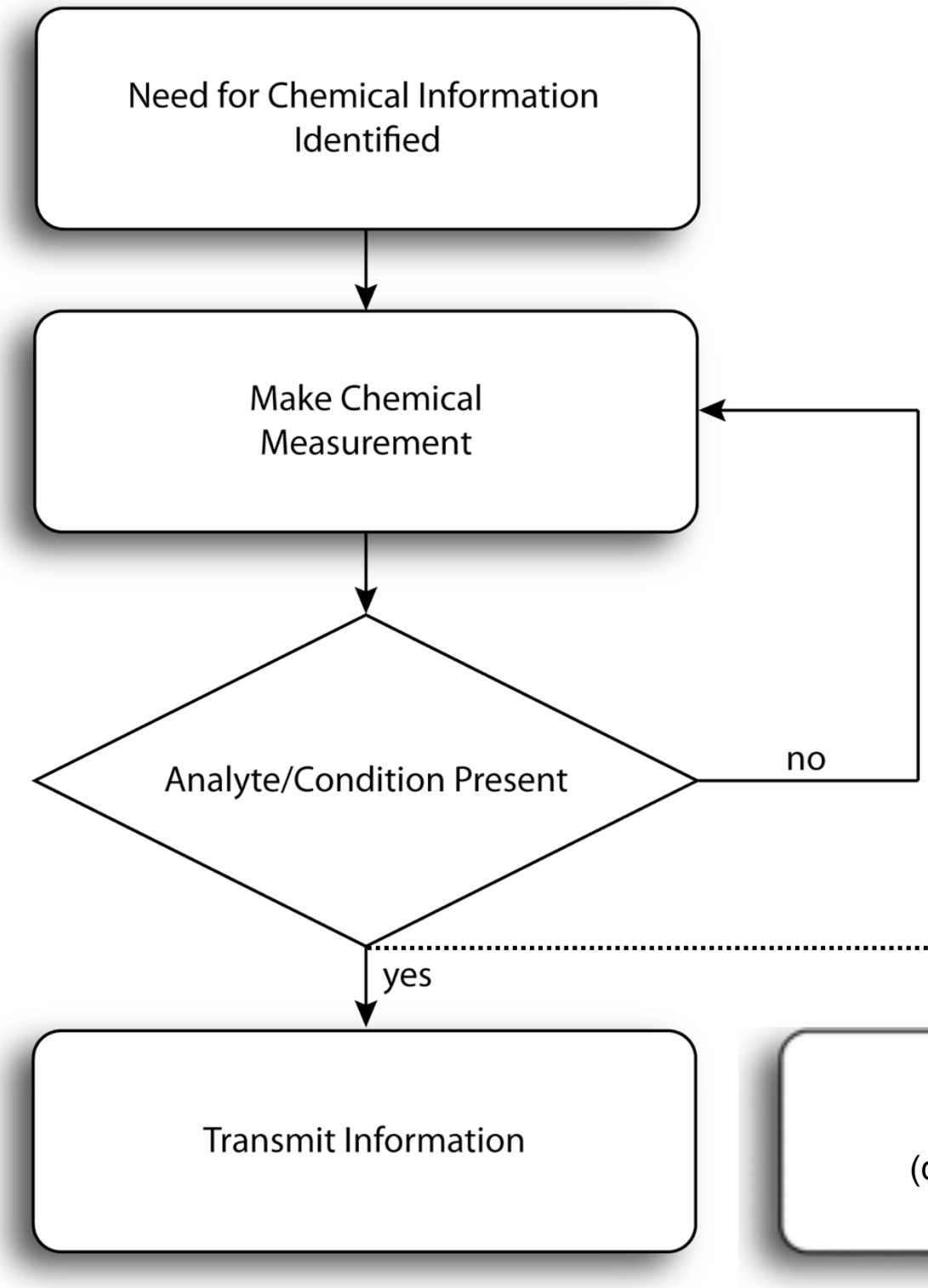

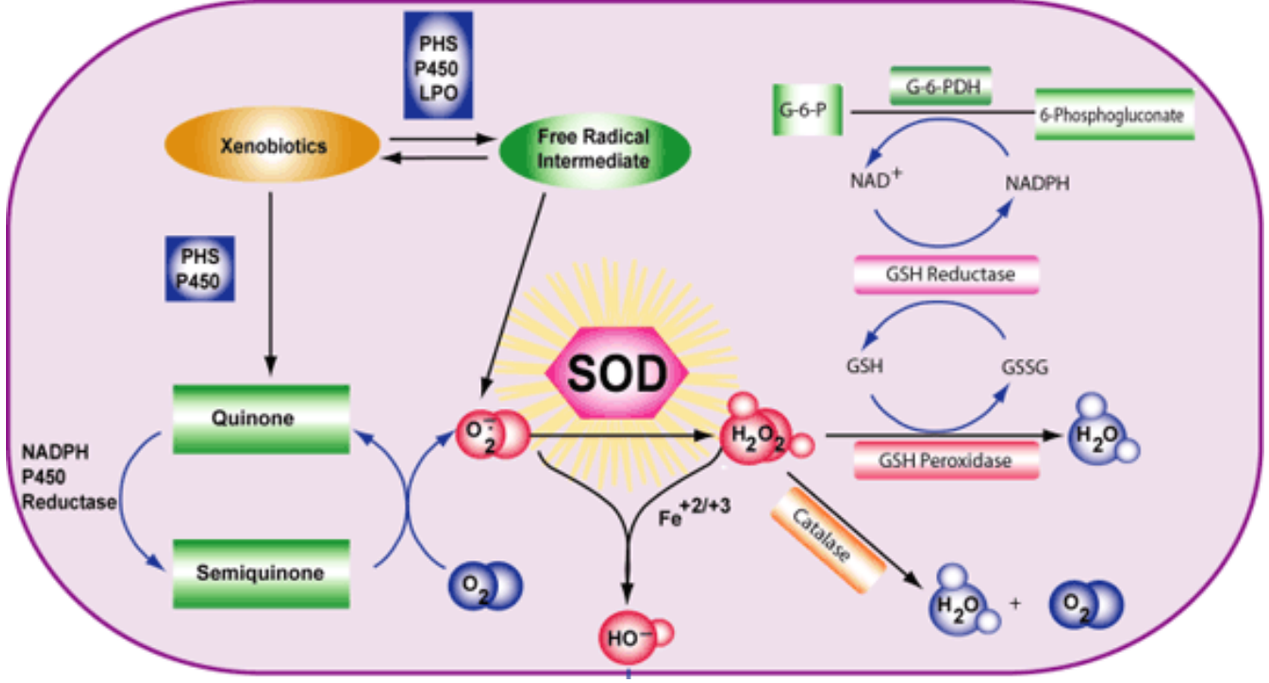

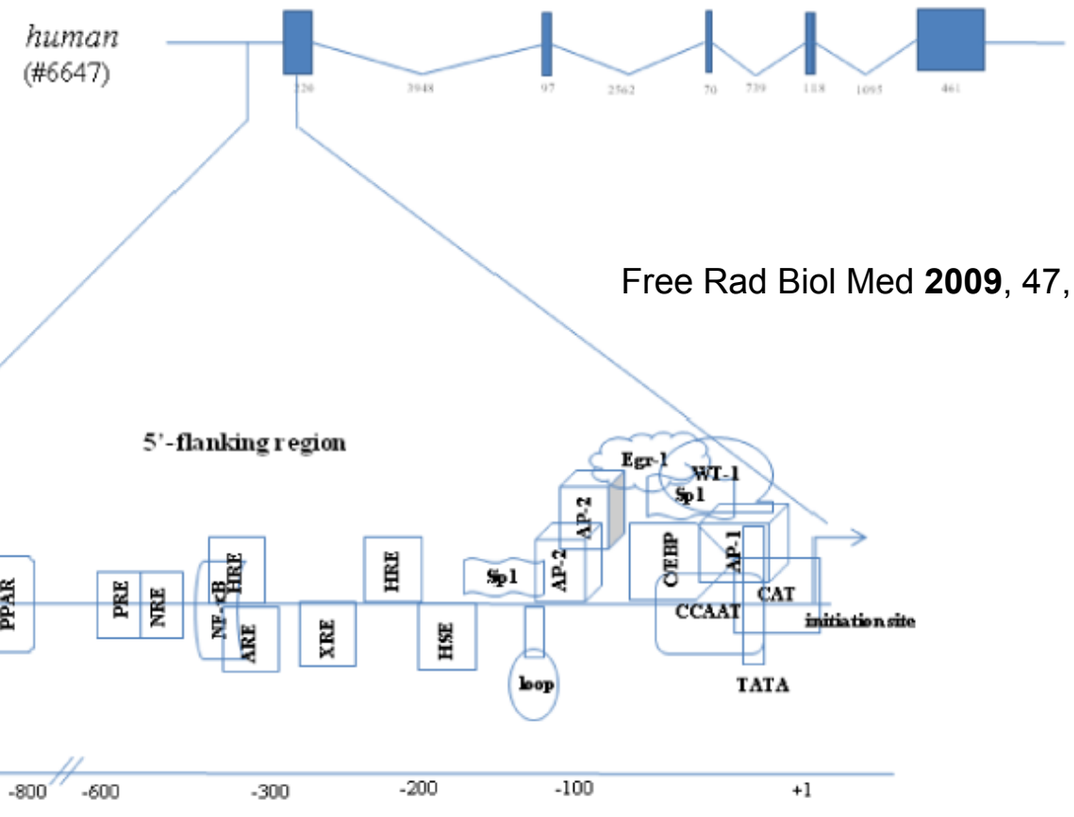

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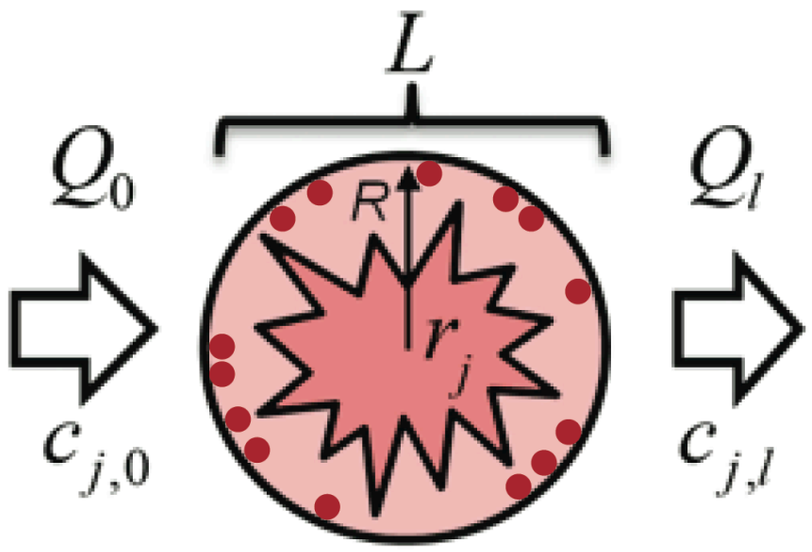
Idealized Nanoreactor

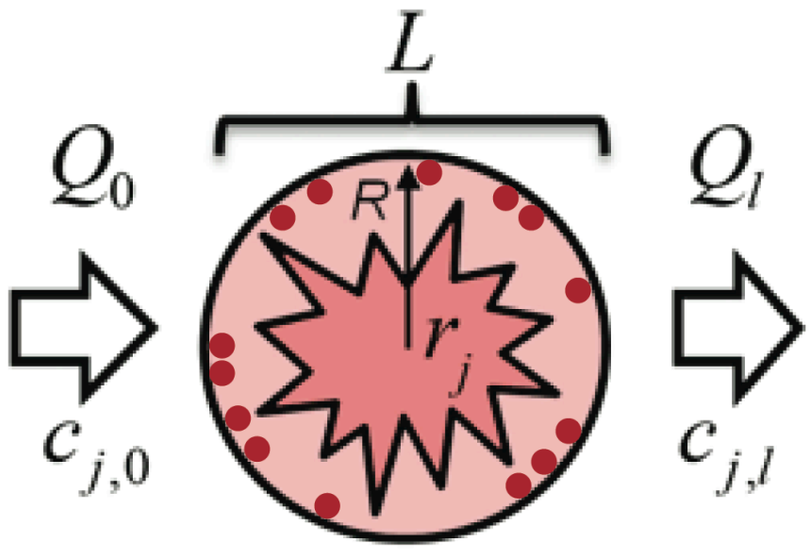


Optimizing Nanoreactors

$$\underbrace{\frac{\partial c_j}{\partial t}}_{accumulation} = \underbrace{\nabla \cdot (D_j \nabla c_j)}_{diffusive} - \underbrace{\nabla \cdot (\vec{v}_j c_j)}_{advective} + \underbrace{r_j}_{source/sink}$$

Optimizing Nanoreactors

Idealized Nanoreactor



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Reaction Limited

$$X = 1-\exp\left(-\frac{v_A}{2D_A}\left(\frac{2D_A k}{v_A^2}\right)L\right) = 1-\exp(-Da) \to 1$$

$$Da = \frac{kL}{v_A} > 10$$

For a mean velocity $v_A \sim 10^{-4}$ m s^{-1},

Da = $(10^3\ s^{-1})(10^{-6}\ m)/(10^{-4}\ m\ s^{-1}) \sim 10$

conversion efficiency is nearly perfect provided $L \geq 1$ μm along the longitudinal direction.

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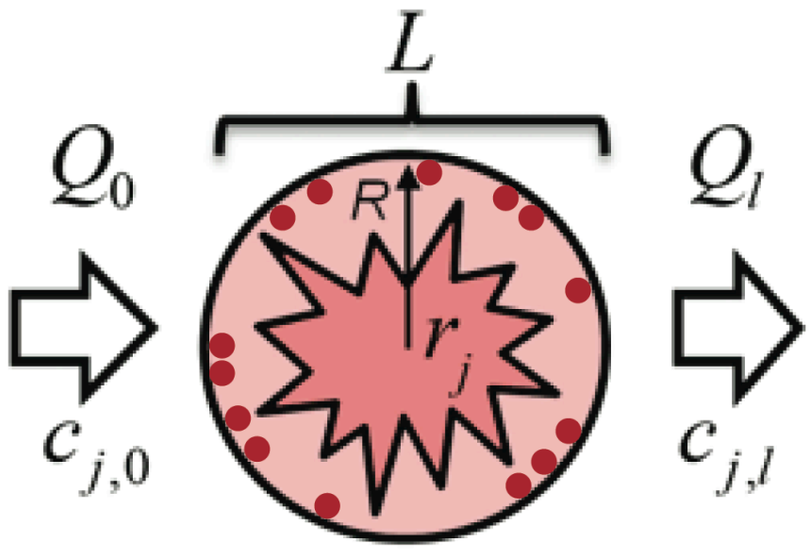

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Mass Transport Limited

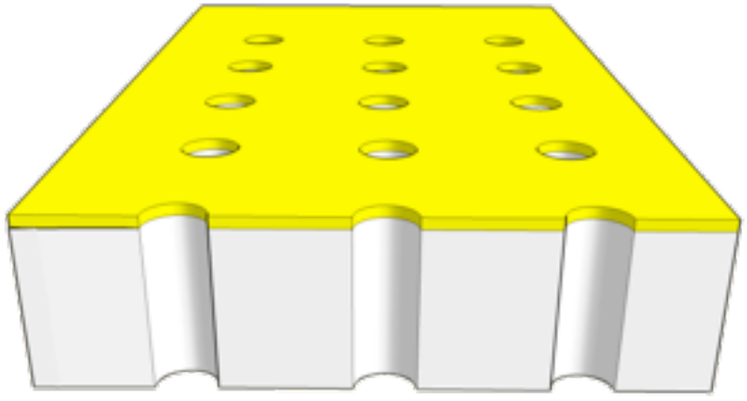
$$X = 1-\exp\left(-2\frac{L}{R}\frac{1}{Pe}\right)$$

$$Pe = \frac{v_A R}{D_A}$$

Aspect ratios are $L/R \sim 100$, so
Pe < 43 produces >99% conversion.

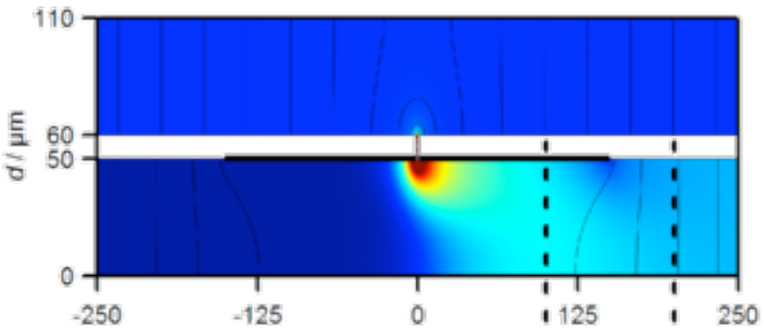
For a small volume reactor with $R < 1$ μm, conversion efficiency is nearly perfect, even with fast advective flow $v_a \sim 10^{-2}$ m·s^{-1}.

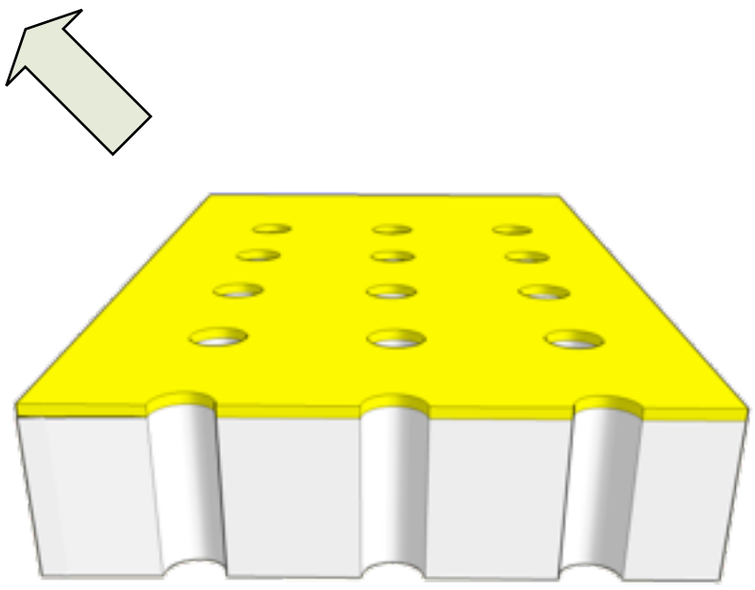
1-D Metal-Dielectric Nanostructures



1-D Metal-Dielectric Nanostructures

Electrokinetic transport





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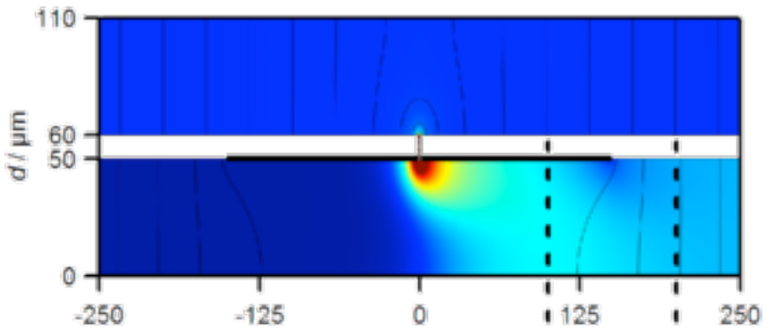
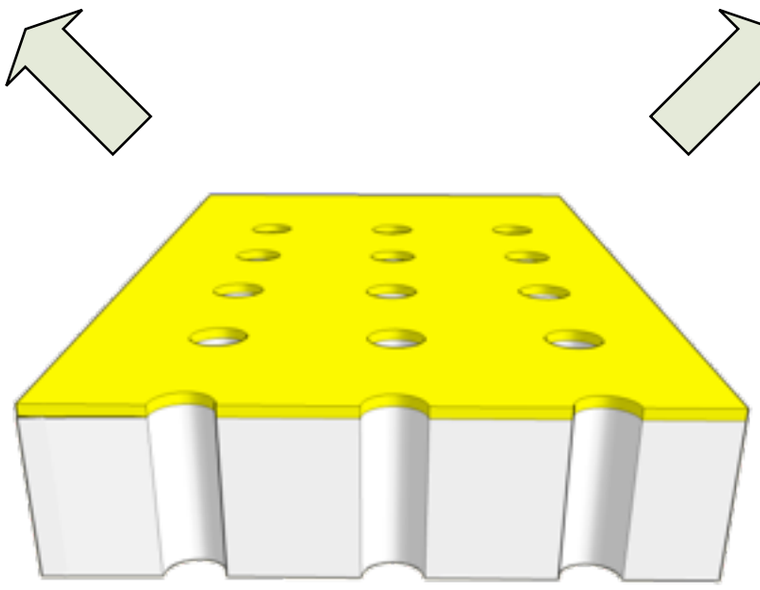
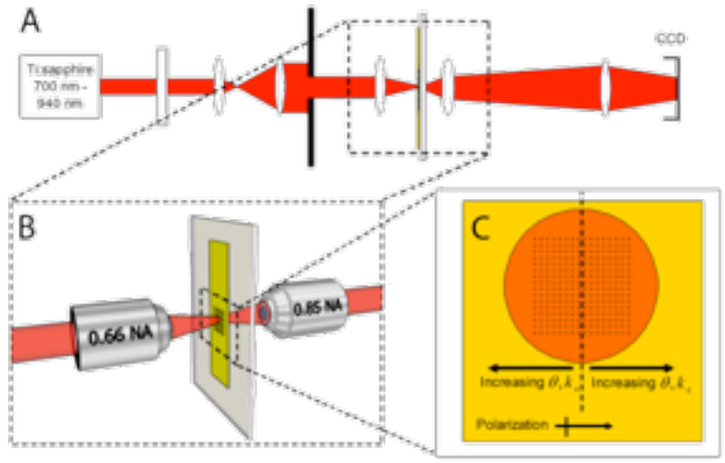




Optical properties



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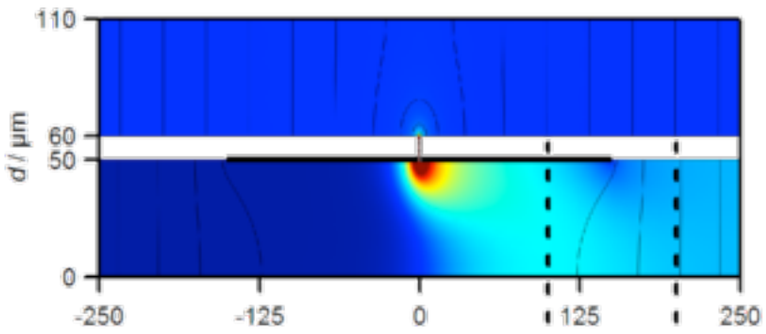
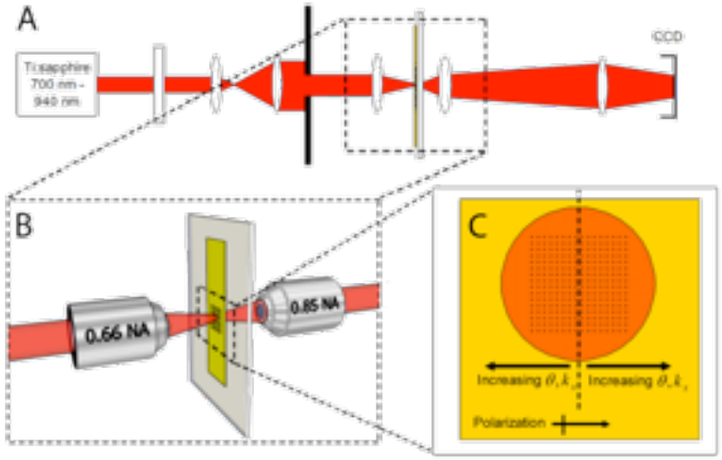
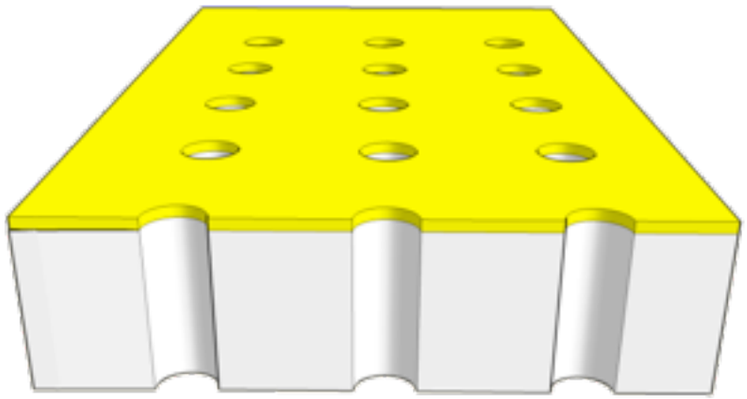
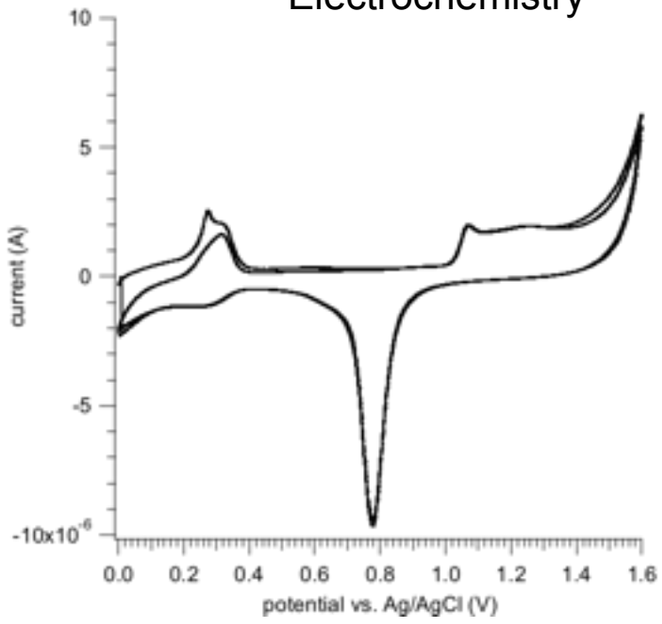


Optical properties



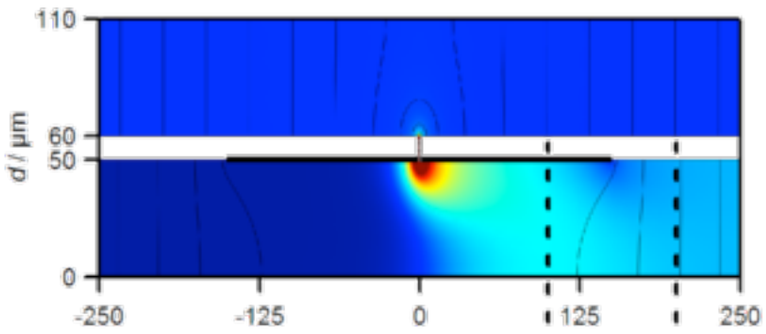


Electrochemistry



1-D Metal-Dielectric Nanostructures

Electrokinetic transport



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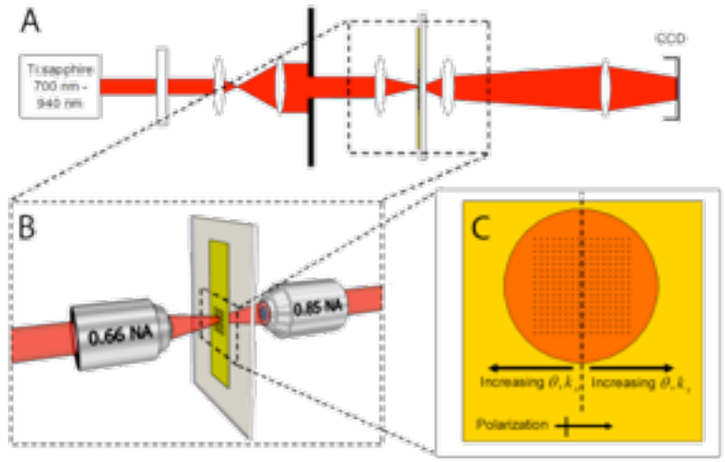
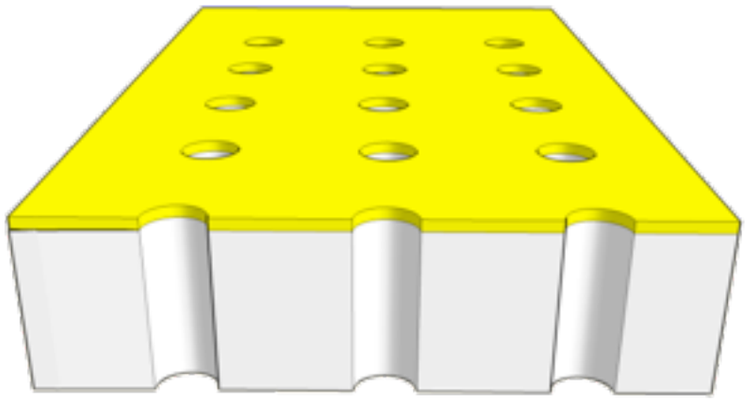
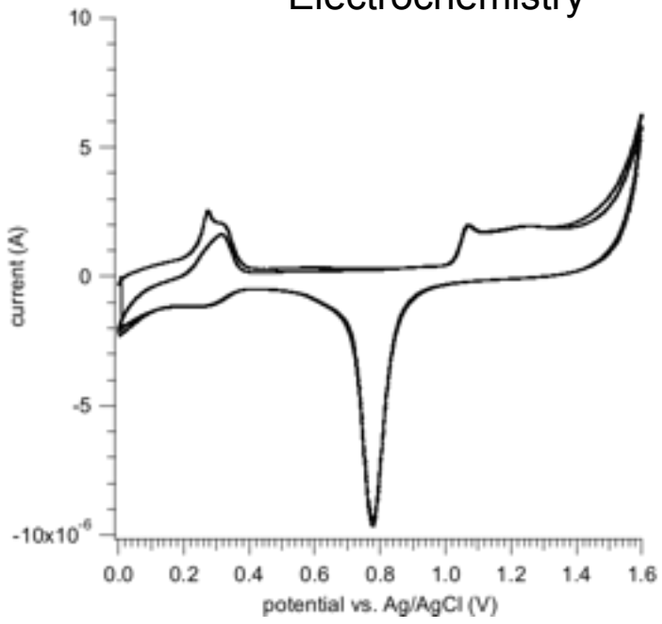
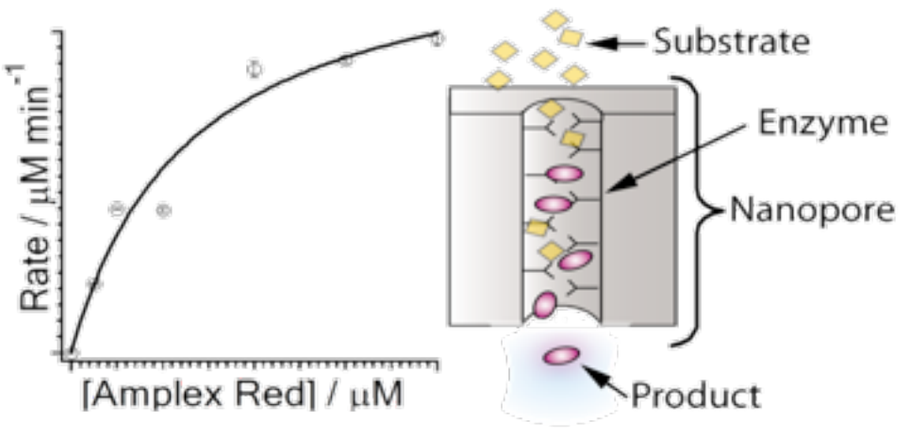




Electrochemistry



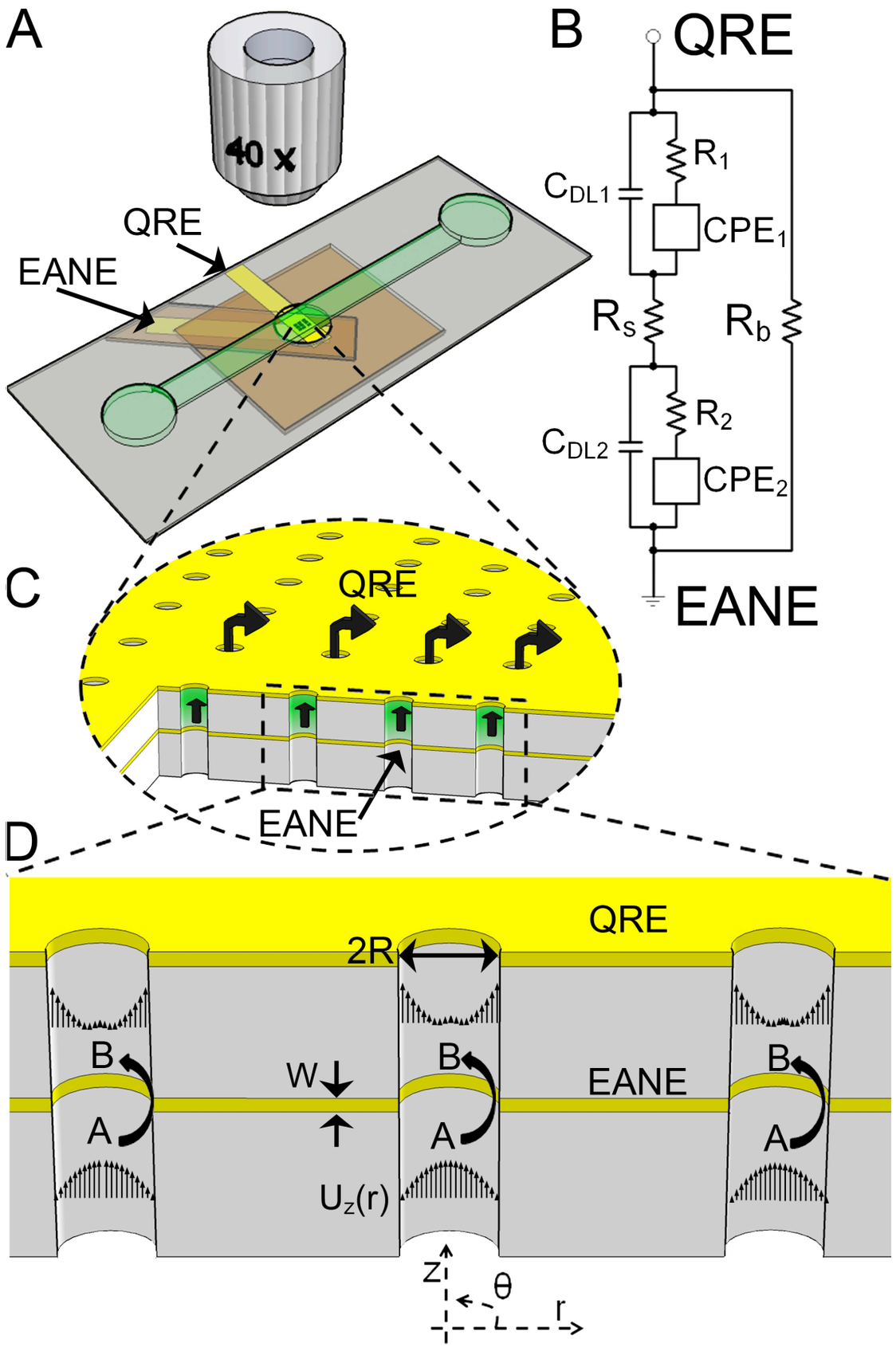
Enzyme-catalytic support



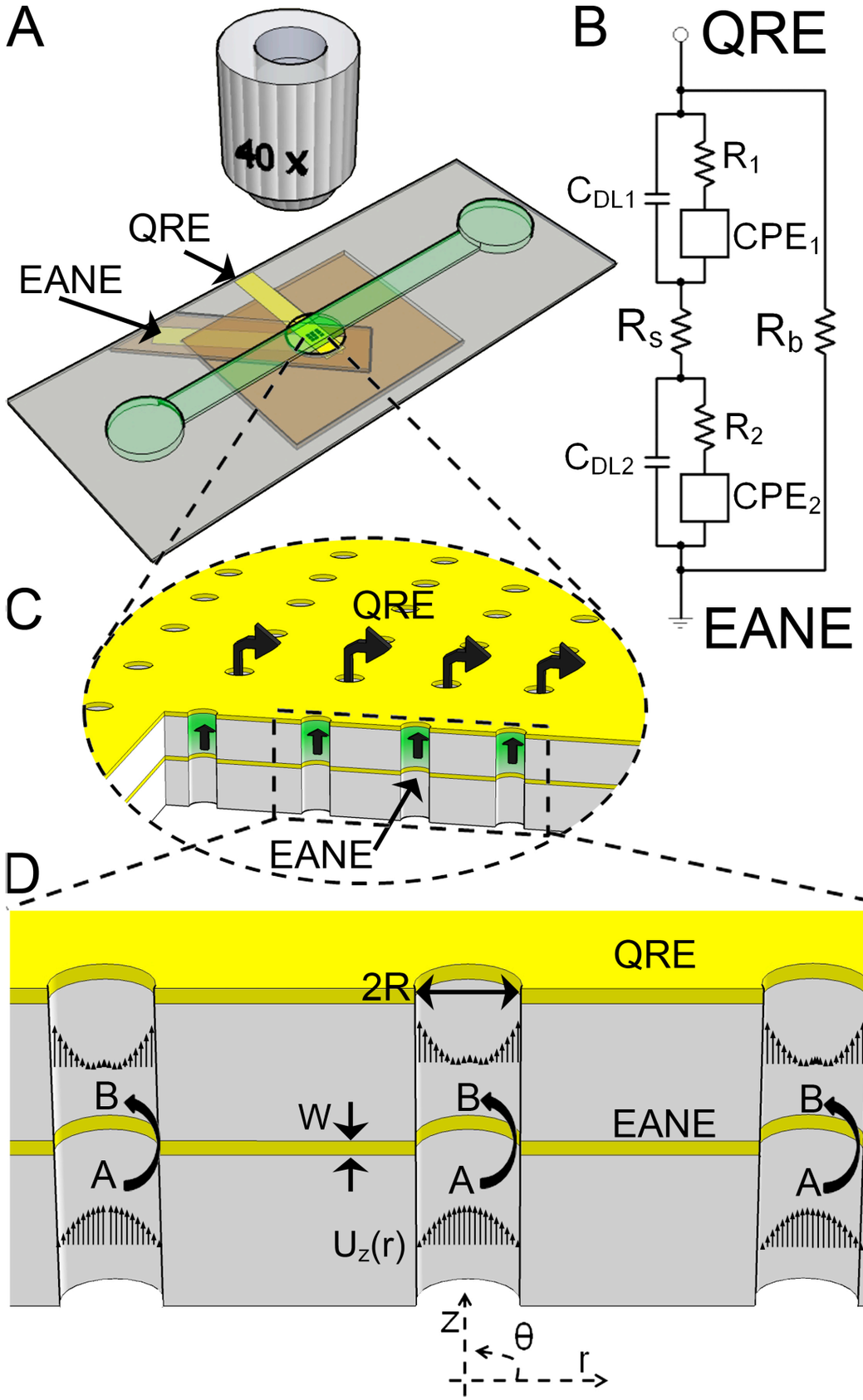
I. 1-Dimensional Nanostructures

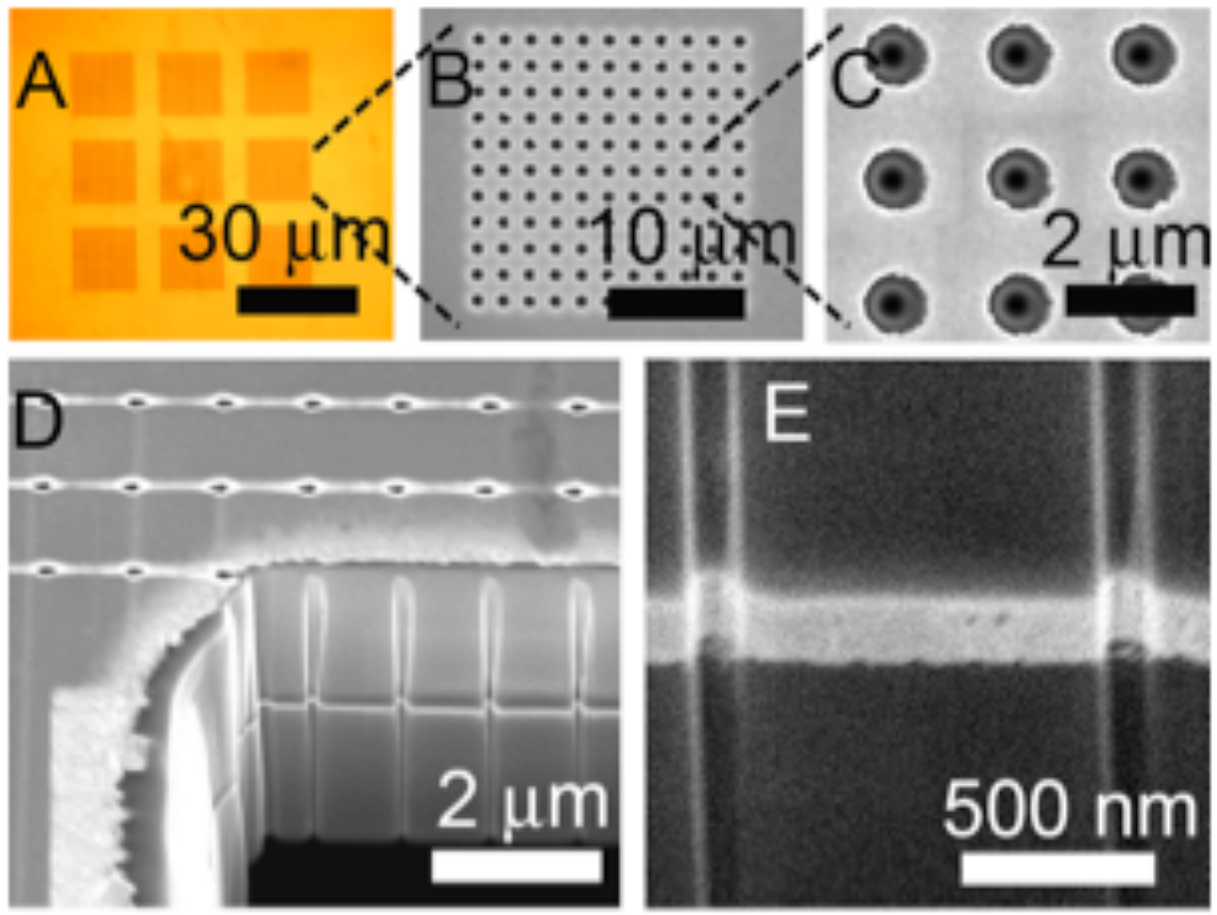
Embedded Annular Nanoband Electrode Arrays

Embedded Annular Nanoband Electrodes



Embedded Annular Nanoband Electrodes





$Fe(CN)_6^{3-/4-}$ EANE Simulations

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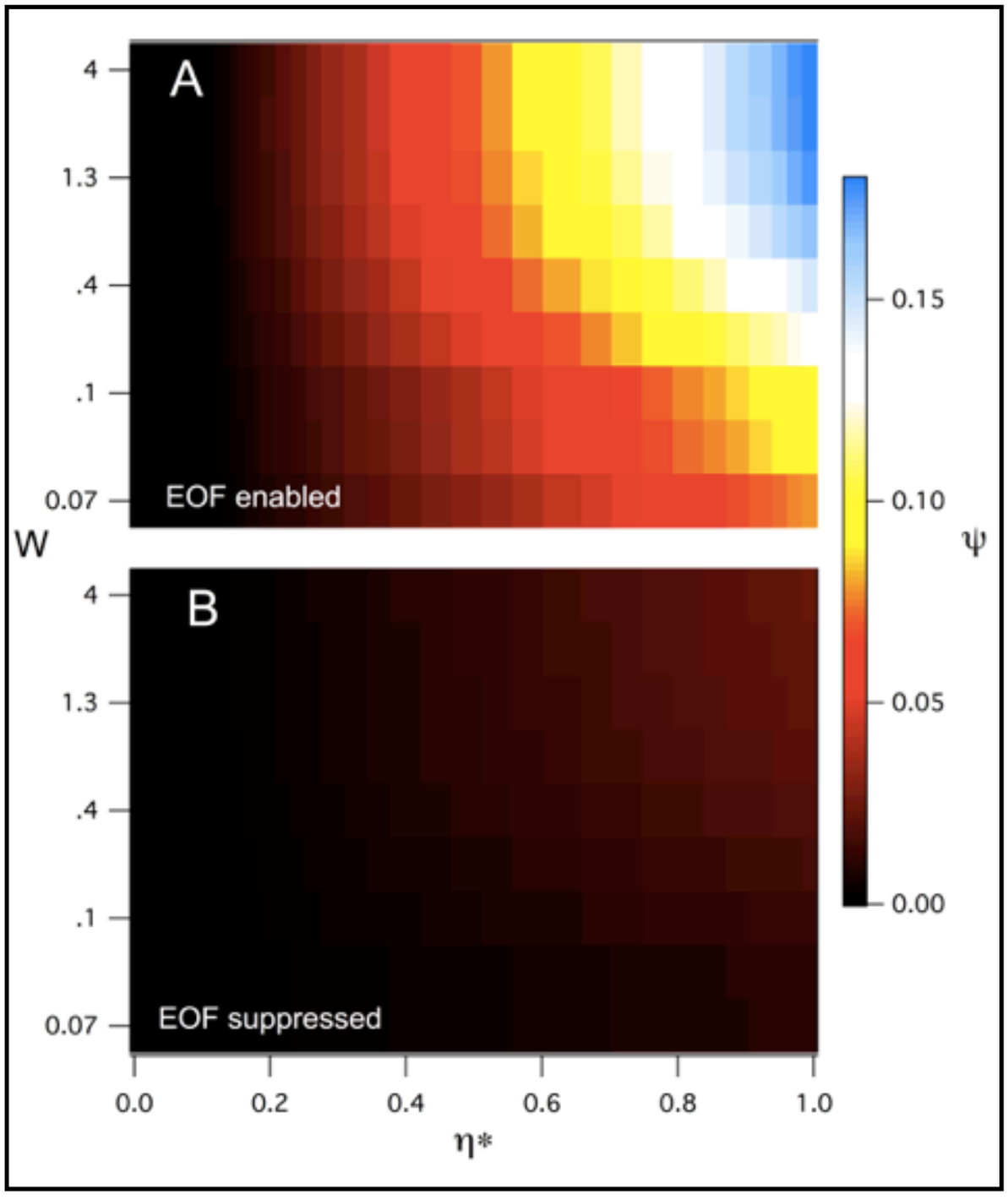

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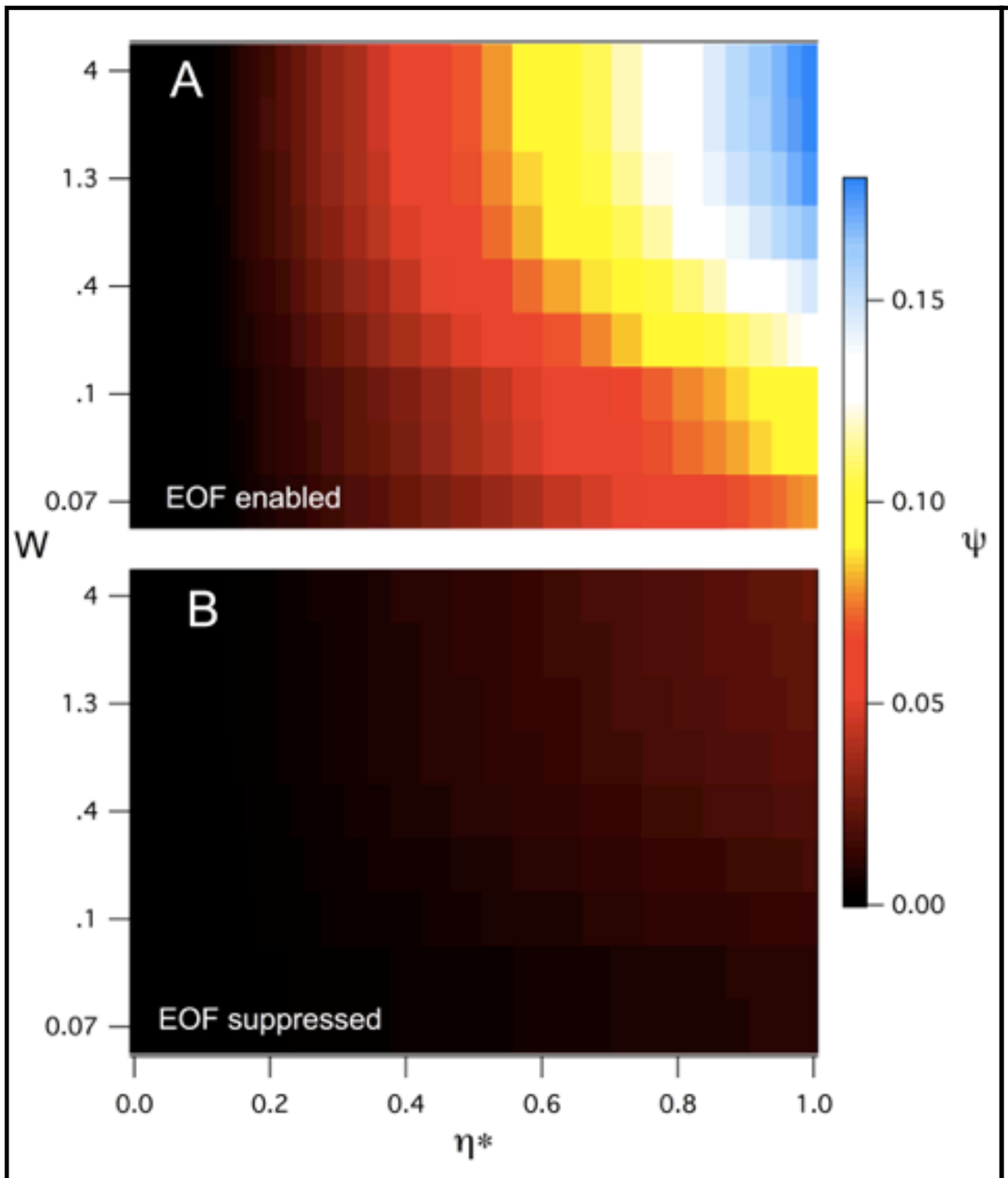

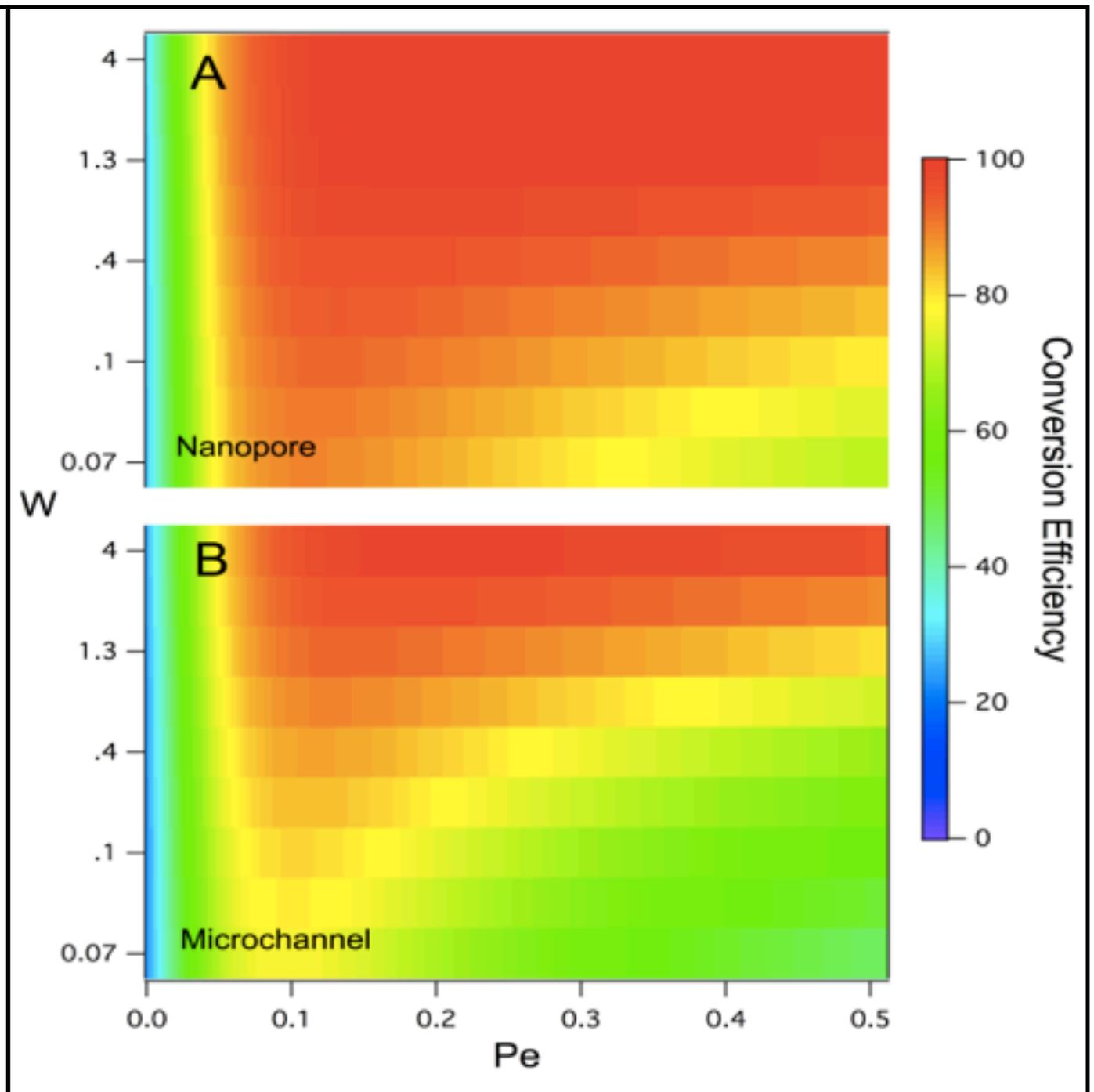

EANE Experiment/Simulation

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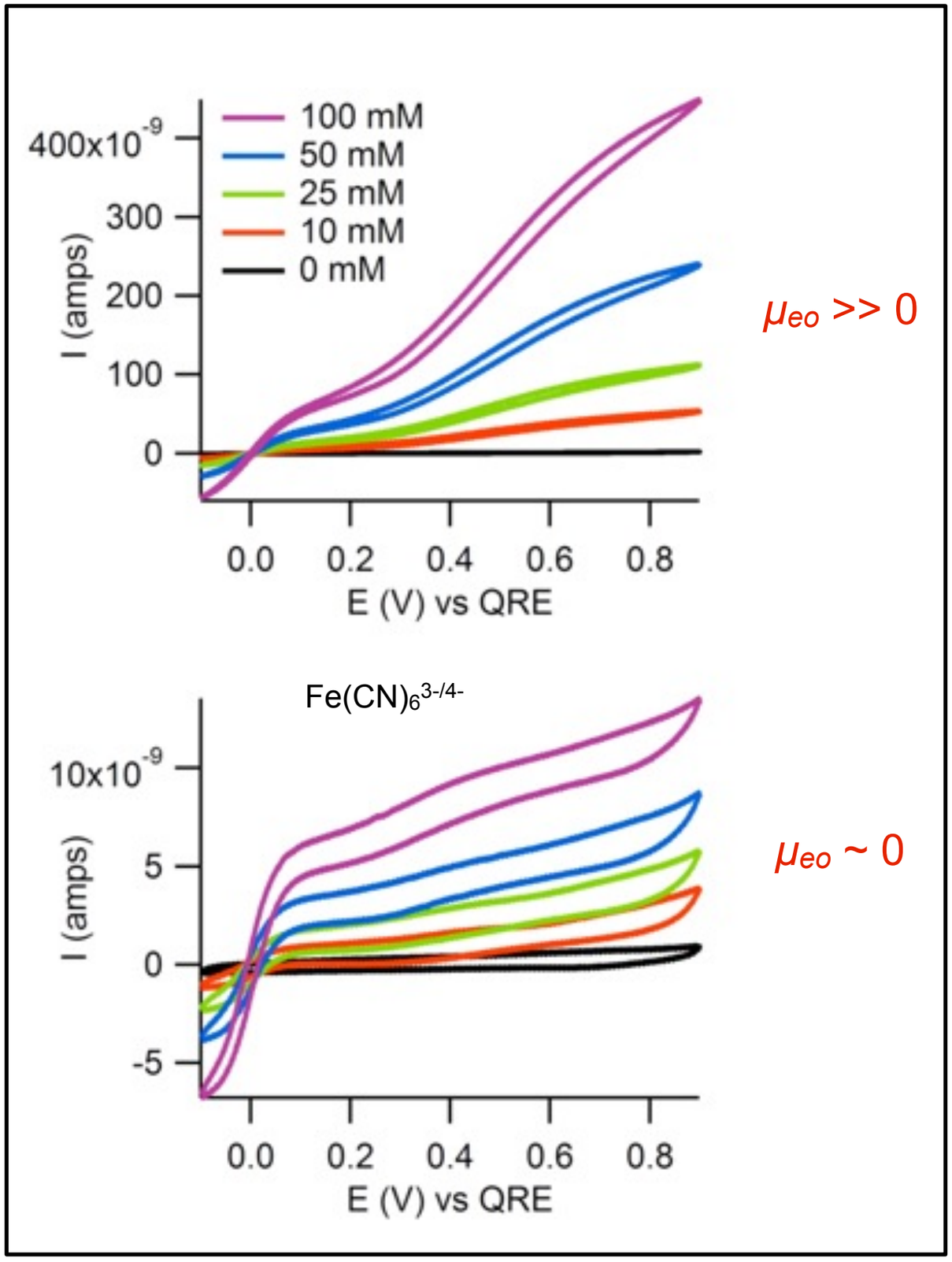
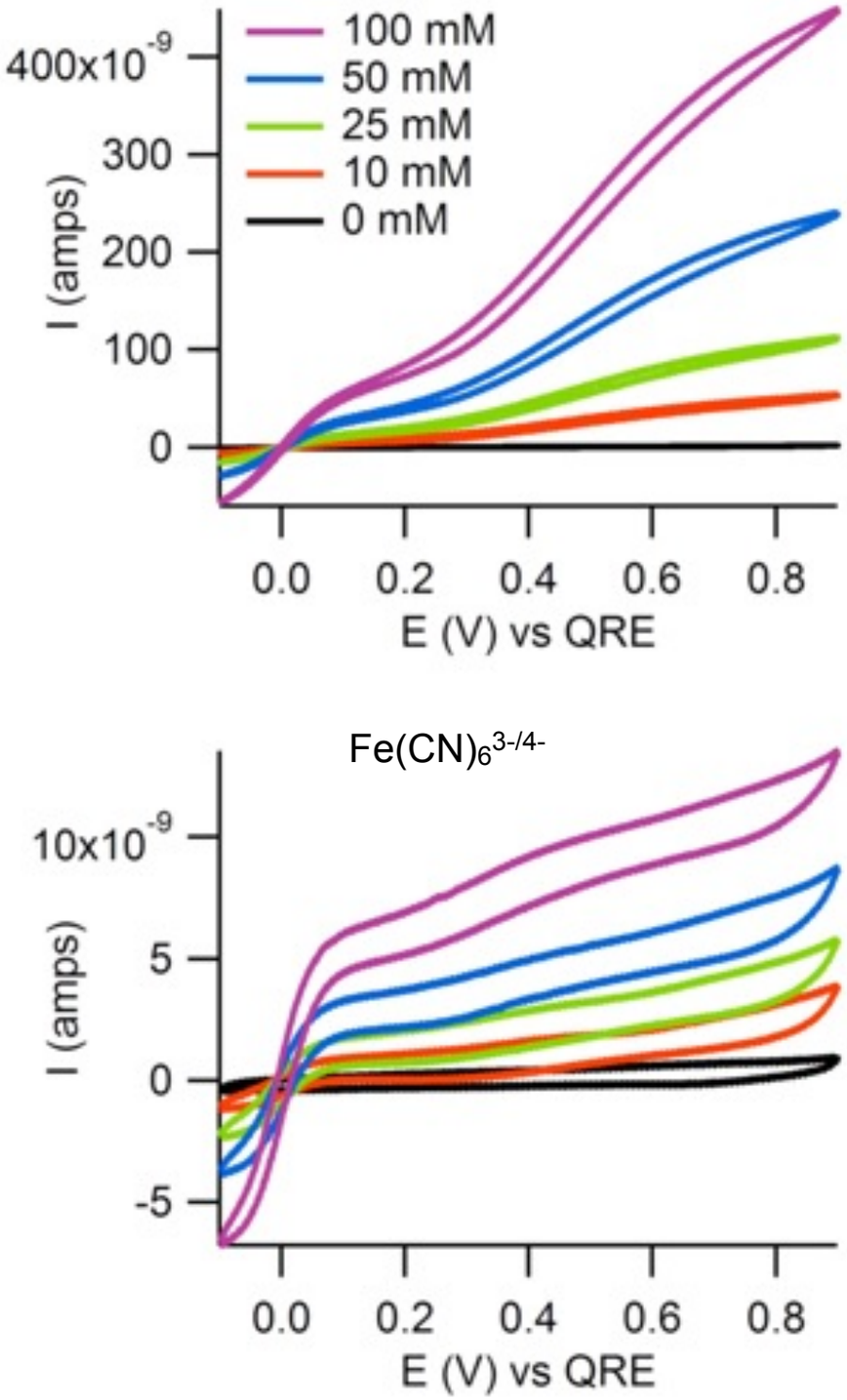


$\mu_{eo} >> 0$

$\mu_{eo} \sim 0$

EANE Experiment/Simulation



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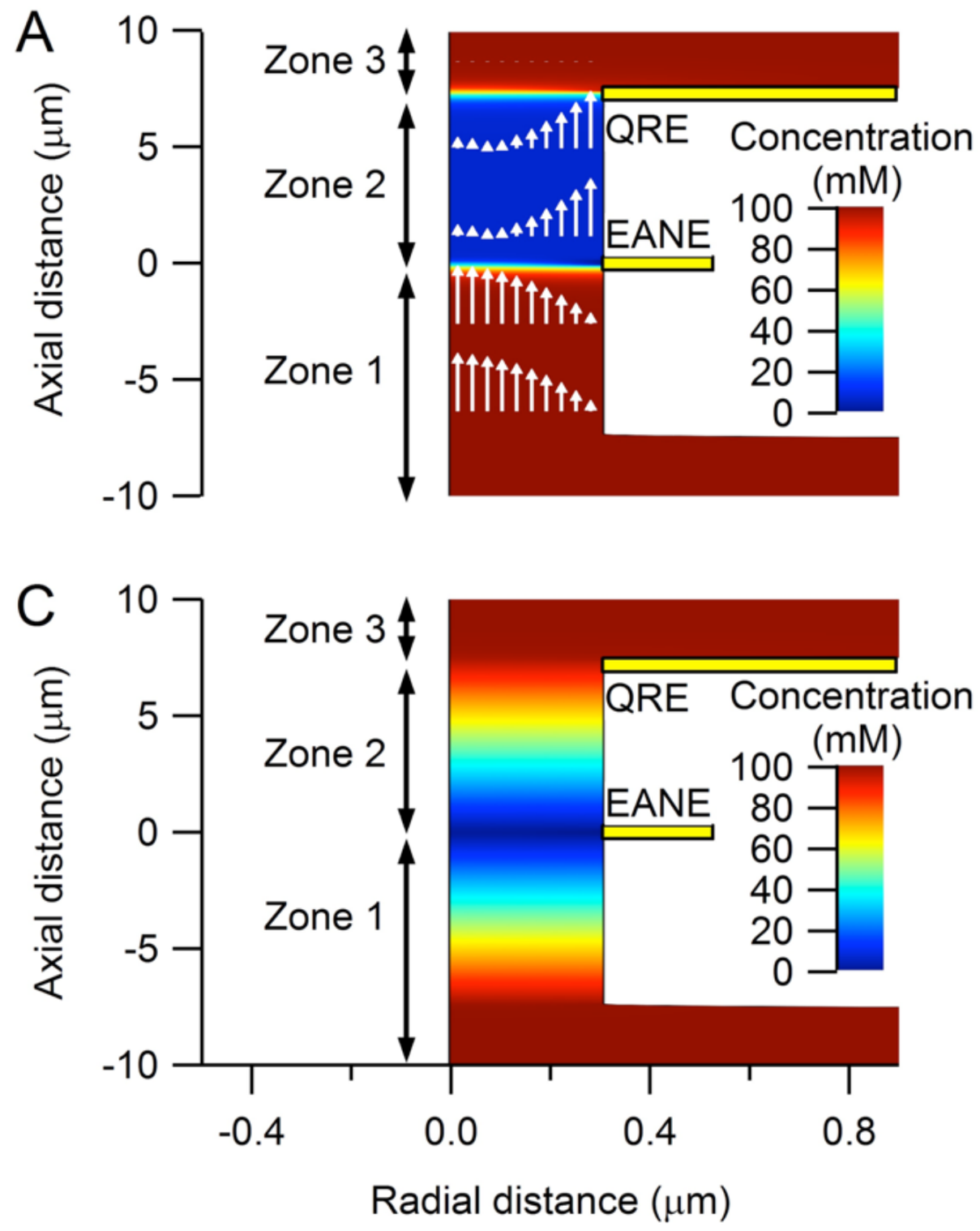
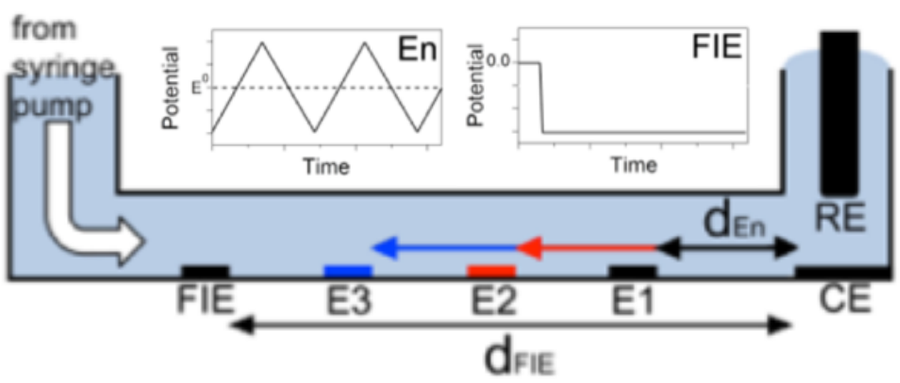


Microchannel-EANE Array Apples-to-Apples Comparison

Description[a]	Flow condition	i_f at $\eta \approx 0.5$ V (nA)	J at $\eta \approx 0.5$ V ($A \cdot cm^{-2}$)	X
EANE experiment: 121 pores Pore dia = 603 ± 60 nm	$u_{avg} \approx 1.5$ mm/s	447	0.979	0.93 ± 0.21
	$u_{avg} \approx 0$ mm/s	12.6	0.028	---
EANE simulation: 1 pore Pore dia = 600 nm	$u_{avg} \approx 1.5$ mm/s	470 (121 pores)	1.03	0.95
	$u_{avg} \approx 0$ mm/s	30.1 (121 pores)	0.066	---
Microchannel experiment: Width = 50 μm Height = 50 μm Electrode width = 40 μm	$u_{avg} \approx 1.1$ mm/s	3100	0.155	0.15
	$u_{avg} \approx 0$ mm/s	1510	0.0755	---
Microchannel theoretical prediction: Width = 50 μm Height = 50 μm Electrode width = 40 μm	$u_{avg} \approx 1.5$ mm/s	1,540	0.0773	0.053

II. A Closer Look at the Coupling of Transport and Electron Transfer


from
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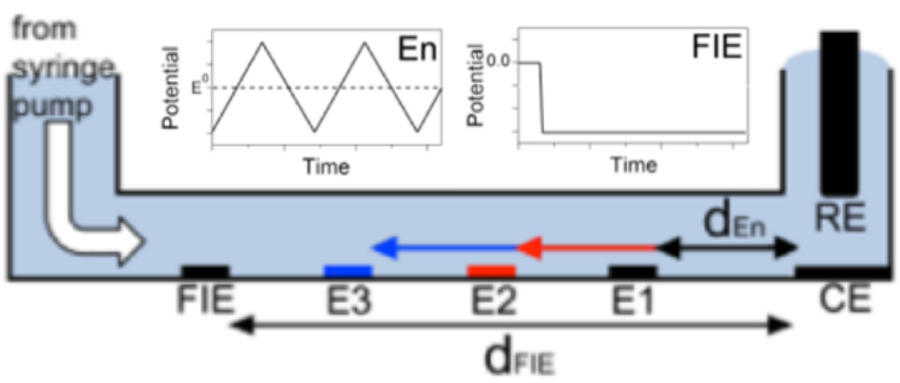
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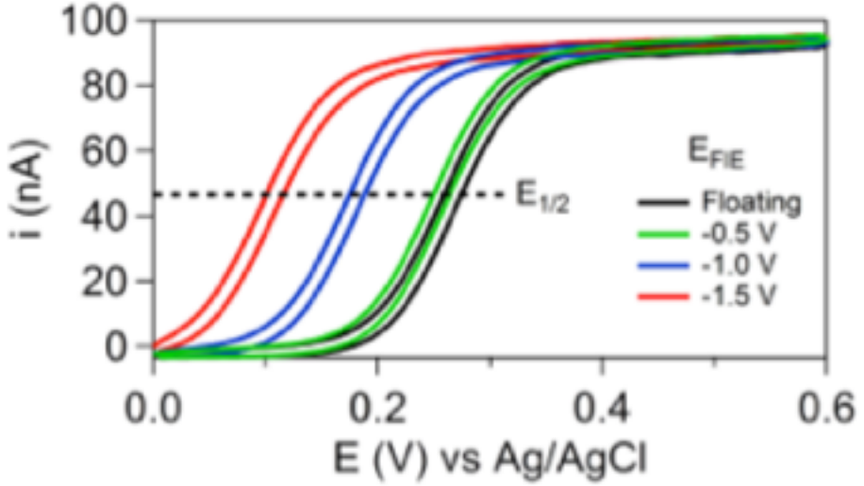
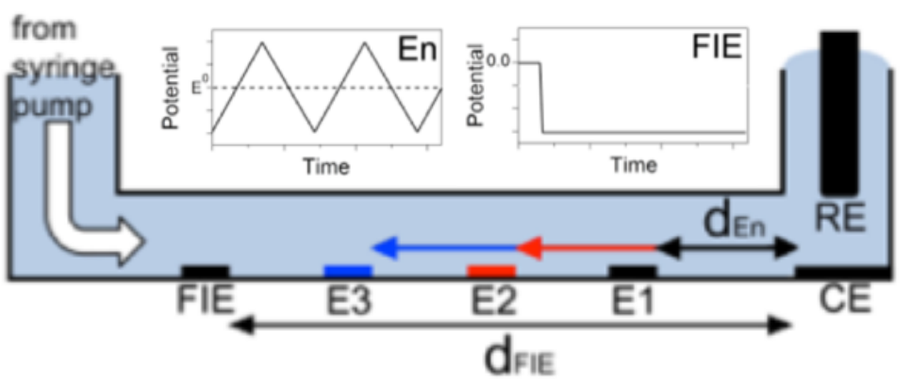

i (nA)
100
80
60
40
20
0
0.0
0.2
0.4
0.6
E (V) vs Ag/AgCl
$E_{1/2}$
E_{FIE}
Floating
-0.5 V
-1.0 V
-1.5 V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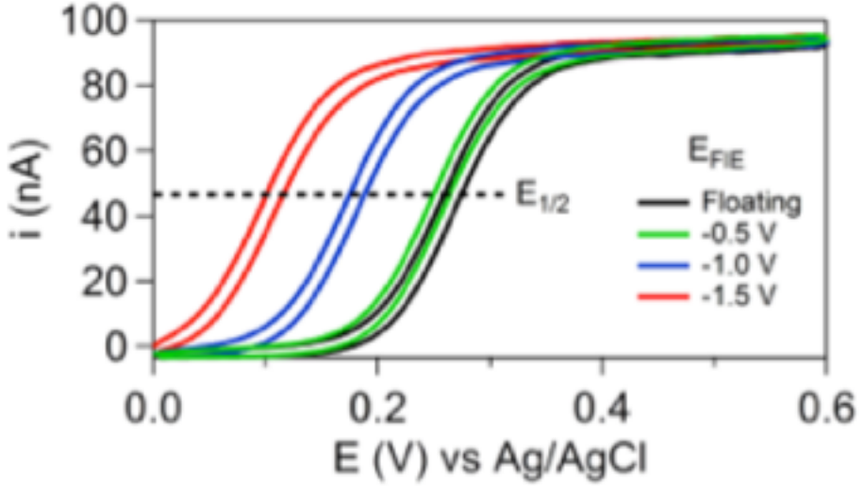
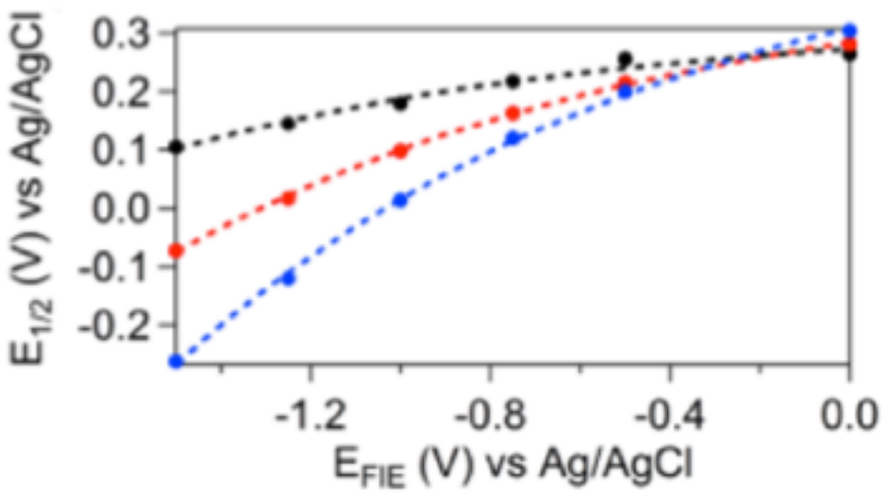
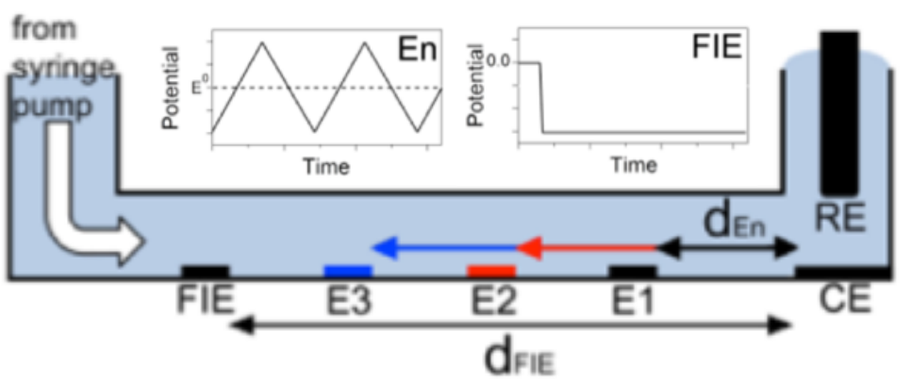

i (nA)
E (V) vs Ag/AgCl
$E_{1/2}$
E_{FIE}
Floating
-0.5 V
-1.0 V
-1.5 V


$E_{1/2}$ (V) vs Ag/AgCl
E_{FIE} (V) vs Ag/AgCl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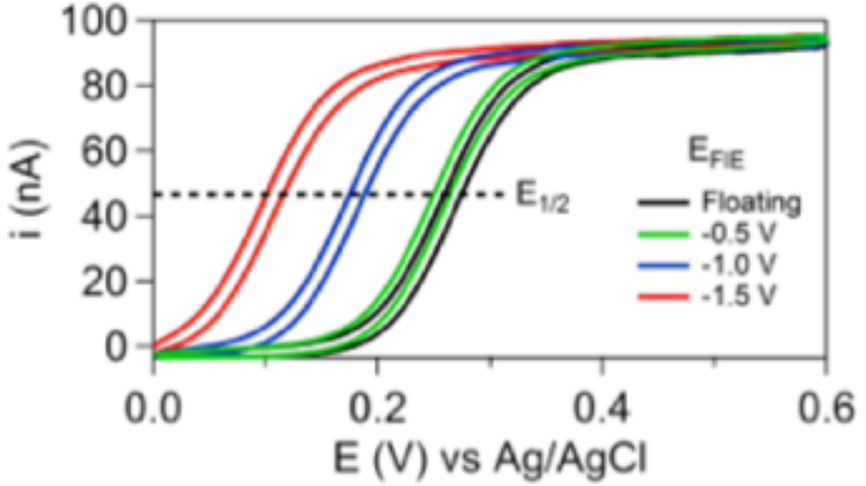
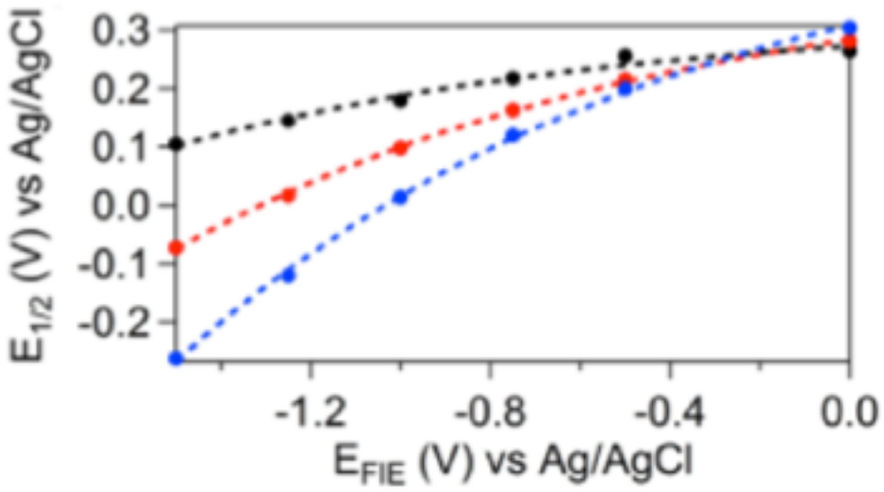
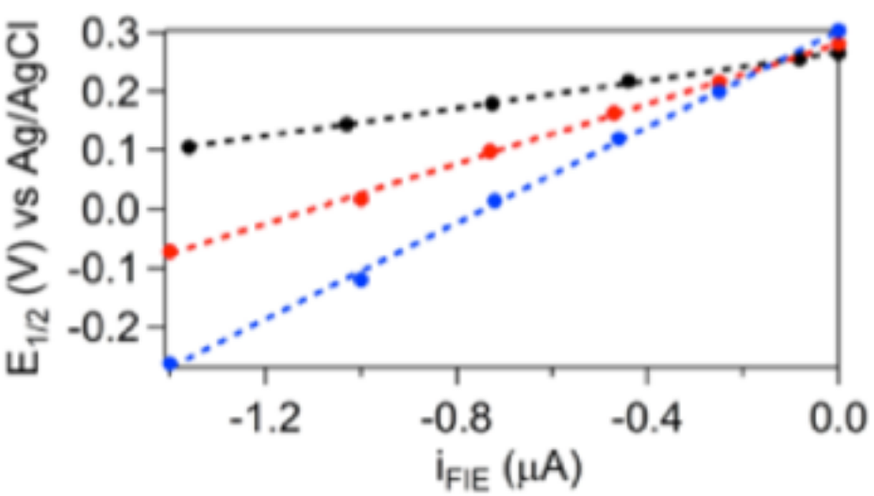
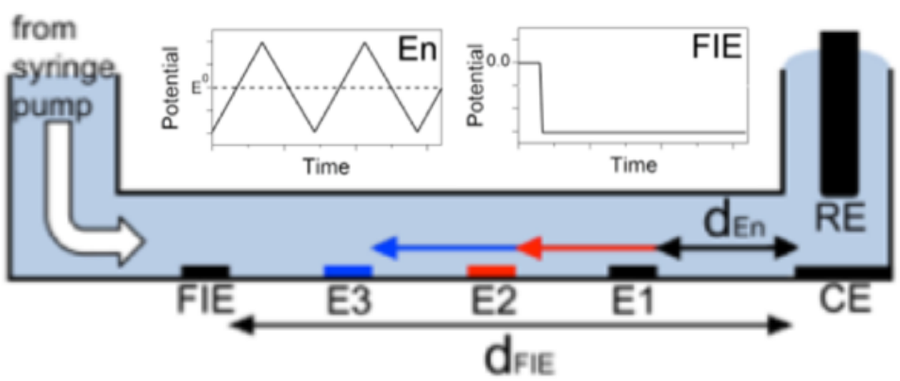

i (nA)
$E_{1/2}$
E_{FIE}
Floating
-0.5 V
-1.0 V
-1.5 V
E (V) vs Ag/AgCl


$E_{1/2}$ (V) vs Ag/AgCl
E_{FIE} (V) vs Ag/AgCl


$E_{1/2}$ (V) vs Ag/AgCl
i_{FIE} (μA)


from
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Potential
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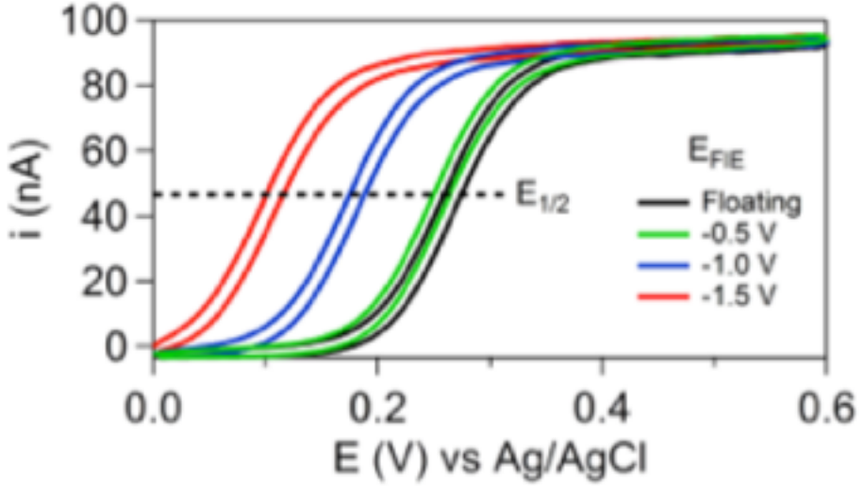
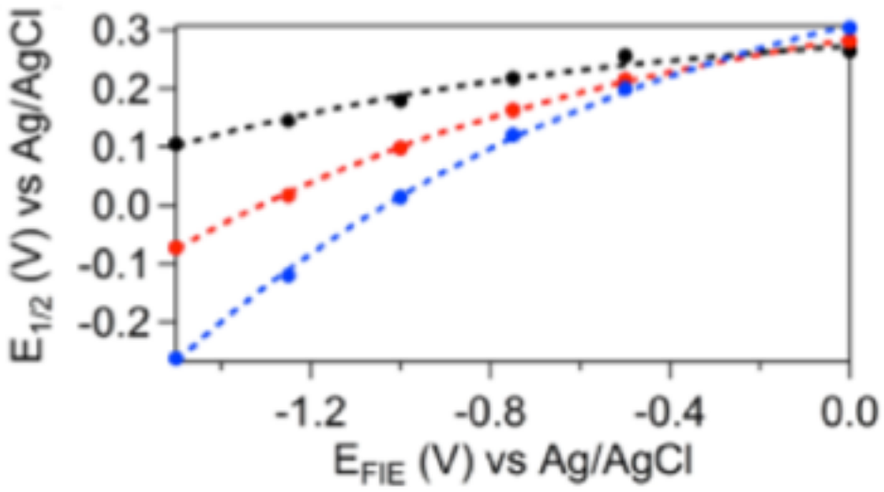
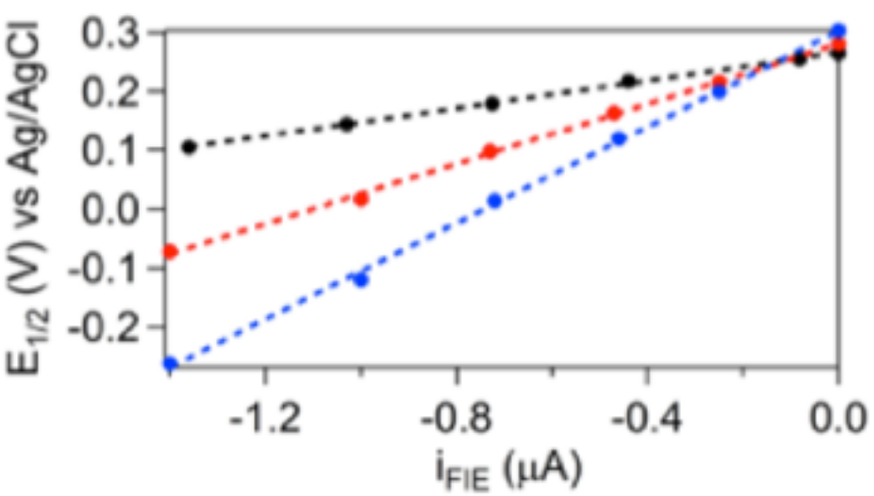
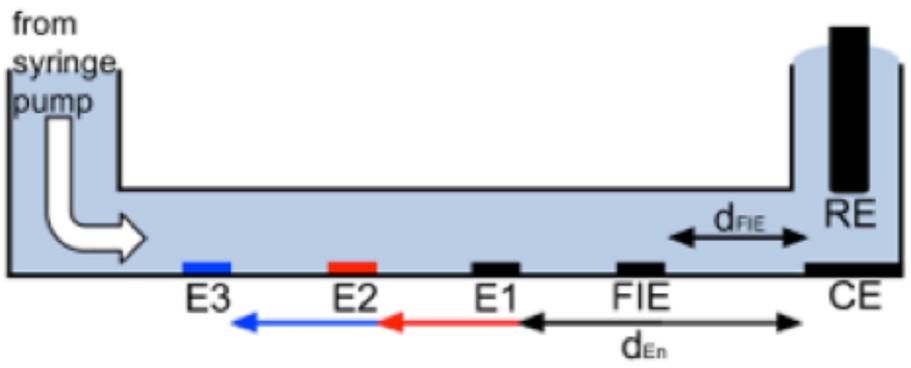
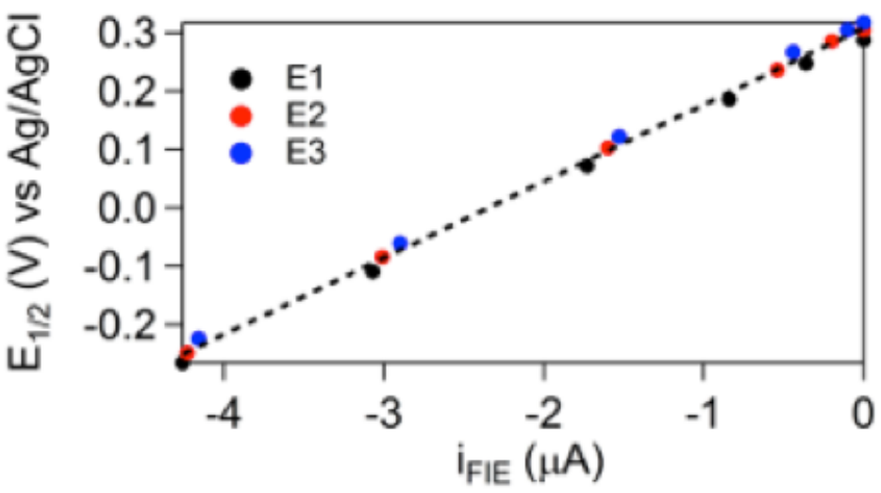
E3
E2
E1
CE
d_{FIE}

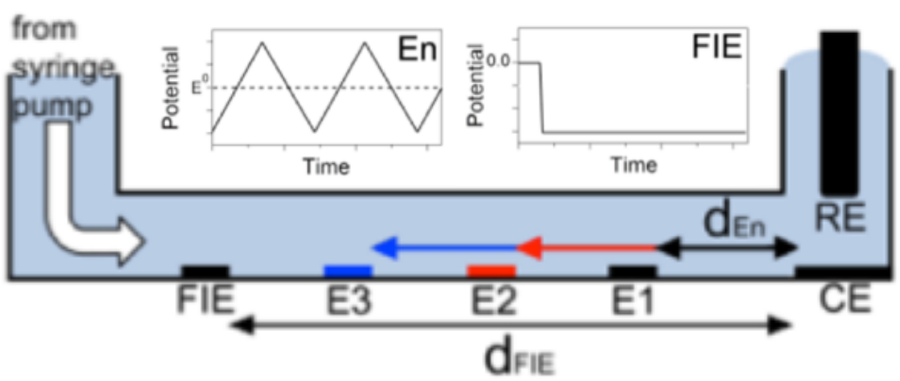

i (nA)
$E_{1/2}$
E_{FIE}
Floating
-0.5 V
-1.0 V
-1.5 V
E (V) vs Ag/AgCl

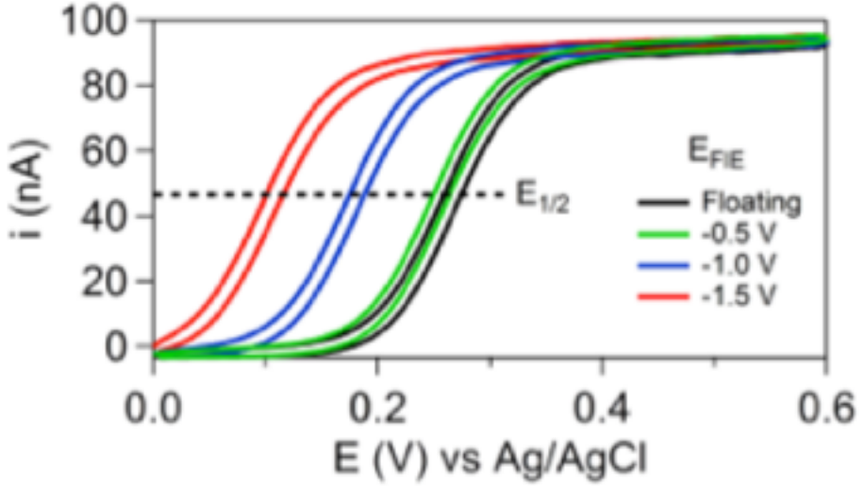

$E_{1/2}$ (V) vs Ag/AgCl
E_{FIE} (V) vs Ag/AgCl

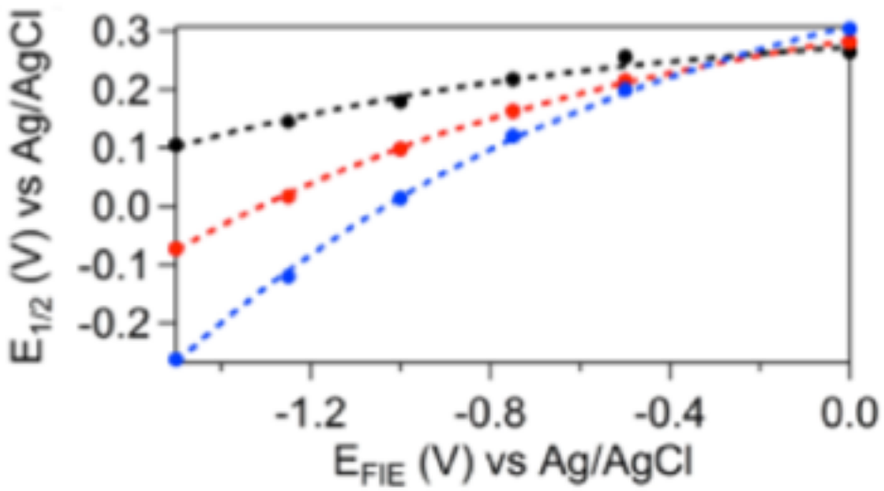

$E_{1/2}$ (V) vs Ag/AgCl
i_{FIE} (μA)

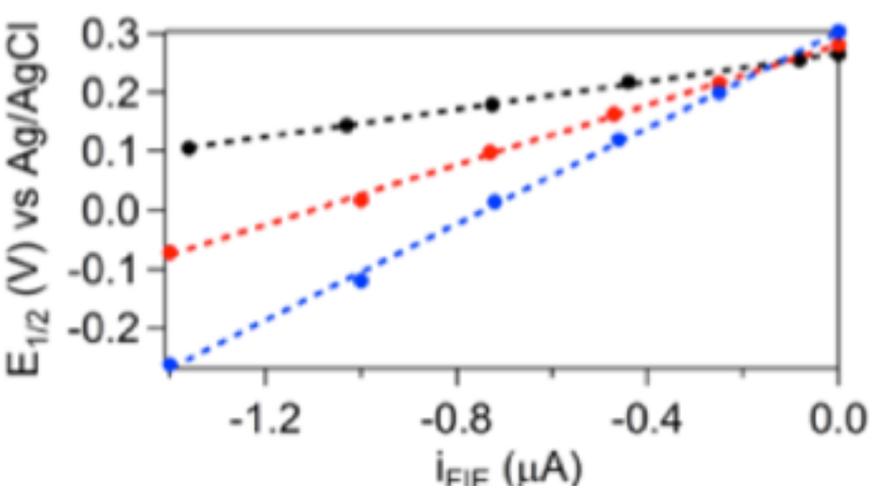

from
syringe
pump
d_{FIE}
RE
E3
E2
E1
FIE
CE
d_{En}

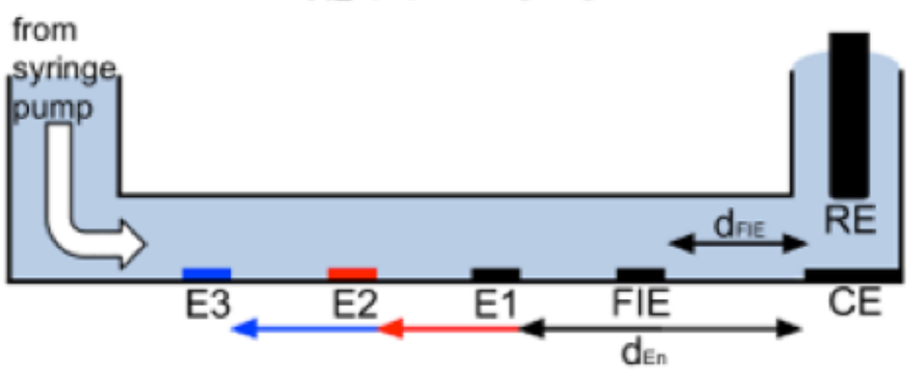

$E_{1/2}$ (V) vs Ag/AgCl
E1
E2
E3
i_{FIE} (μA)

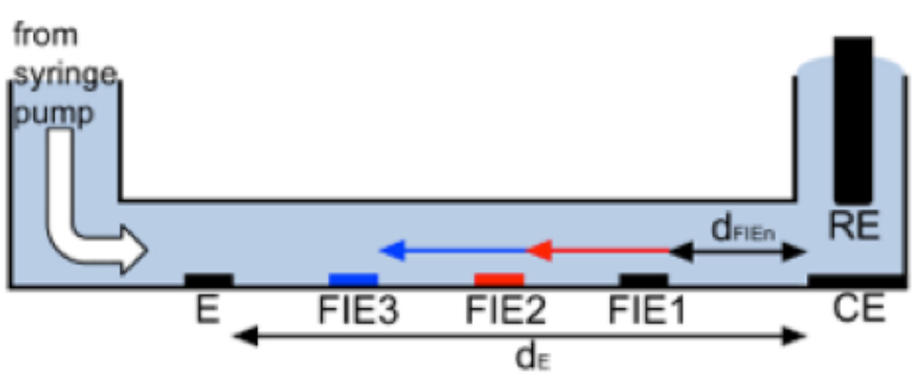

from
syringe
pump
Potential
En
Time
Potential
FIE
Time
RE
d_{En}
FIE
E3
E2
E1
CE
d_{FIE}

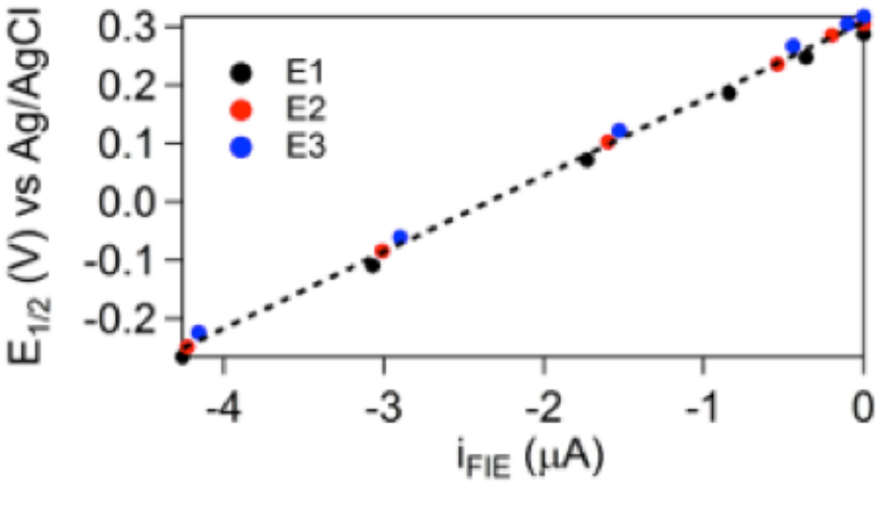

i (nA)
$E_{1/2}$
E_{FIE}
Floating
-0.5 V
-1.0 V
-1.5 V
E (V) vs Ag/AgCl

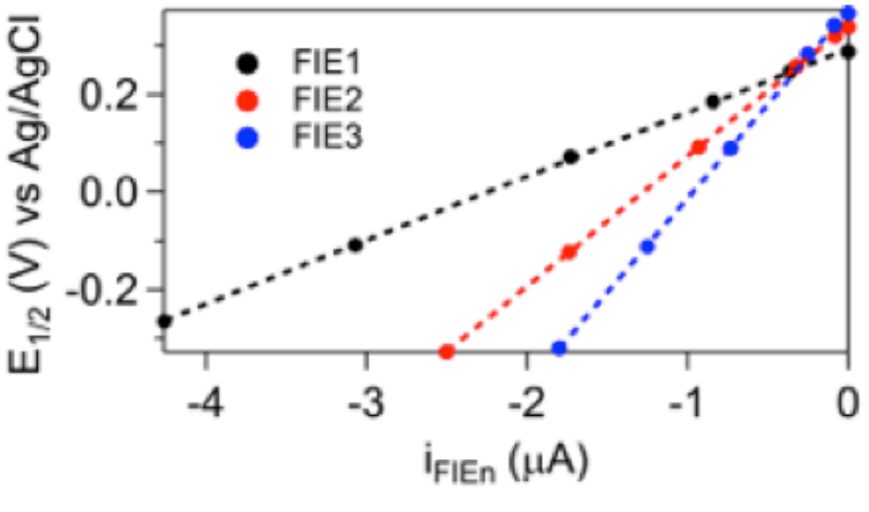

$E_{1/2}$ (V) vs Ag/AgCl
E_{FIE} (V) vs Ag/AgCl


$E_{1/2}$ (V) vs Ag/AgCl
i_{FIE} (μA)

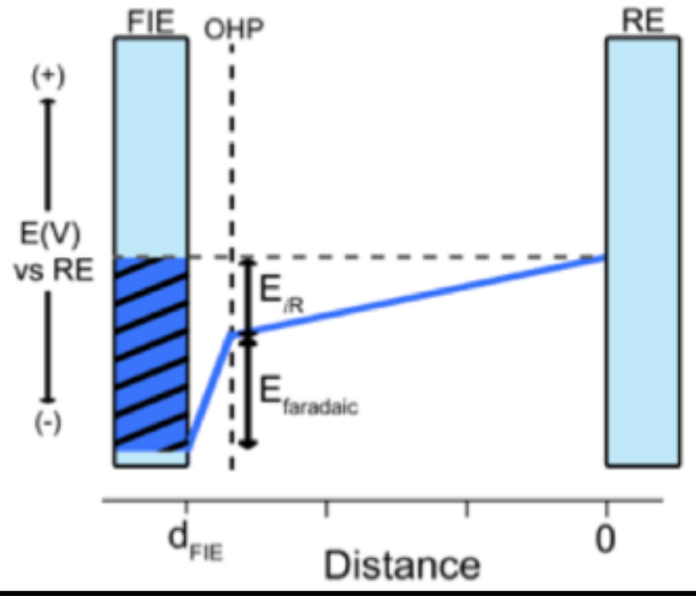

from
syringe
pump
d_{FIE}
RE
E3
E2
E1
FIE
CE
d_{En}


from
syringe
pump
d_{FIEn}
RE
E
FIE3
FIE2
FIE1
CE
d_E


$E_{1/2}$ (V) vs Ag/AgCl
E1
E2
E3
i_{FIE} (μA)

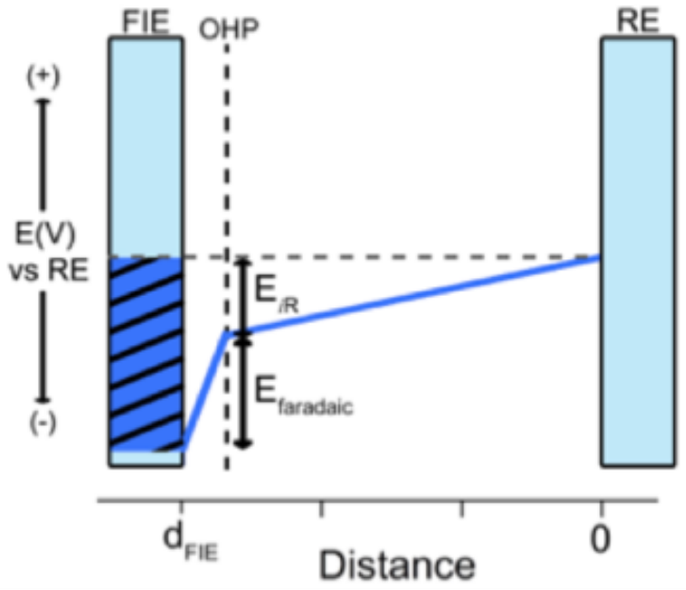

$E_{1/2}$ (V) vs Ag/AgCl
FIE1
FIE2
FIE3
i_{FIEn} (μA)

General Behavior in the Weak Coupling Limit



$$E_{1/2} = E_{1/2}(i=0) + i_{FIE}\frac{d_{FIE}}{A\sigma}$$

General Behavior in the Weak Coupling Limit



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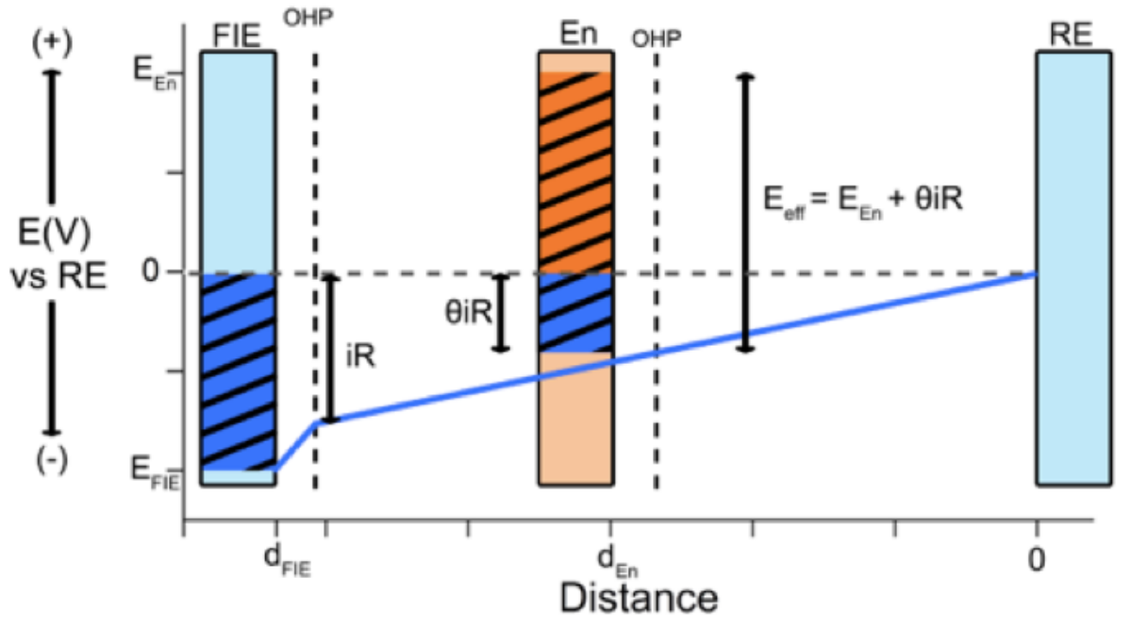
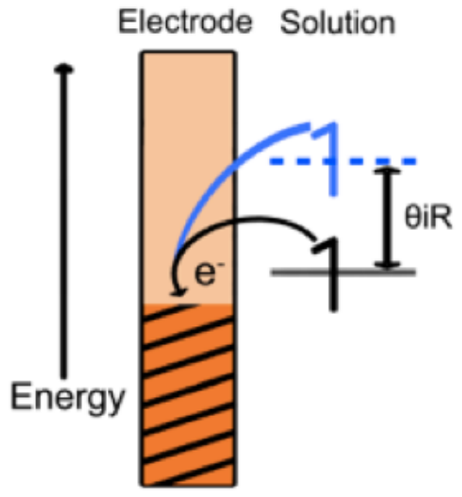
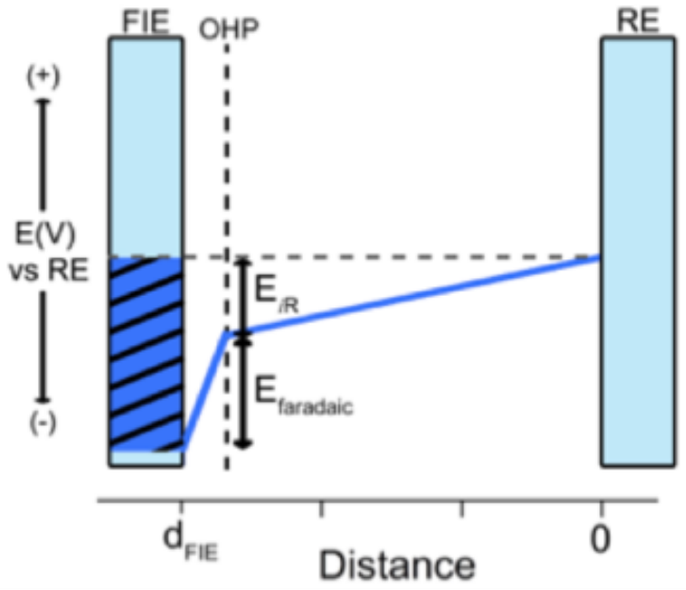
Case I: Working Electrode in Field





General Behavior in the Weak Coupling Limit



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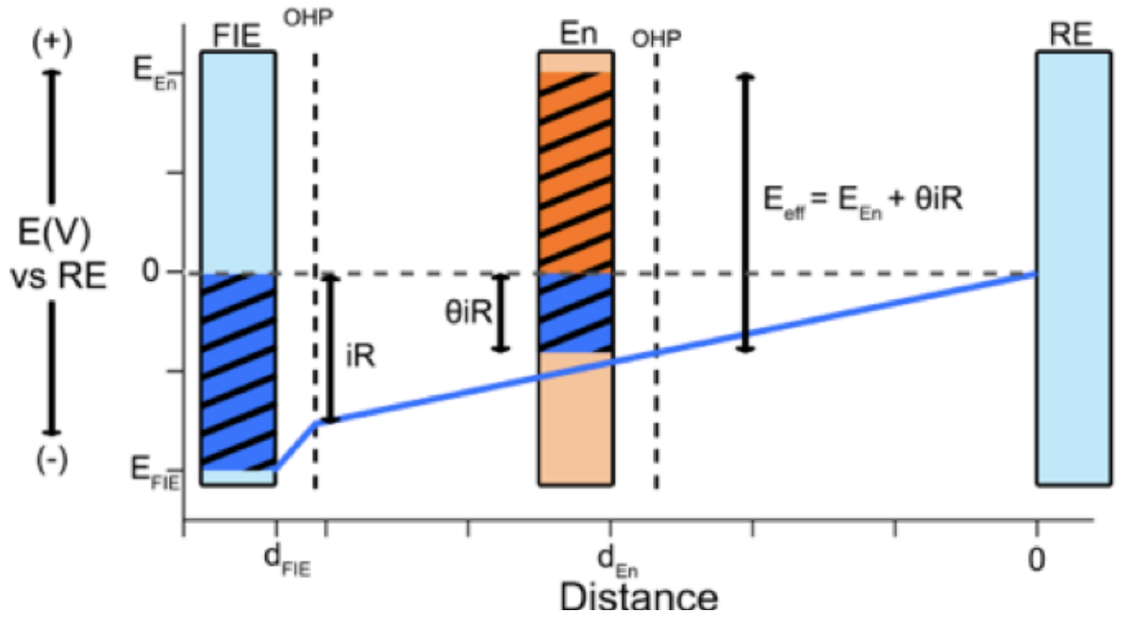
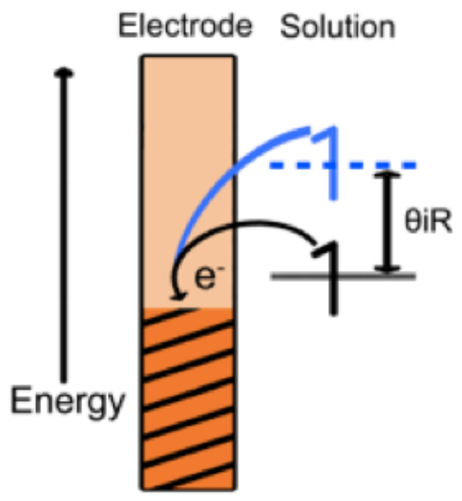
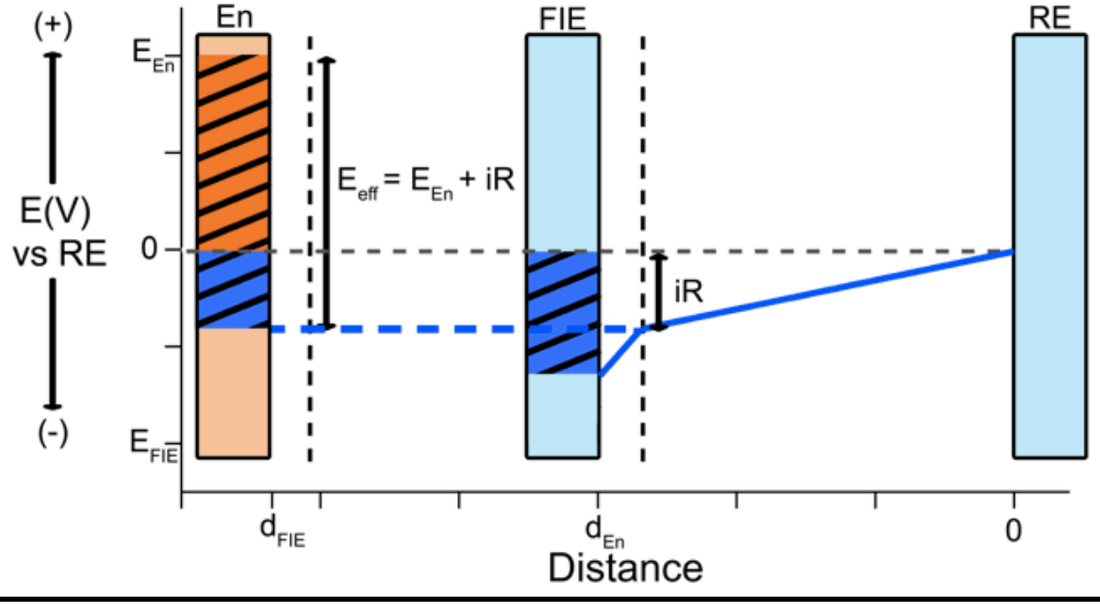
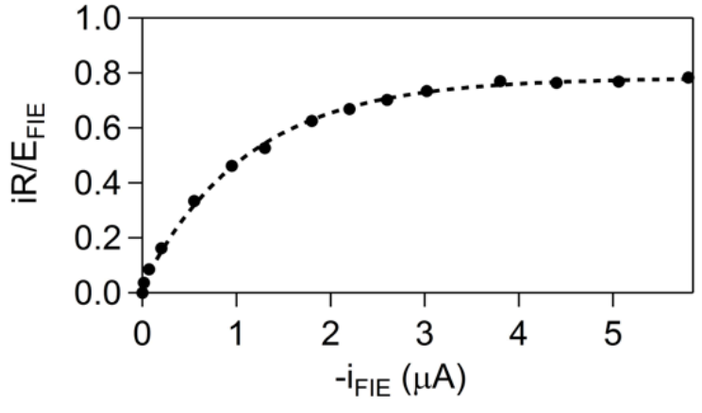


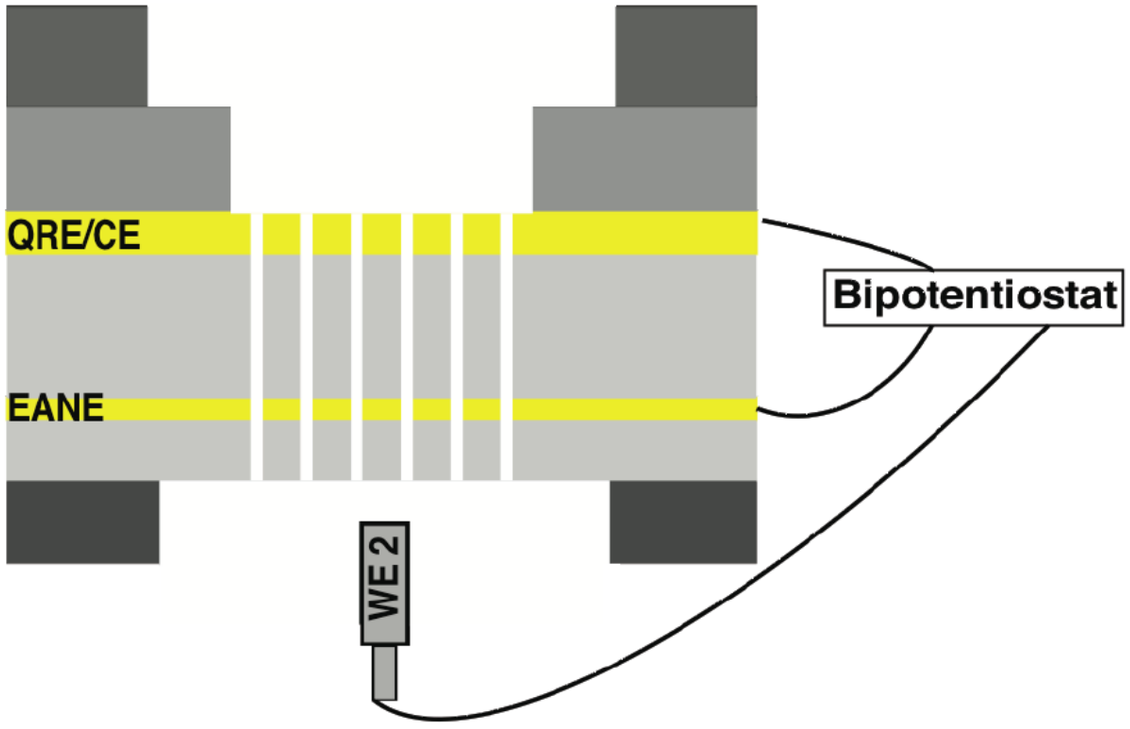


Case II: Working Electrode in Field-Free Region

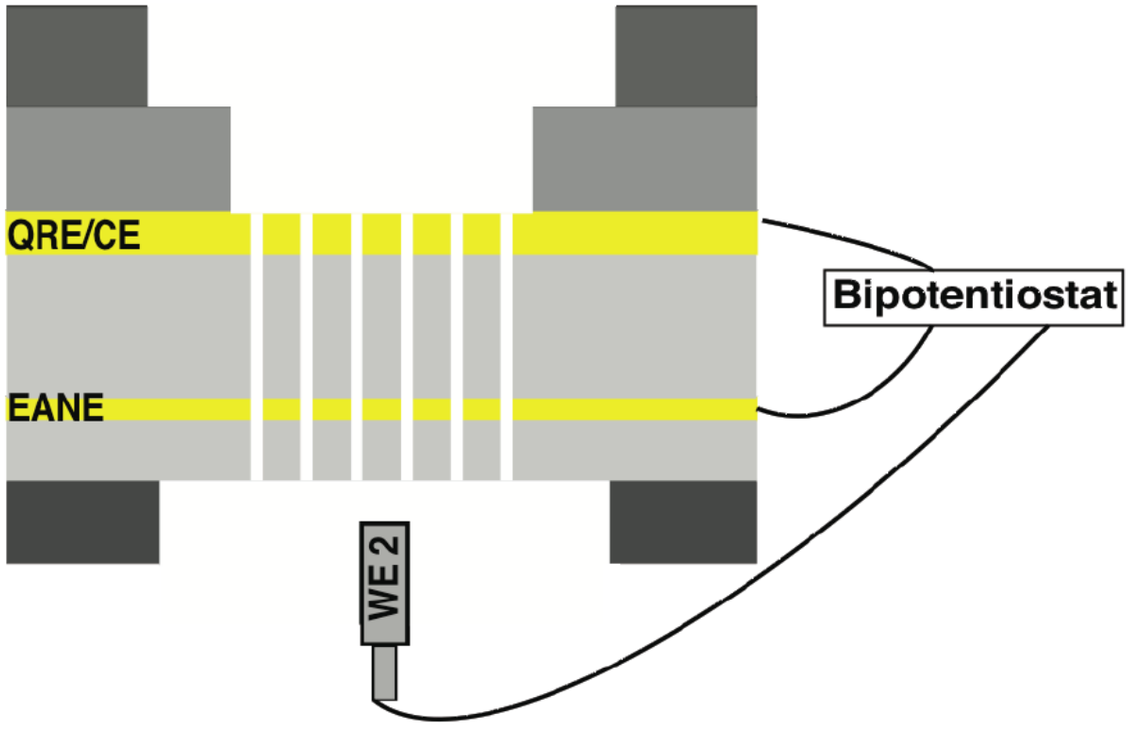


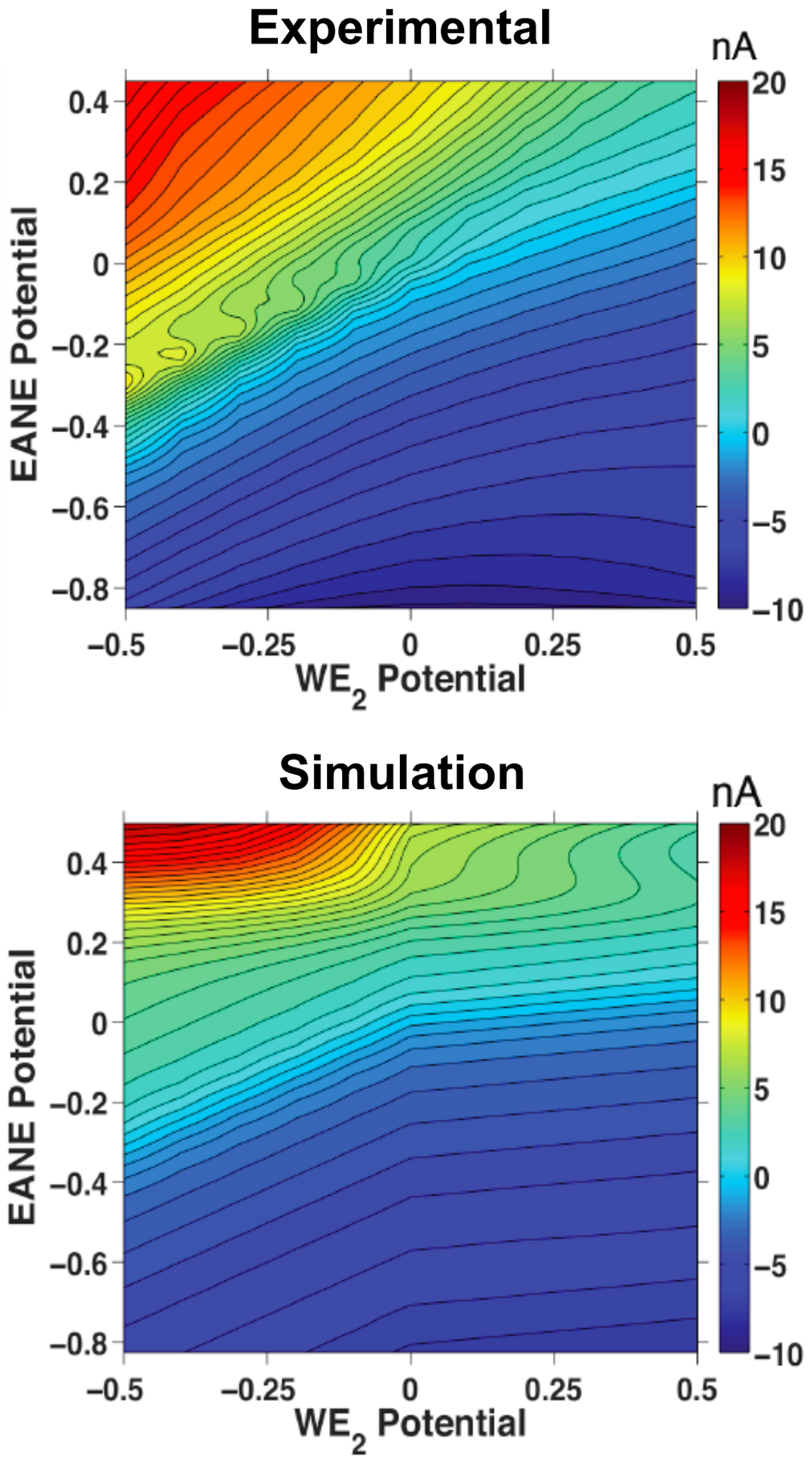


Strong Coupling at the Nanoscale

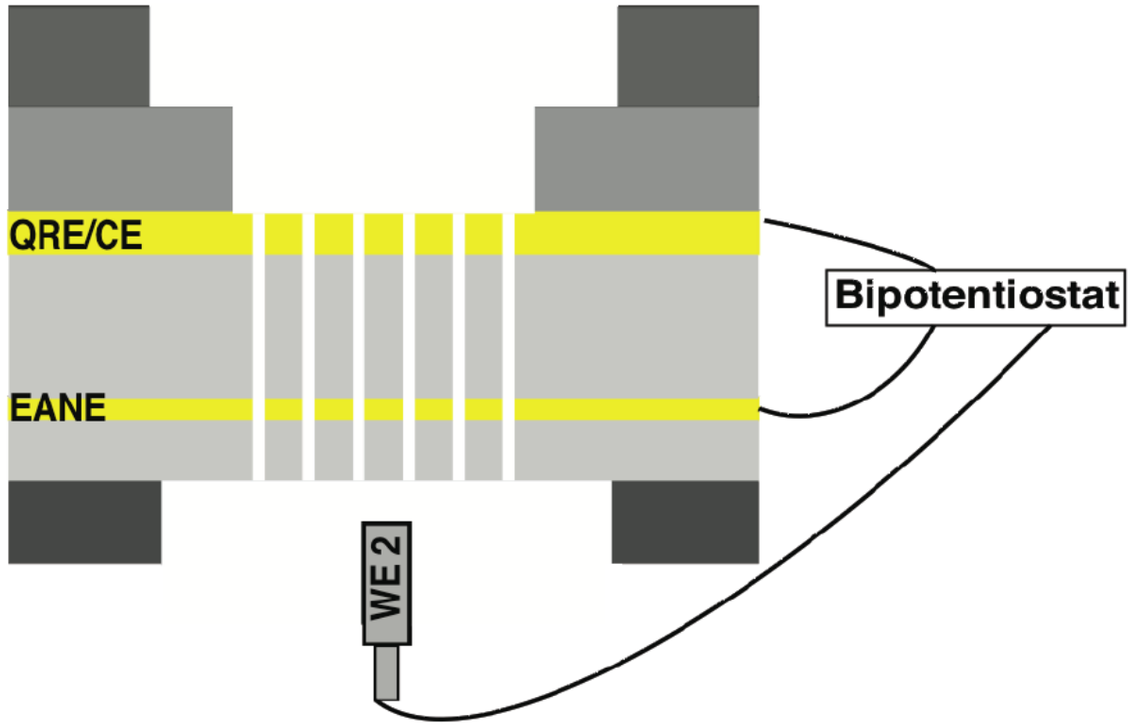


Strong Coupling at the Nanoscale

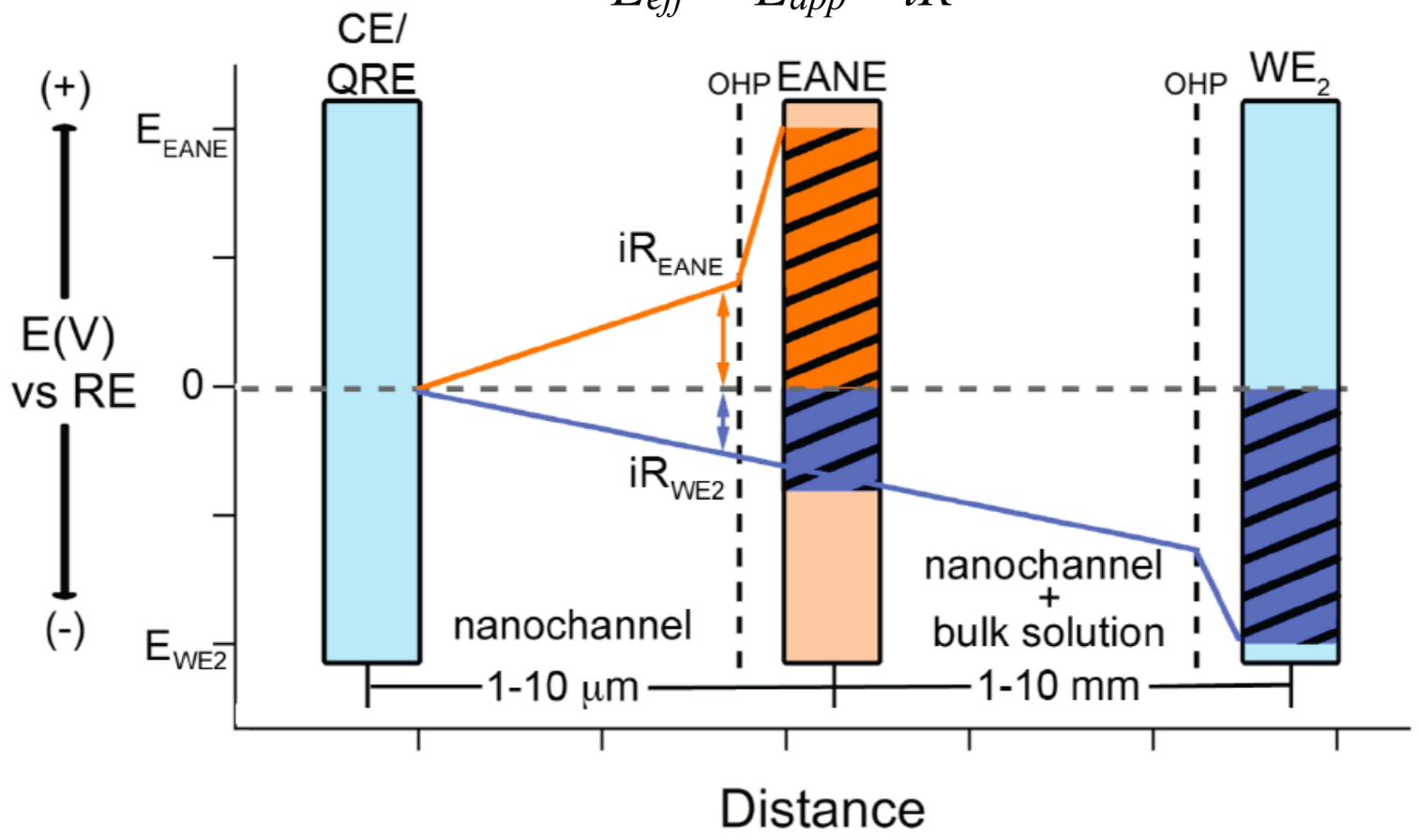


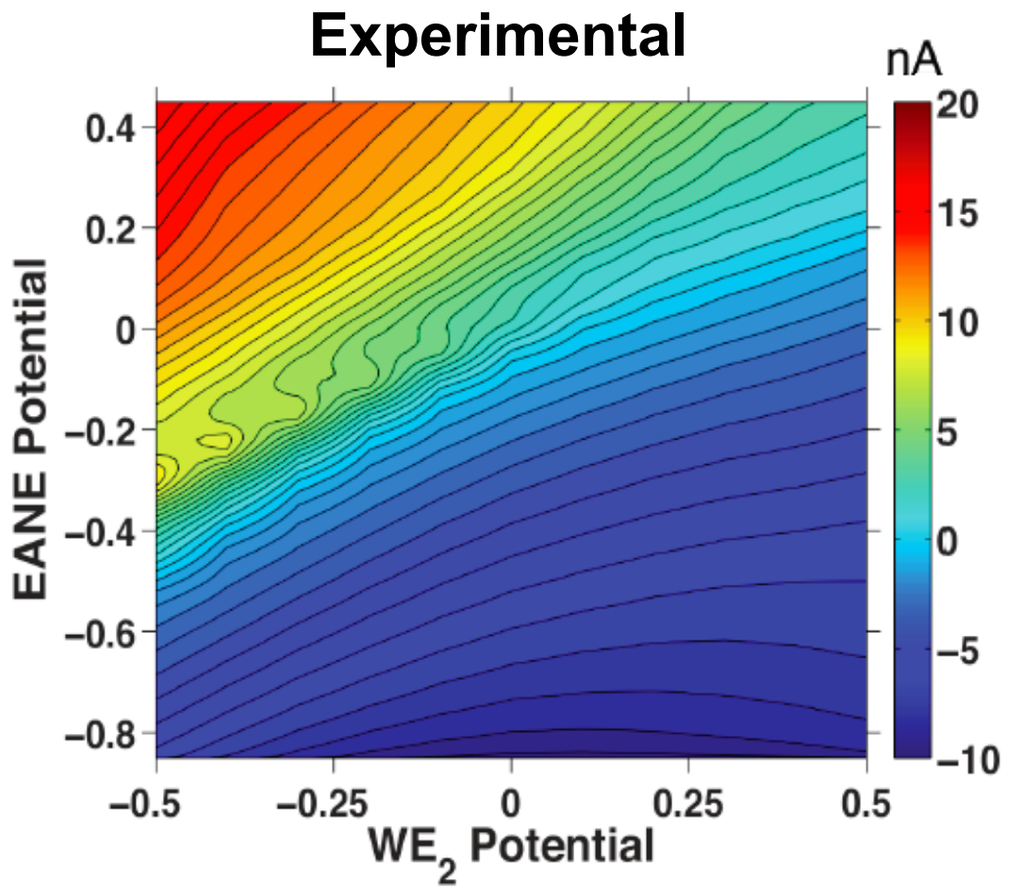


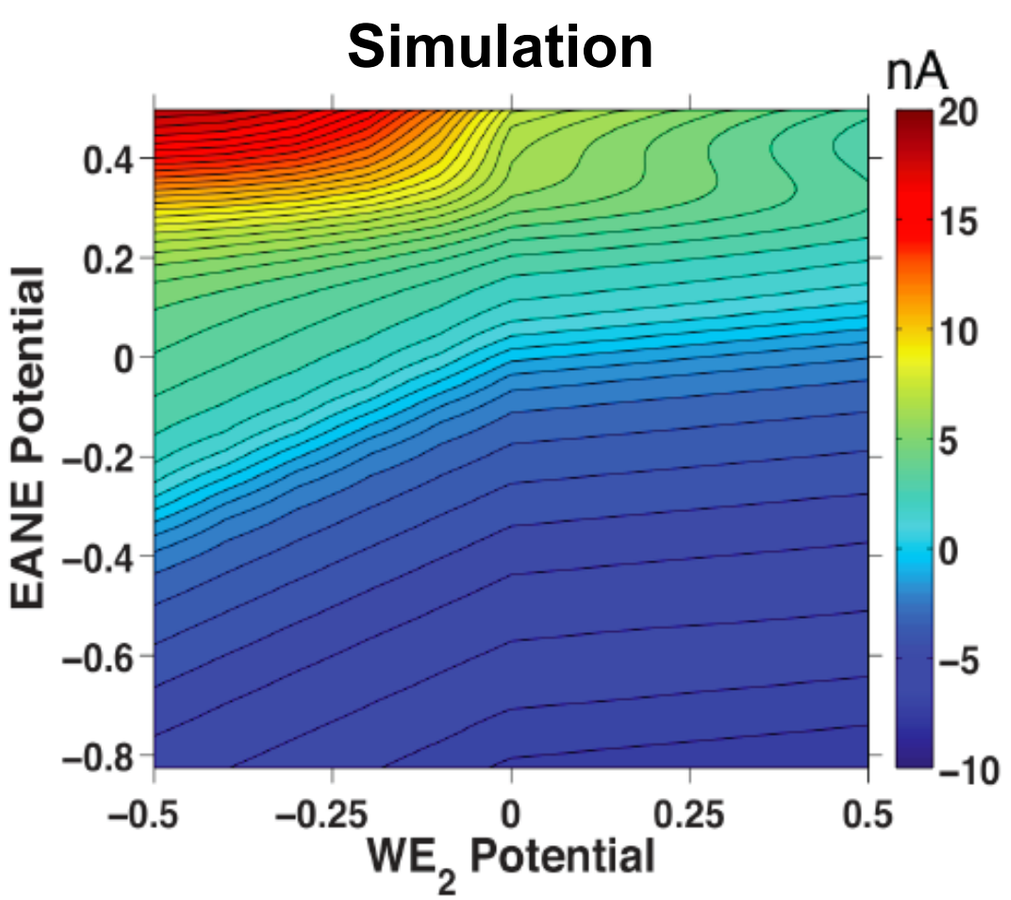
Strong Coupling at the Nanoscale



$$E_{eff} = E_{app} - iR$$



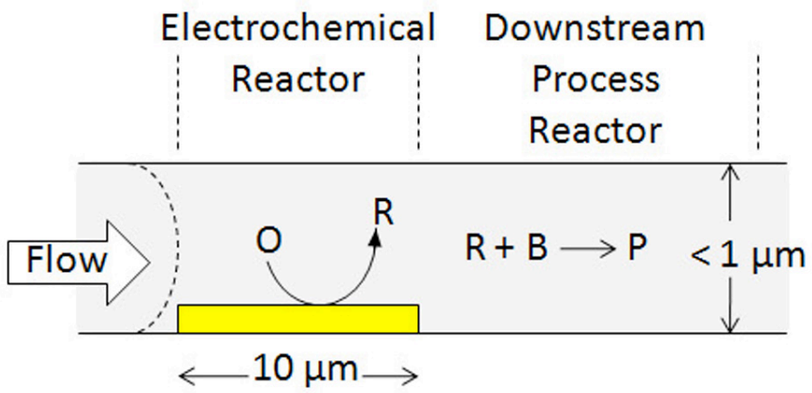


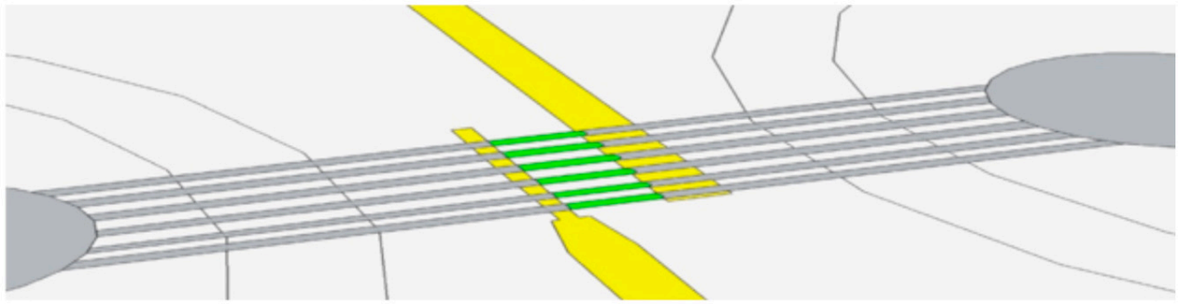


III. *In Situ* Reagent Generation

Reagent Generation in Nanochannels

$$2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^-$$





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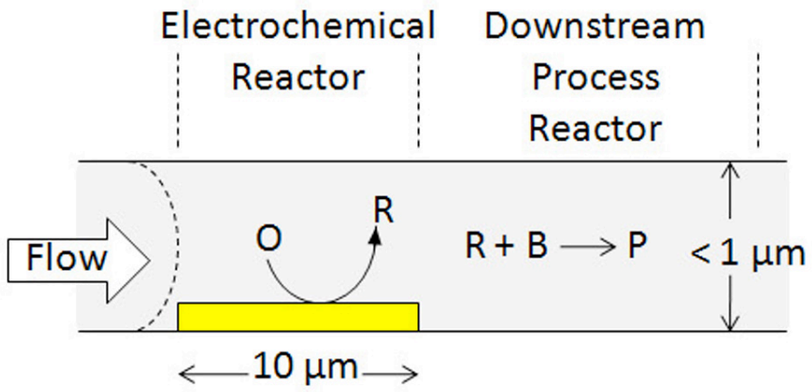

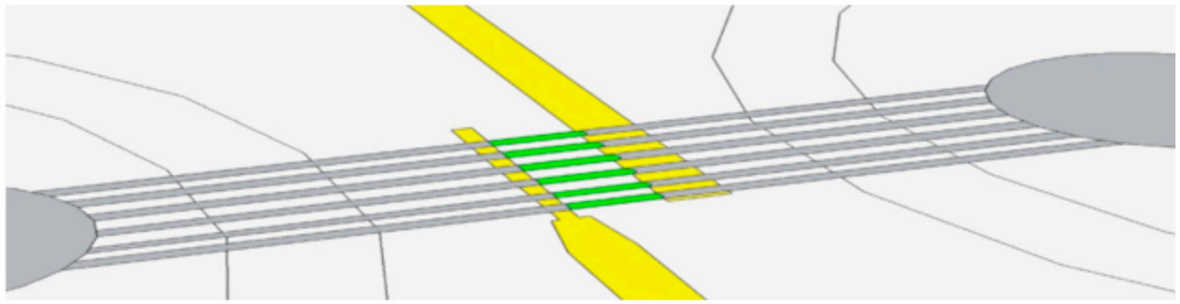

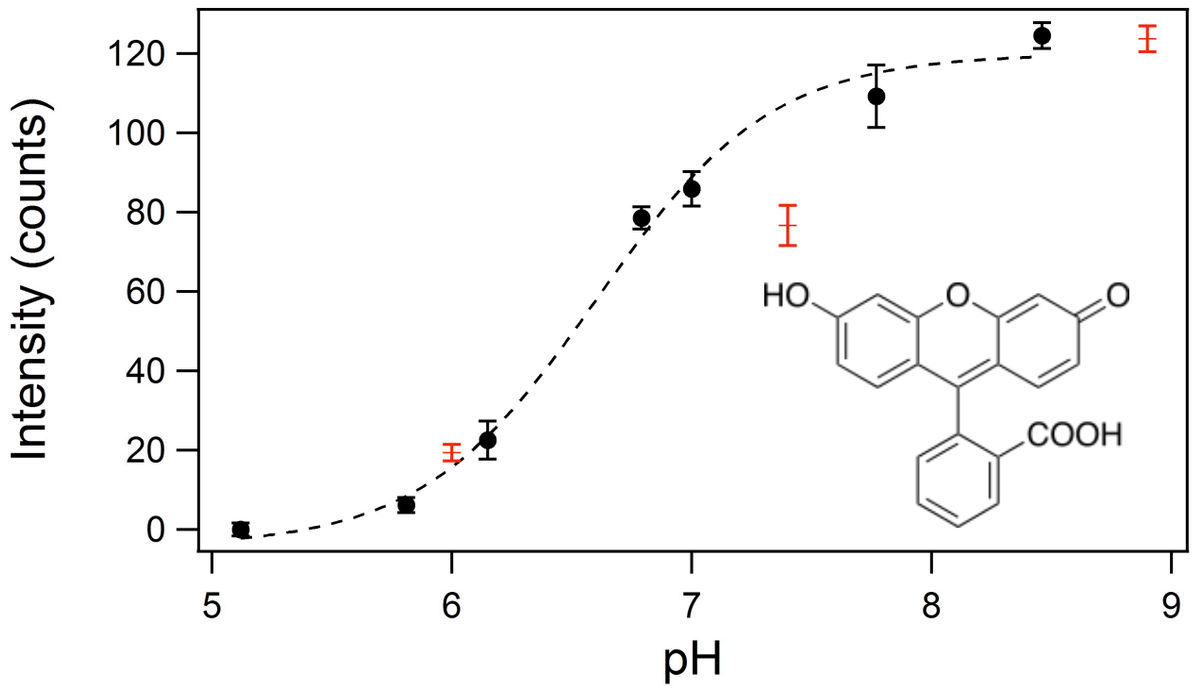

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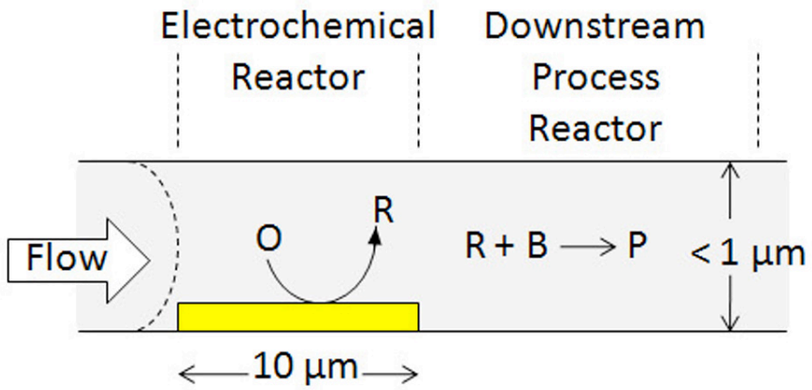

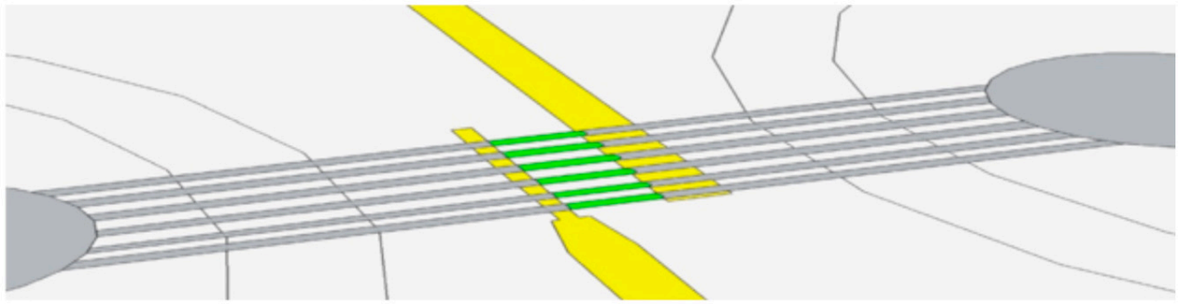

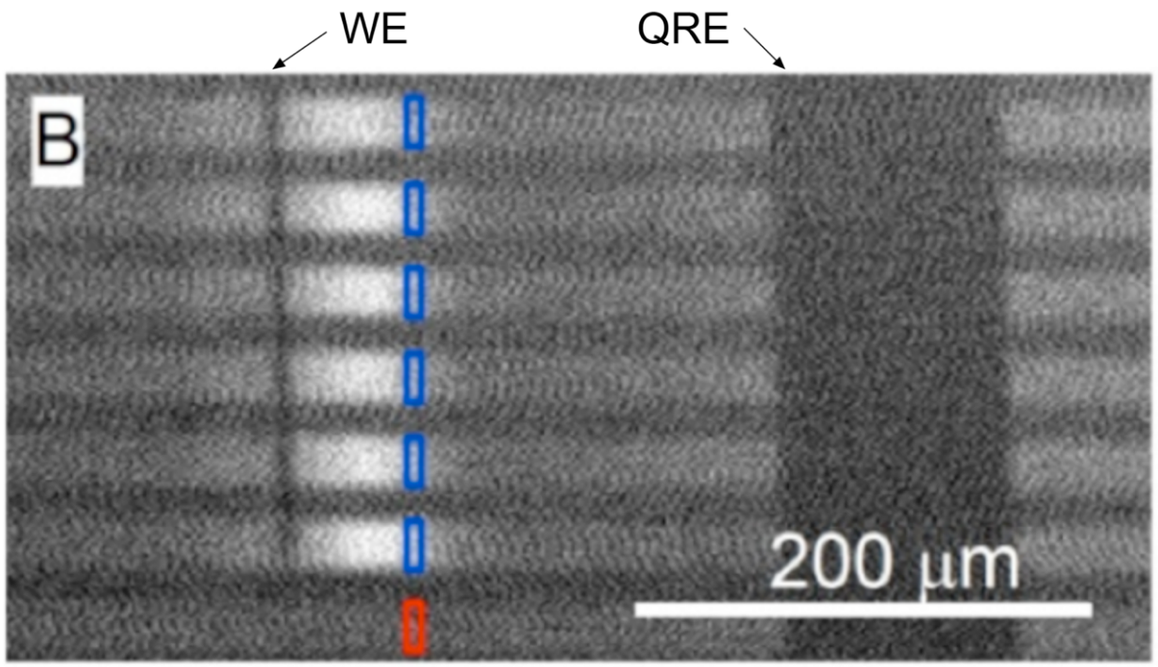

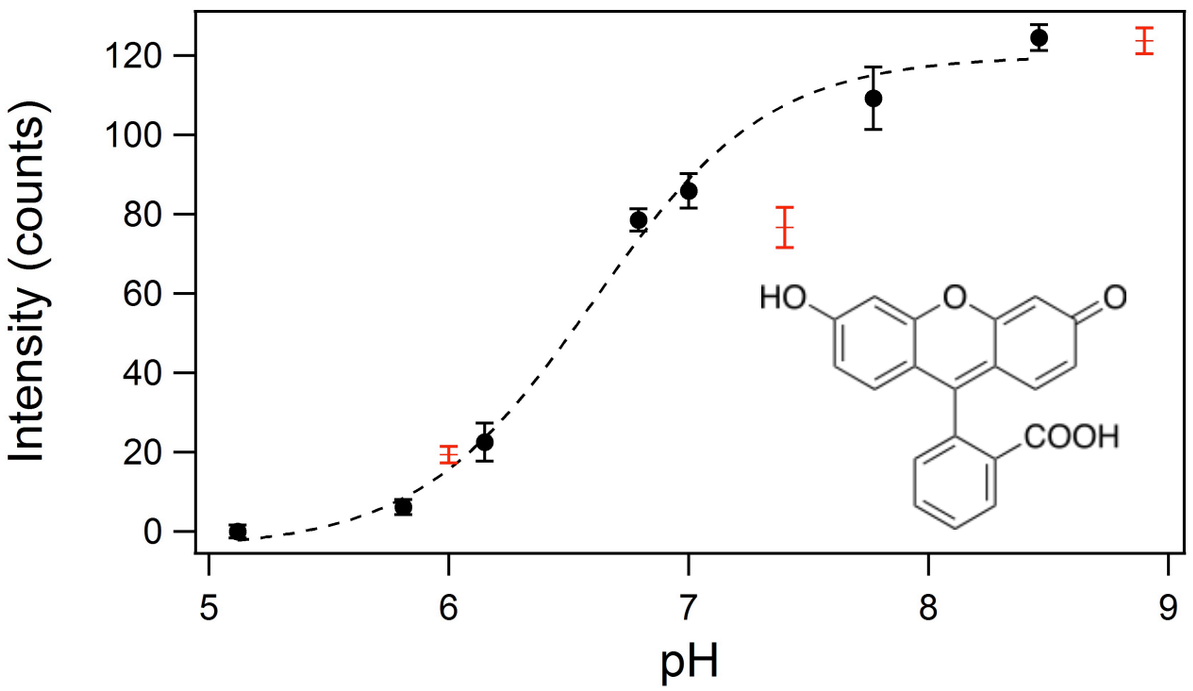

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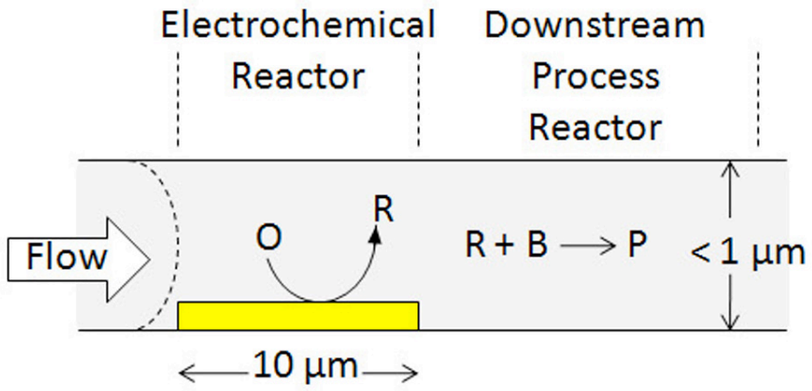
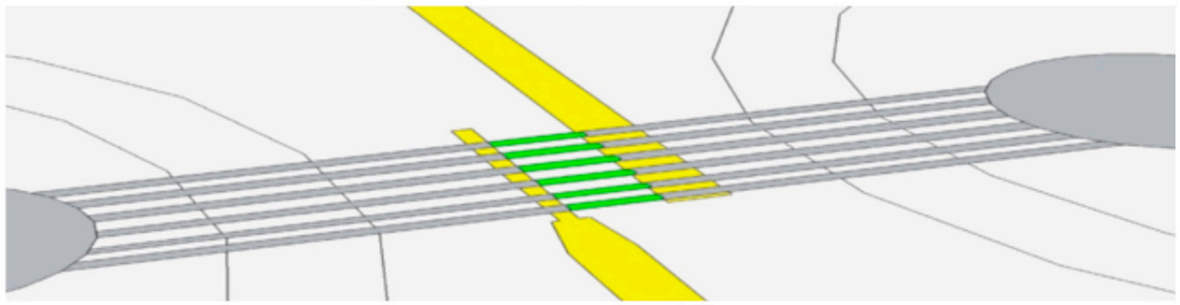
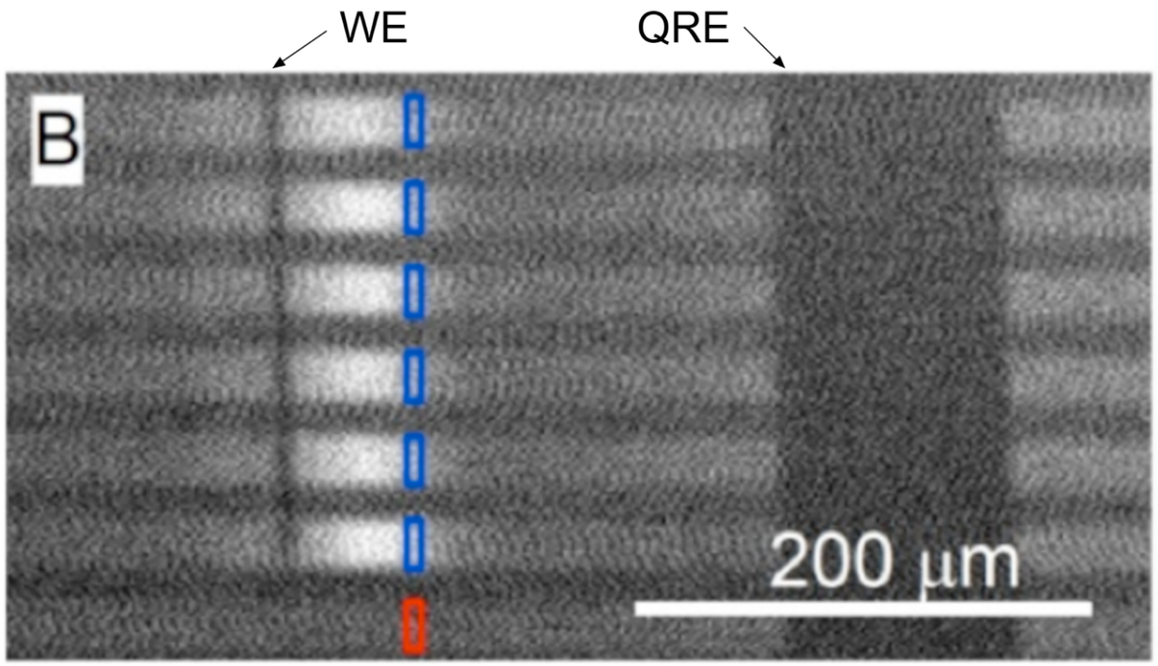
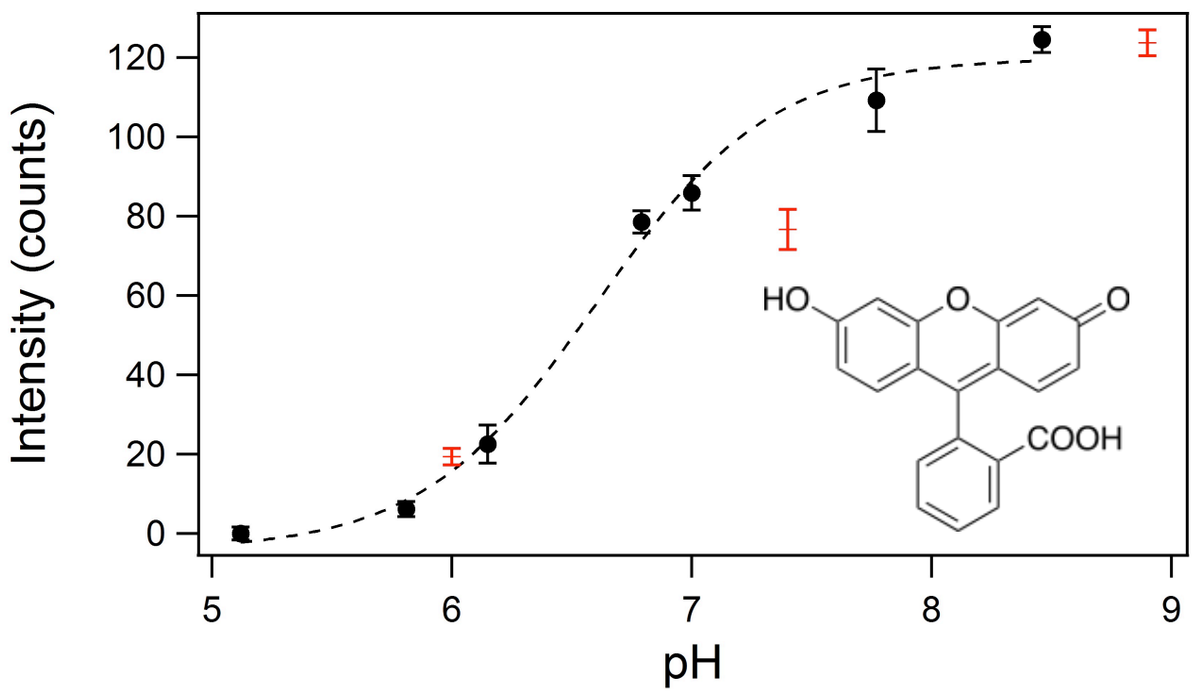
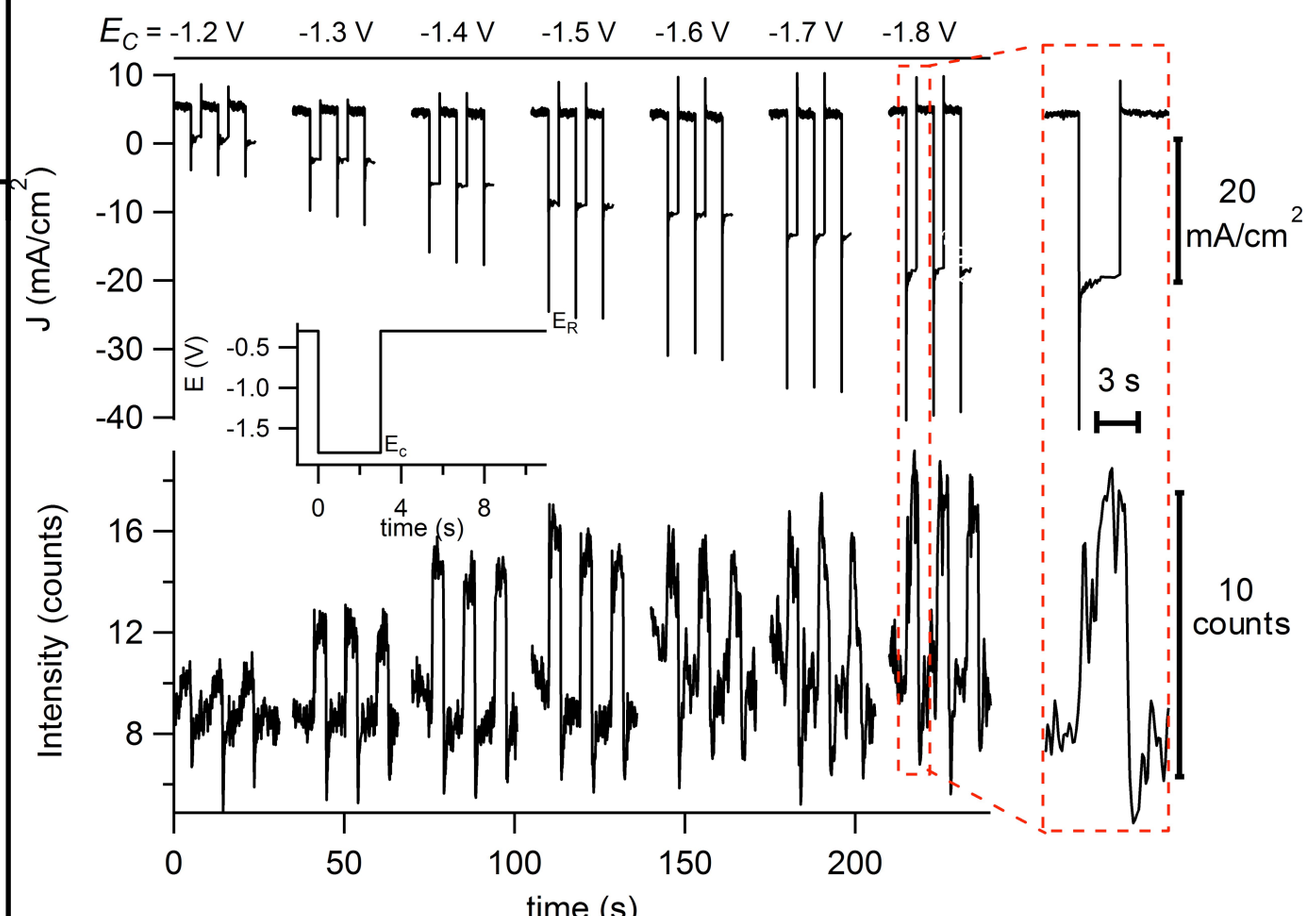
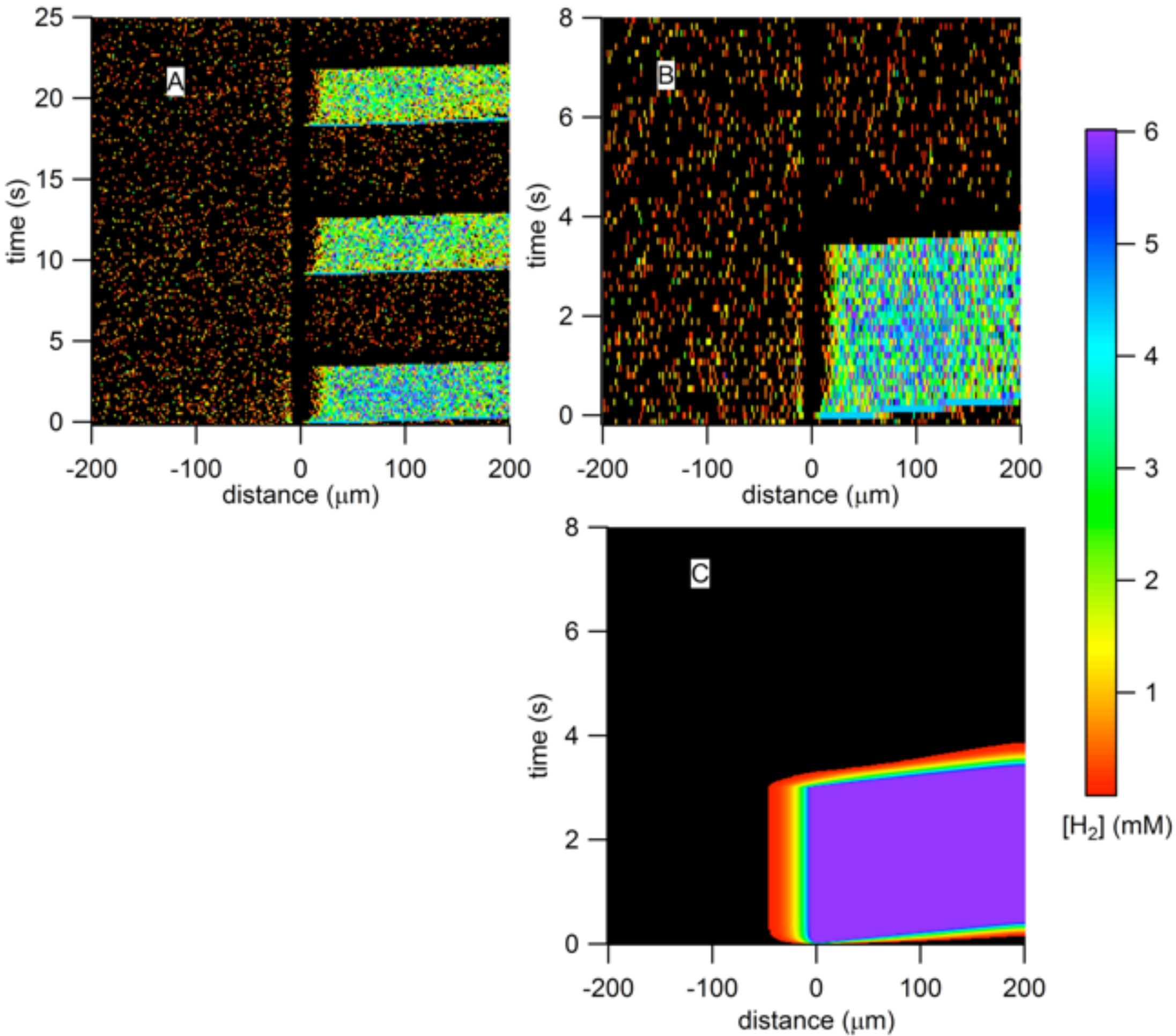


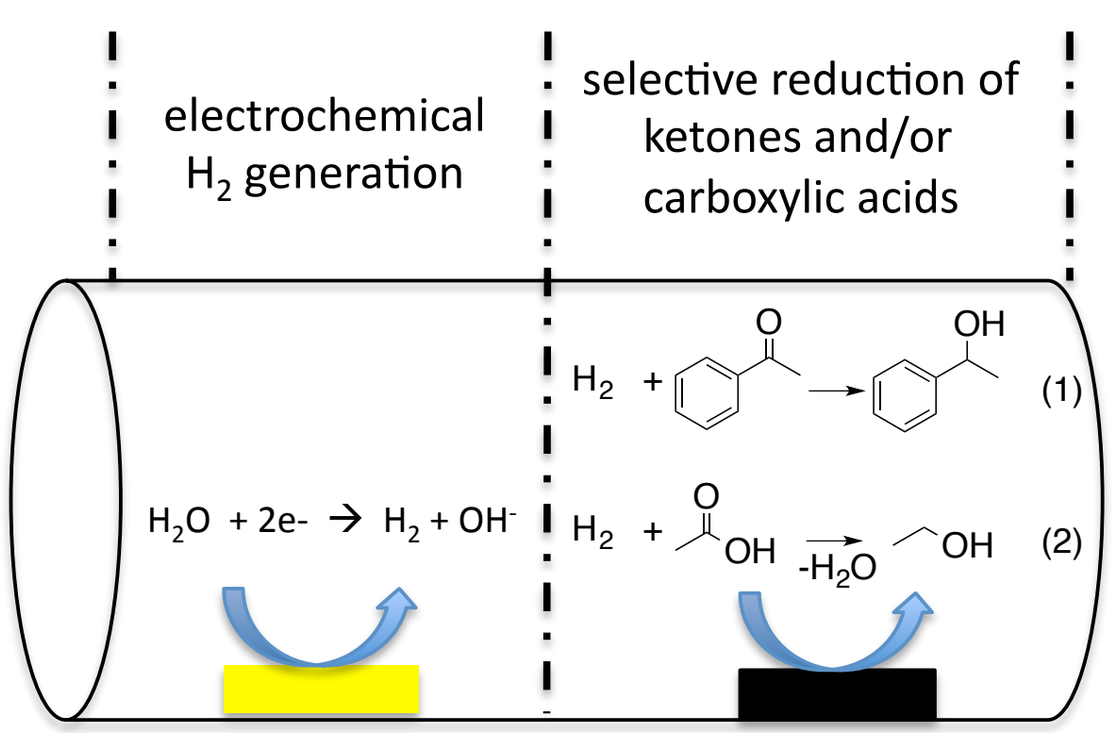


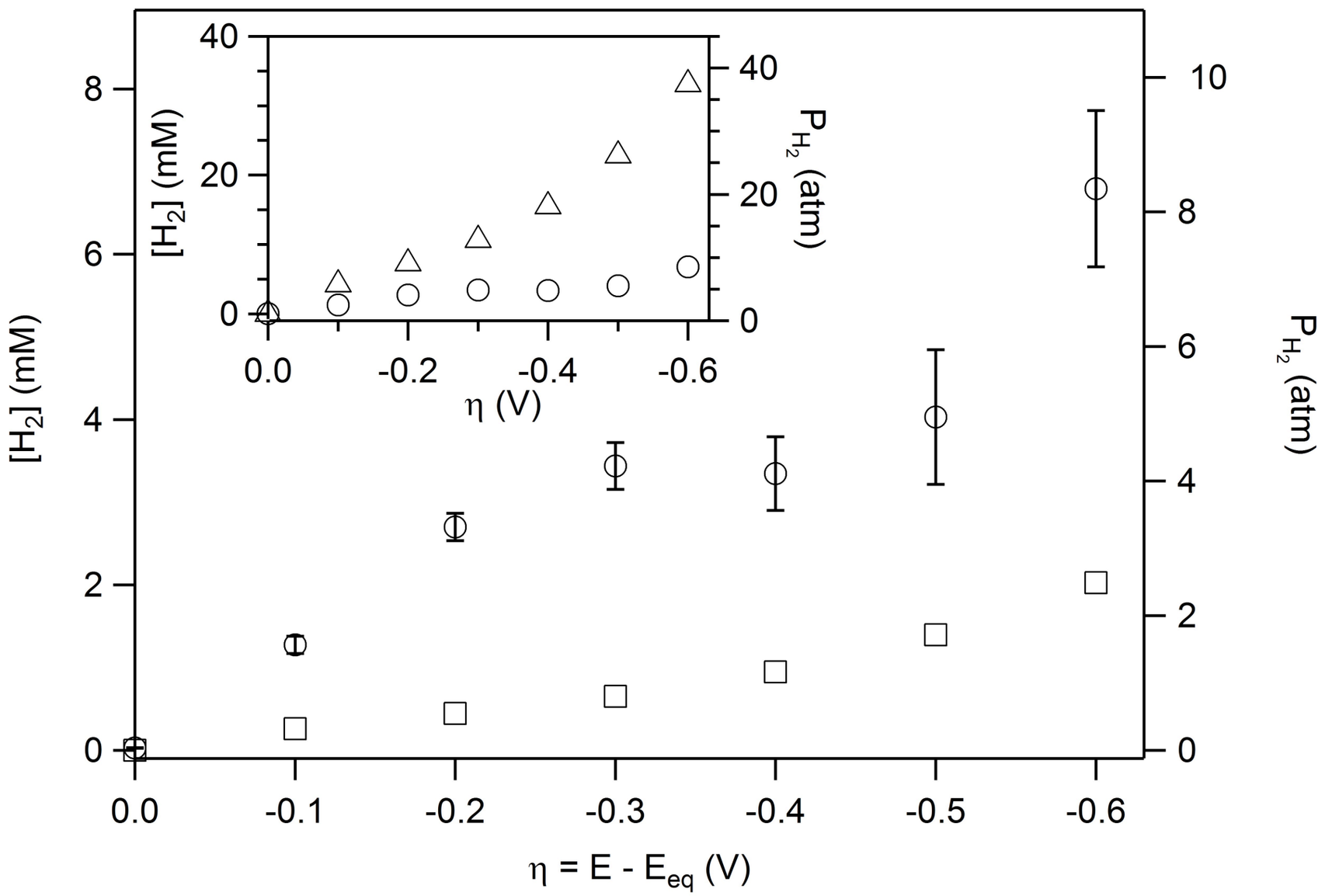







A
B
C
time (s)
distance (μm)
[H2] (mM)
25
20
15
10
5
0
8
6
4
2
-200
-100
0
100
200
1
3


electrochemical
H_2 generation
selective reduction of
ketones and/or
carboxylic acids
$H_2O + 2e- \rightarrow H_2 + OH^-$
H_2 +
OH
(1)
H_2 +
OH
$-H_2O$
OH
(2)


[H2] (mM)
P_{H_2} (atm)
η = E - E_{eq} (V)
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
0
2
4
6
8
10
[H2] (mM)
P_{H_2} (atm)
η (V)
0.0
-0.2
-0.4
-0.6
0
20
40

Conclusions

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- *NCAMs with metallic elements integrate electrokinetic transport, electrochemistry and plasmonic sensing.*

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Challenges

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Challenges

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- *Coupling electron transfer to spectroscopic detection (see single electron transfer events - a topic for another day!).*

Bohn Group

Dorothy Ahlf
Nameera Baig
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Jiyuan Hu
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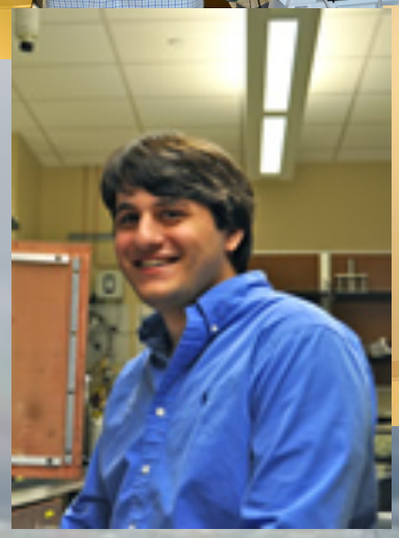
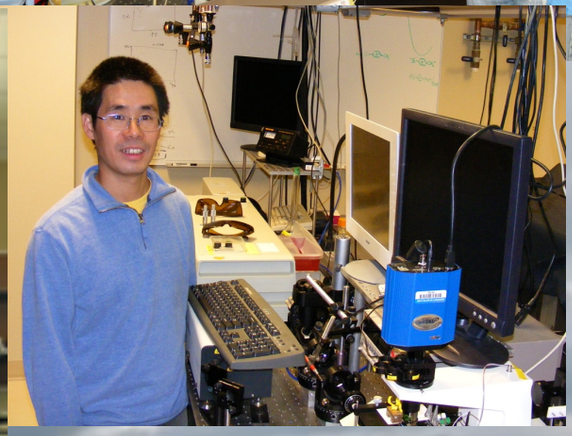
Rachel Masyuko
Sneha Polisetti
Kayla Shaw
Billy Wichert
Wei Xu
Larry Zaino





Bohn Group

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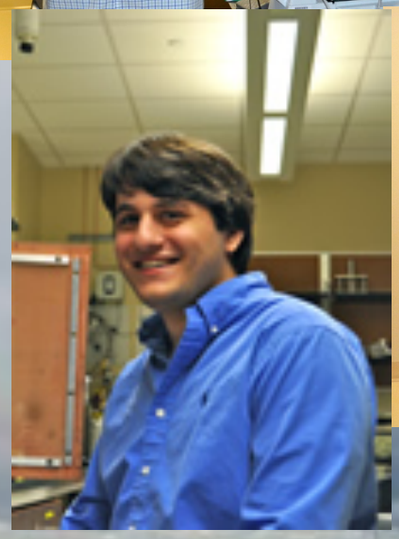
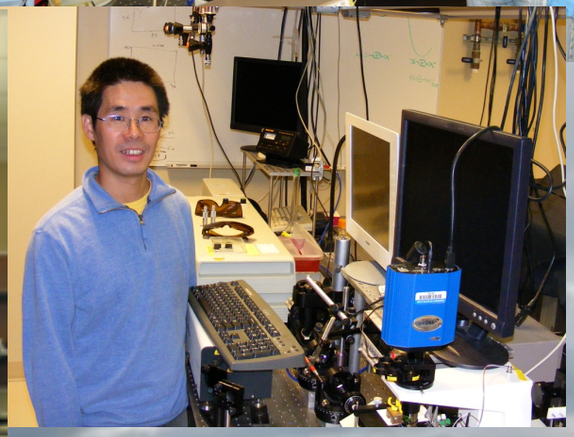
Wei Xu
Larry Zaino

U.S. DEPARTMENT OF ENERGY | Office of Science

National Science Foundation
WHERE DISCOVERIES BEGIN





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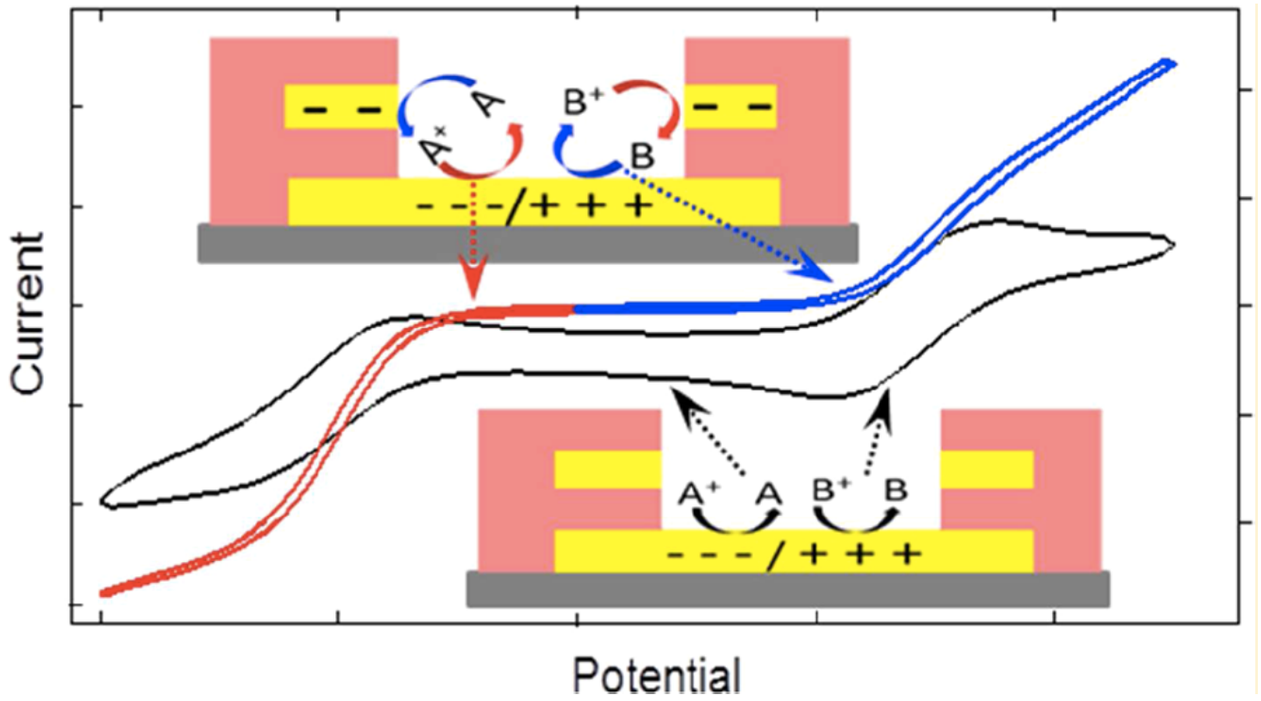
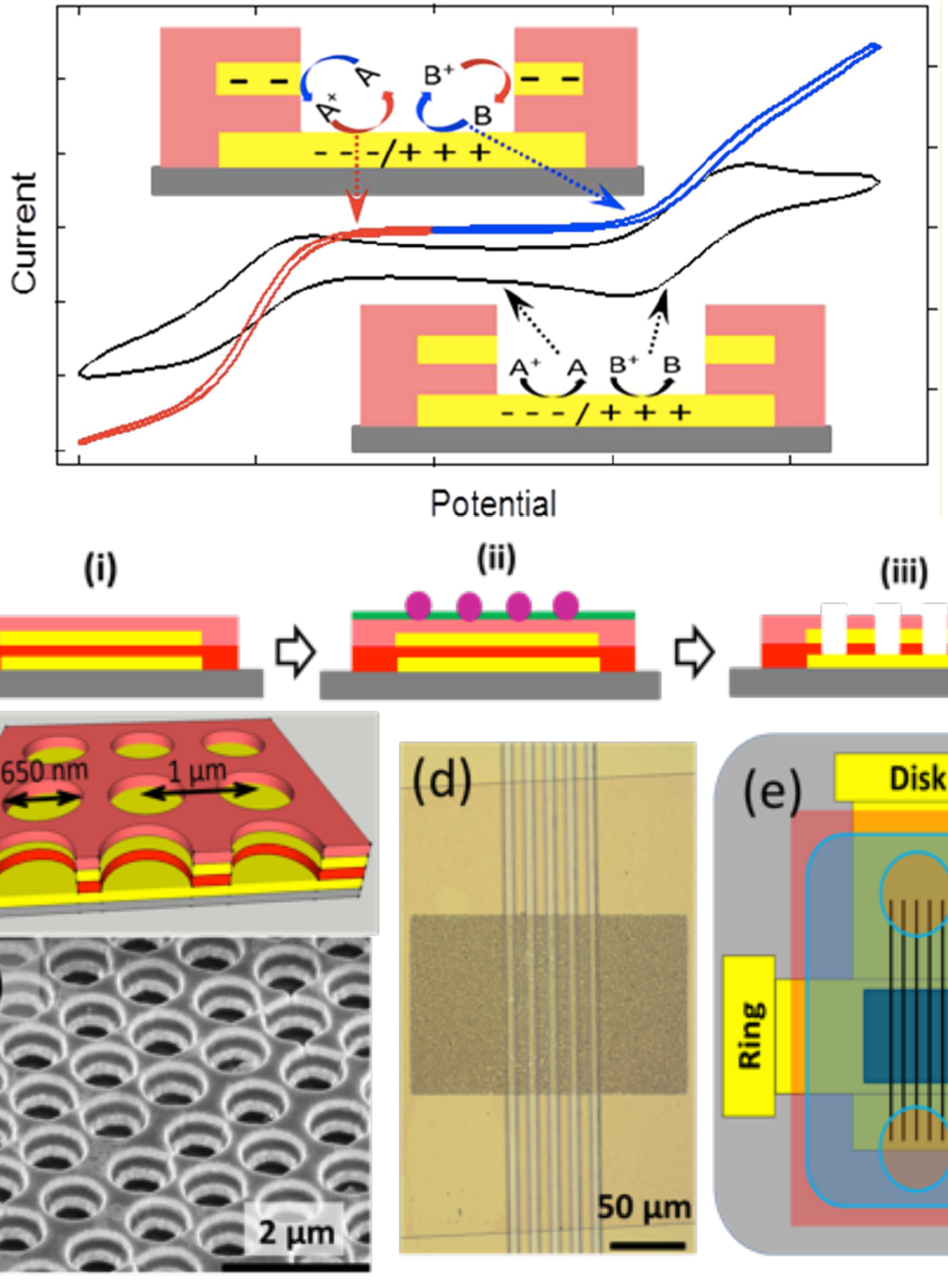
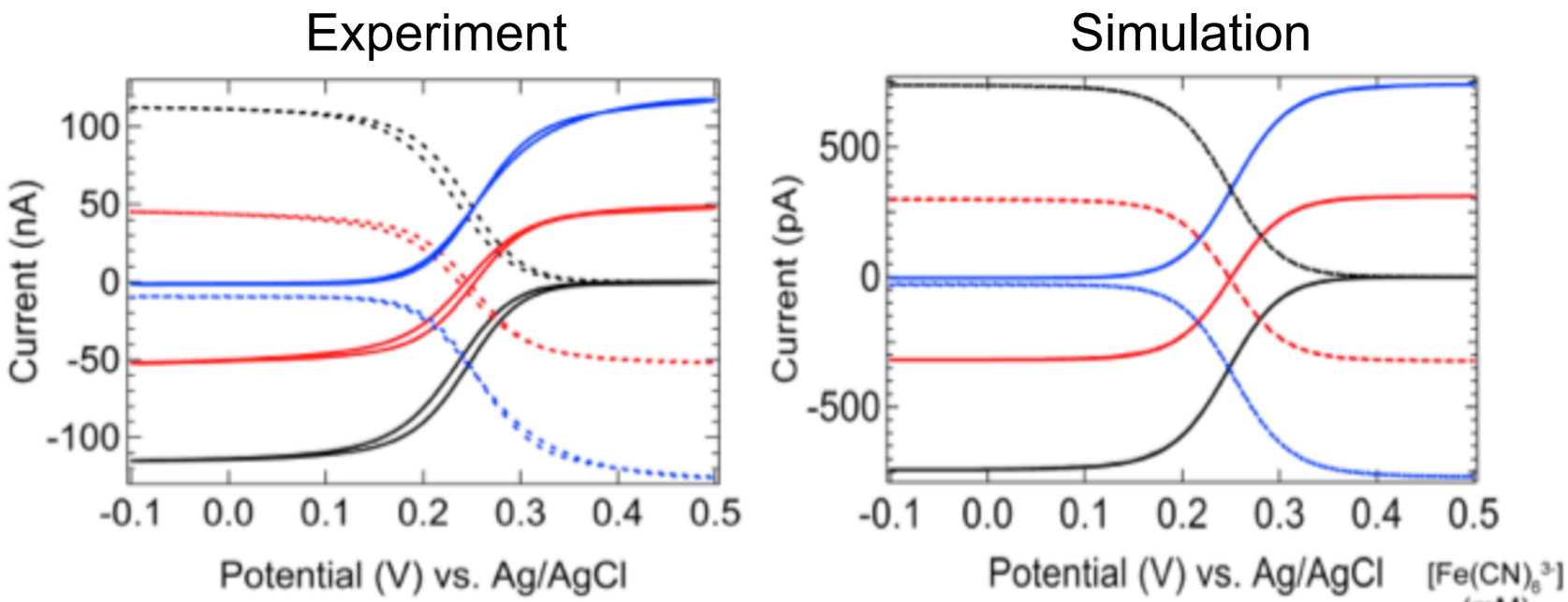
Recessed Ring-Disk Arrays

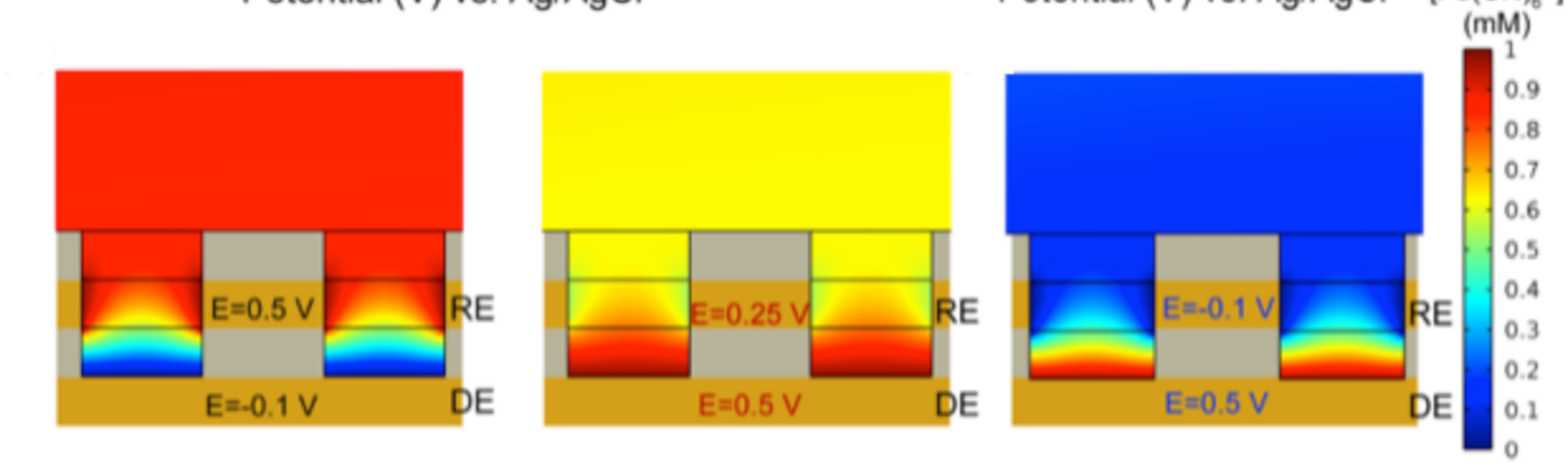


Recessed Ring-Disk Arrays

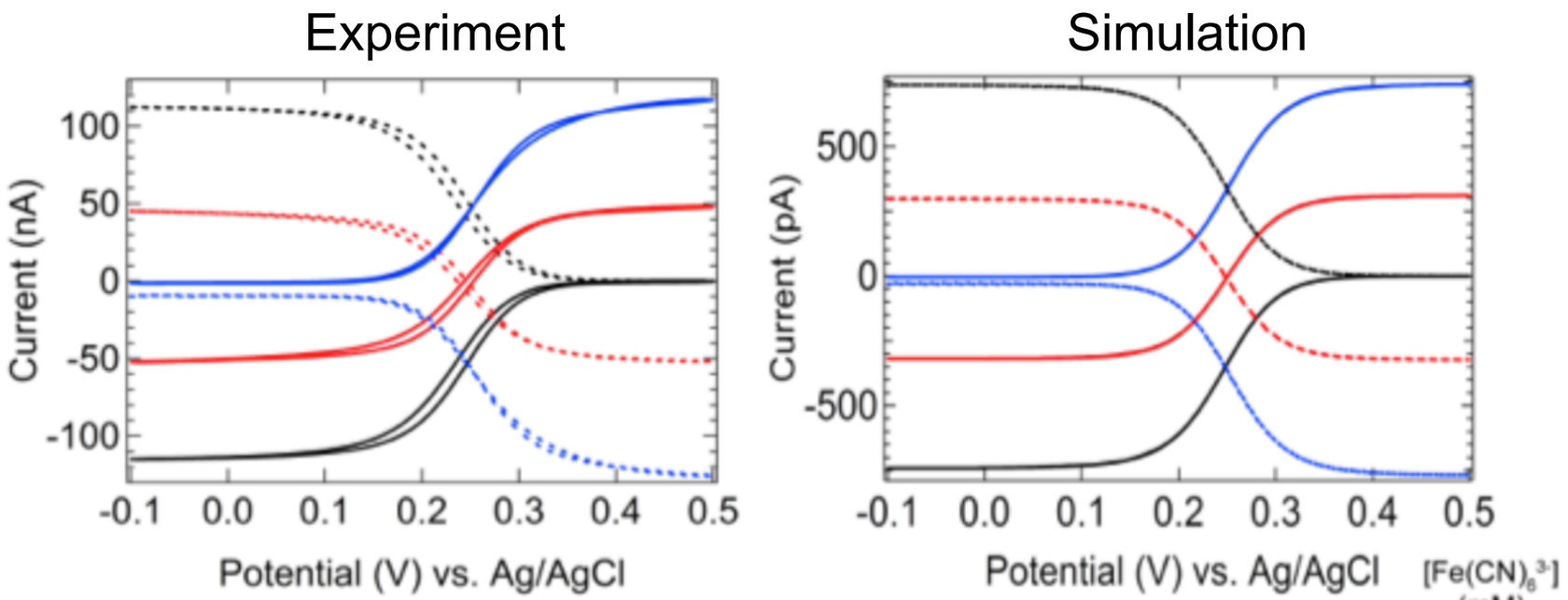


Generator-Collector Operating Characteristics in 0-D RRDE Arrays





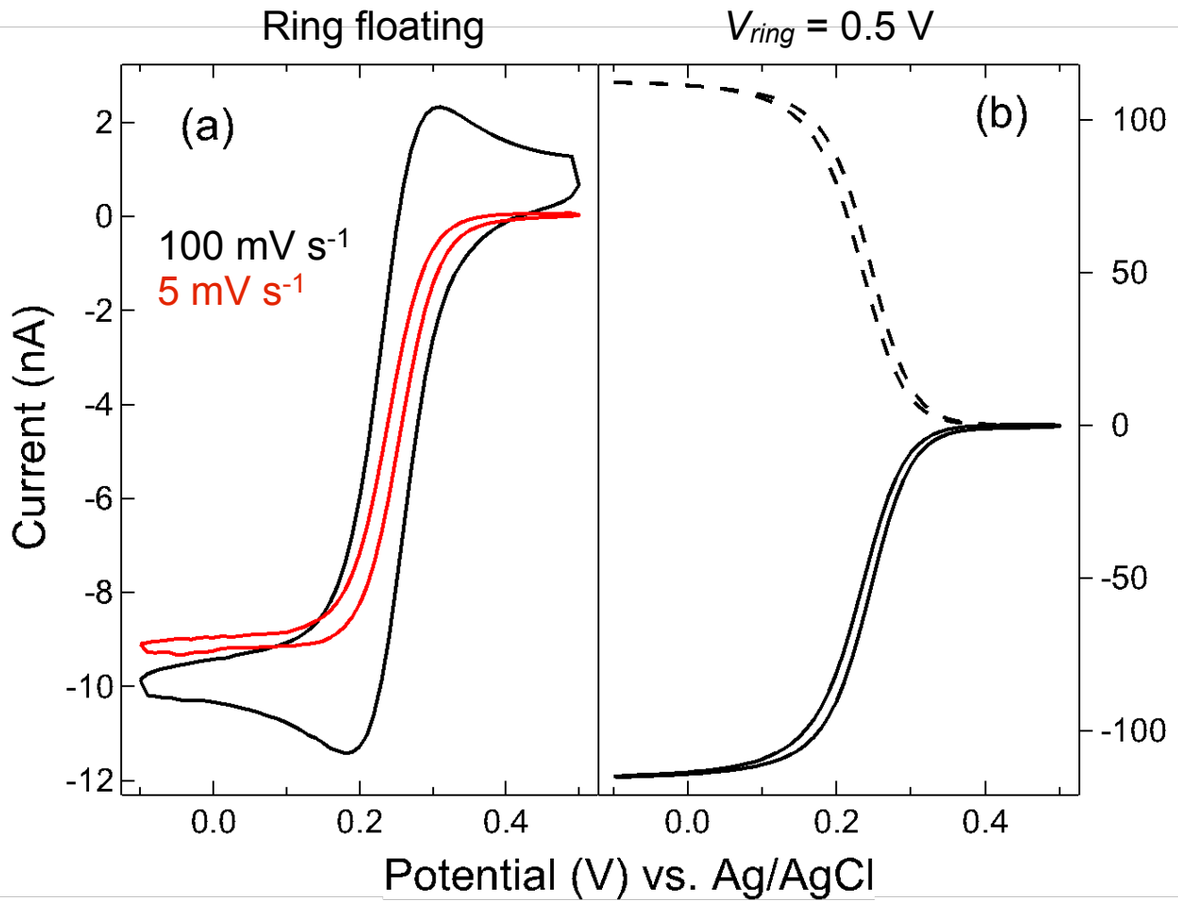
Generator-Collector Operating Characteristics in 0-D RRDE Arrays

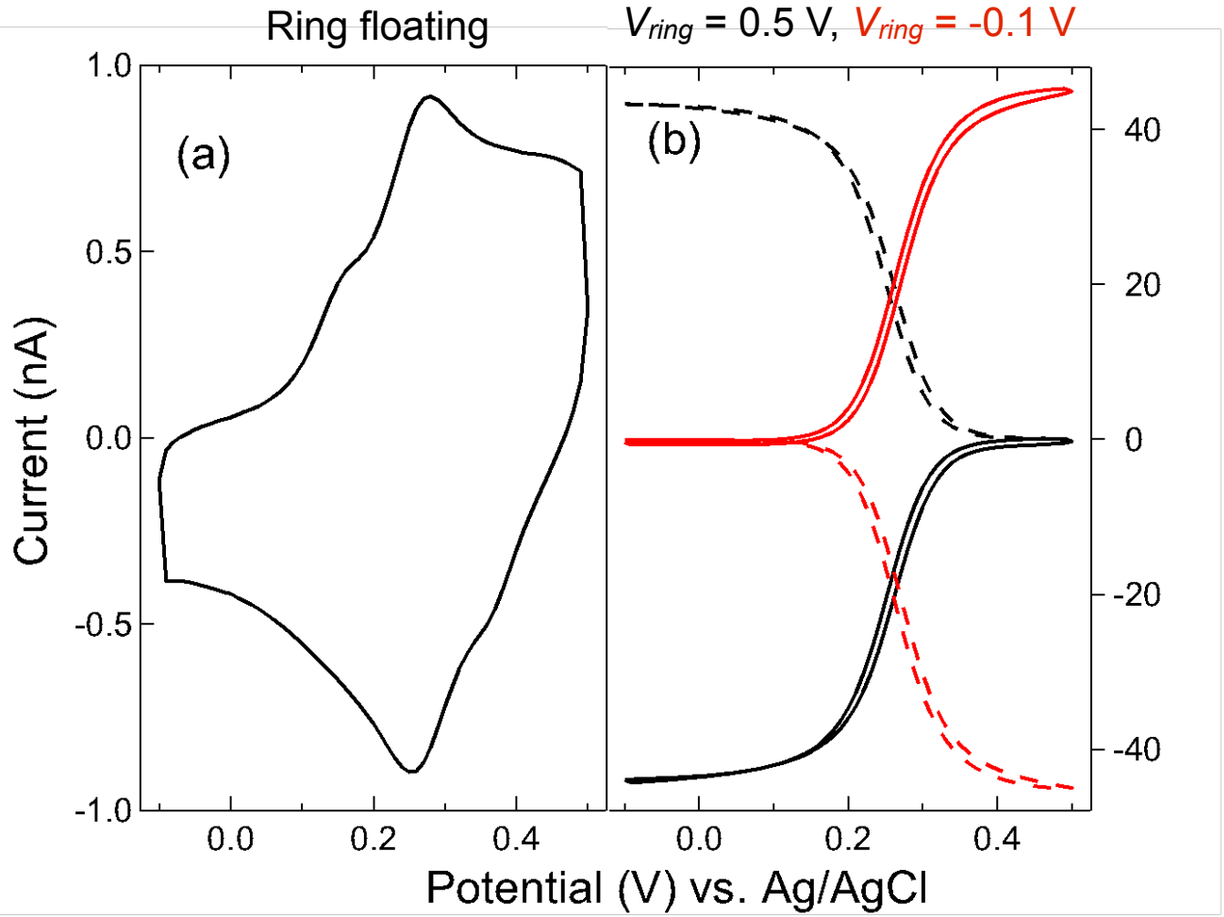


Electrode Separation (nm)	Φ_r	Φ_d	AF^a	N_{rc}	η
100	0.98	0.91	12.3	12.5	0.98
200	0.98	0.90	7.8	8.3	0.99
300	0.96	0.84	5.2	5.5	0.97
300 (low density)	0.74	0.34	1.4	1.4	0.67

Open Channel Configuration

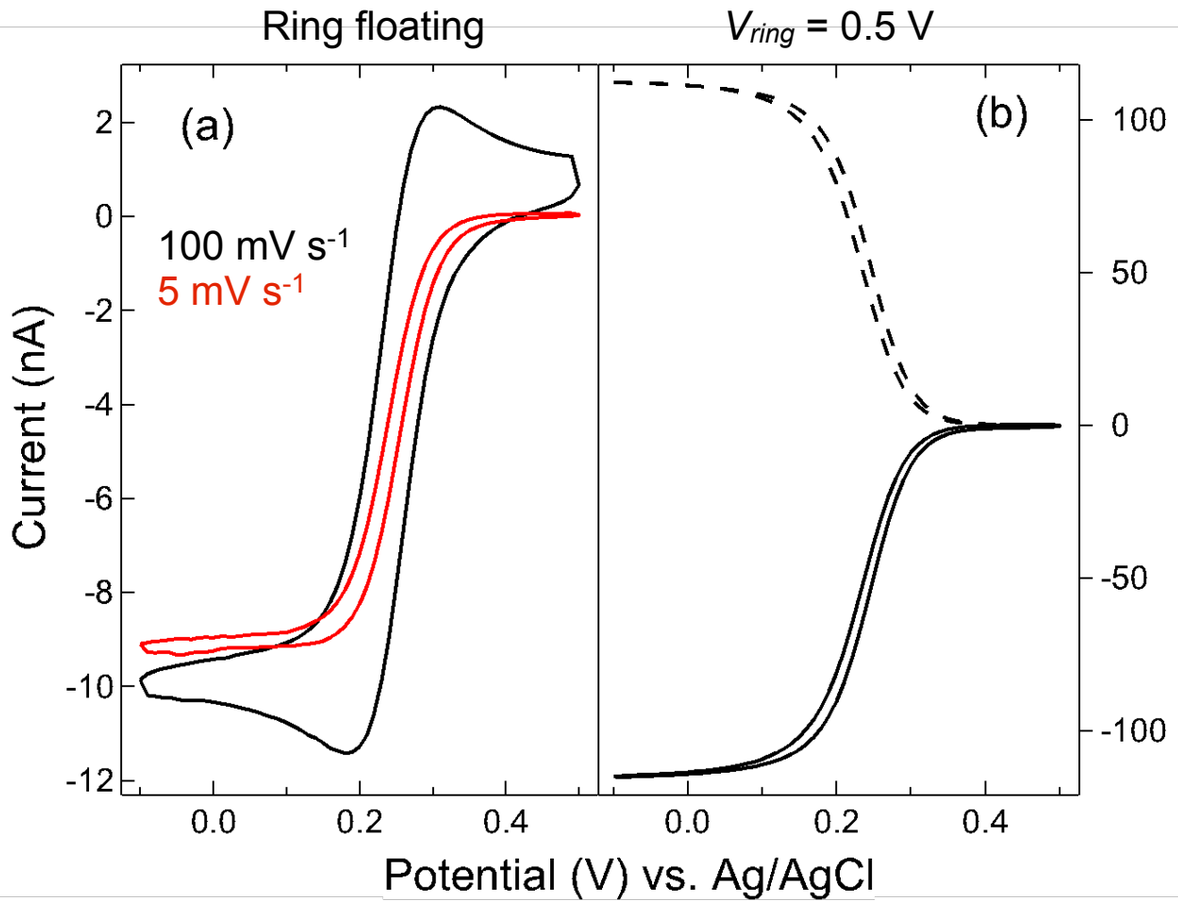
Nanochannel Confined

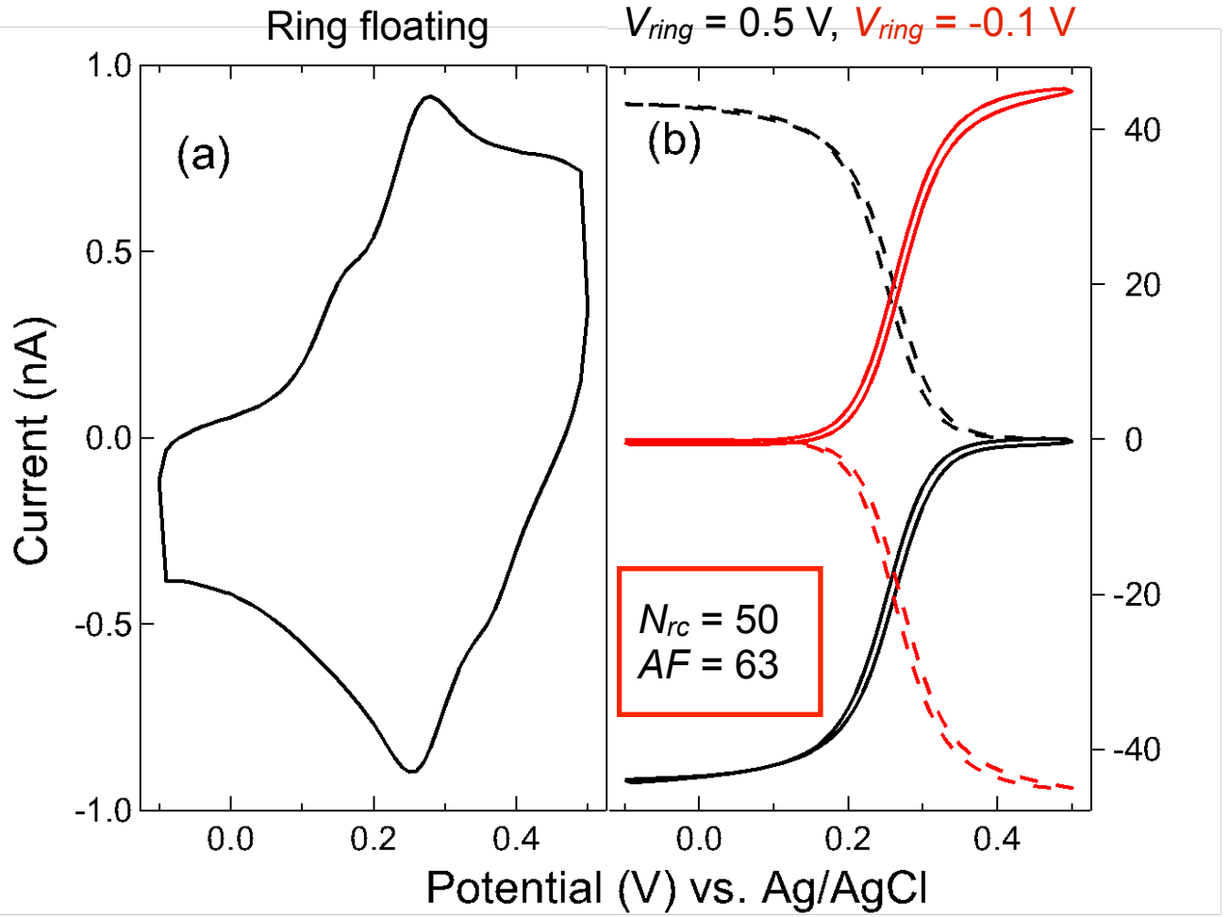




Open Channel Configuration

Nanochannel Confined





Open Channel Configuration

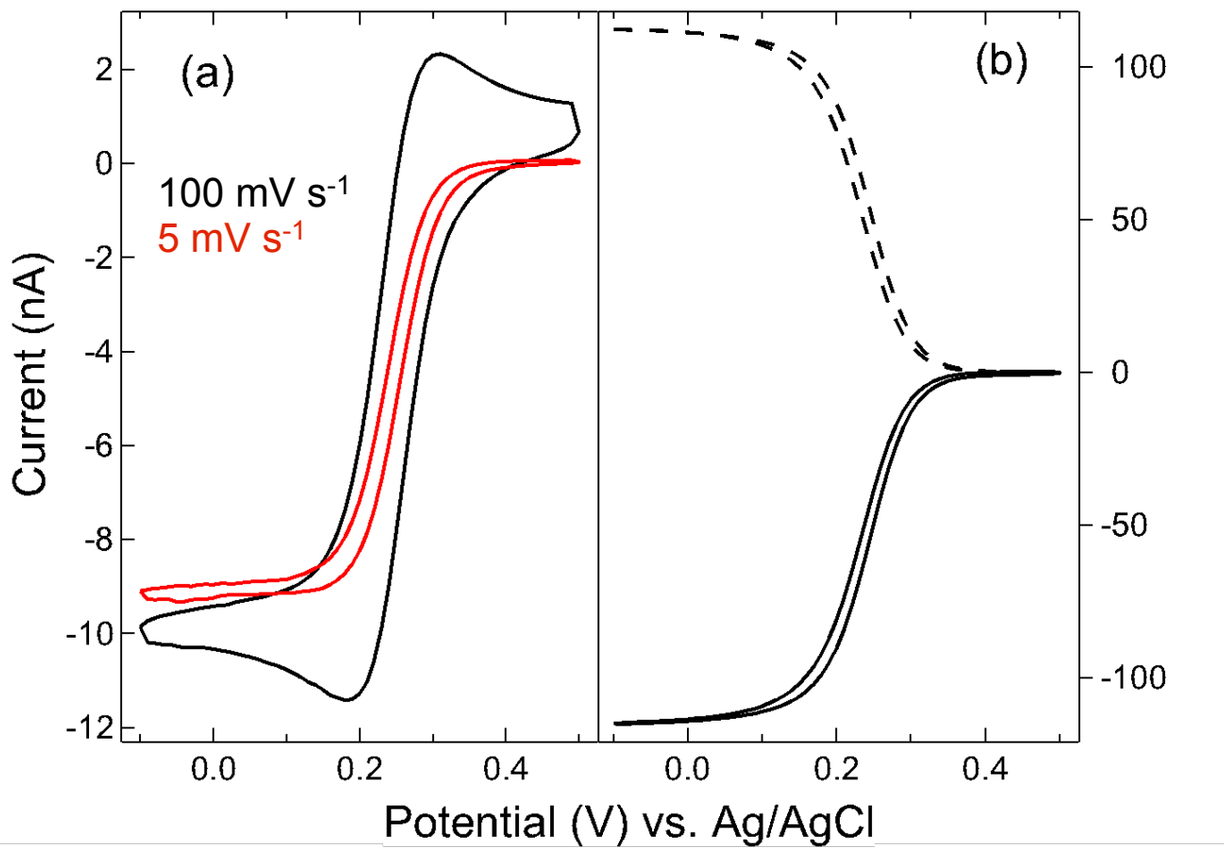
Nanochannel Confined

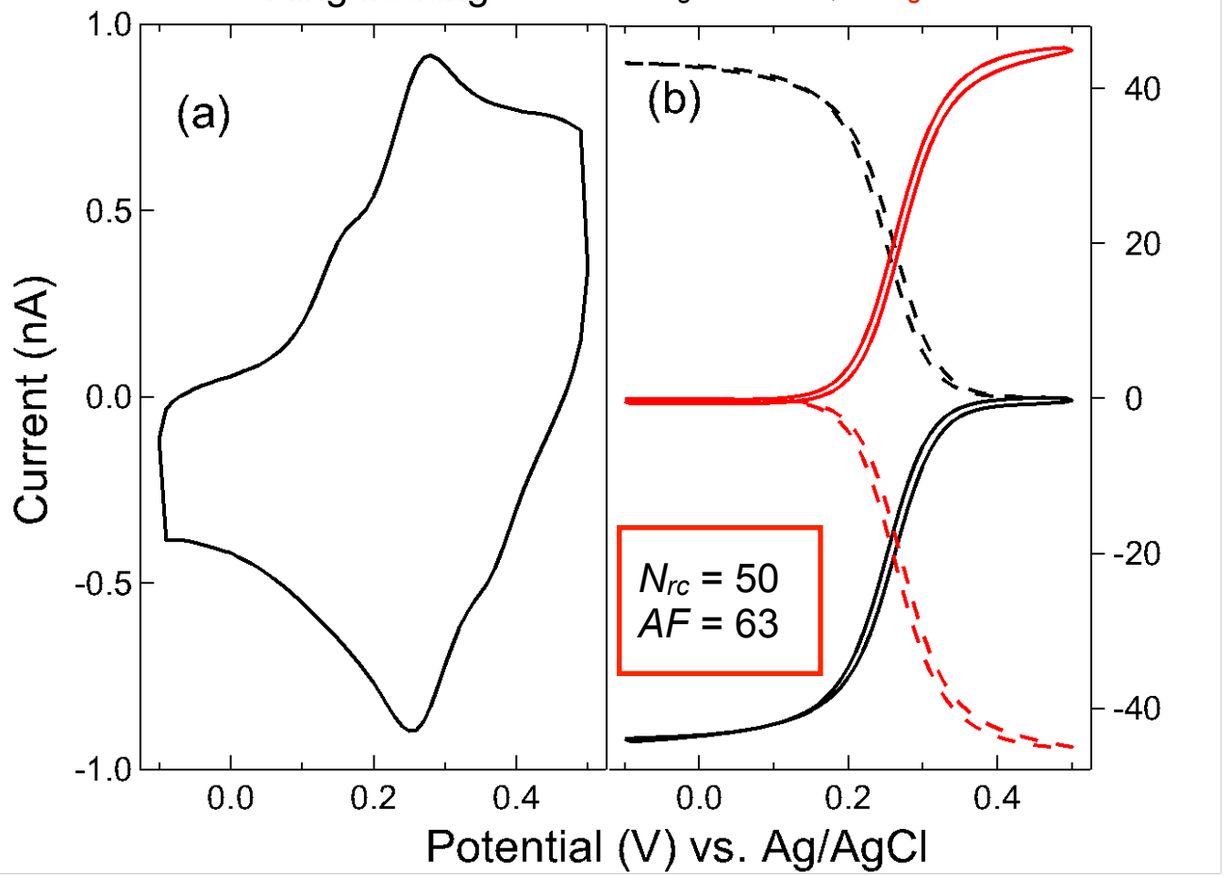
Ring floating

V_{ring} = 0.5 V

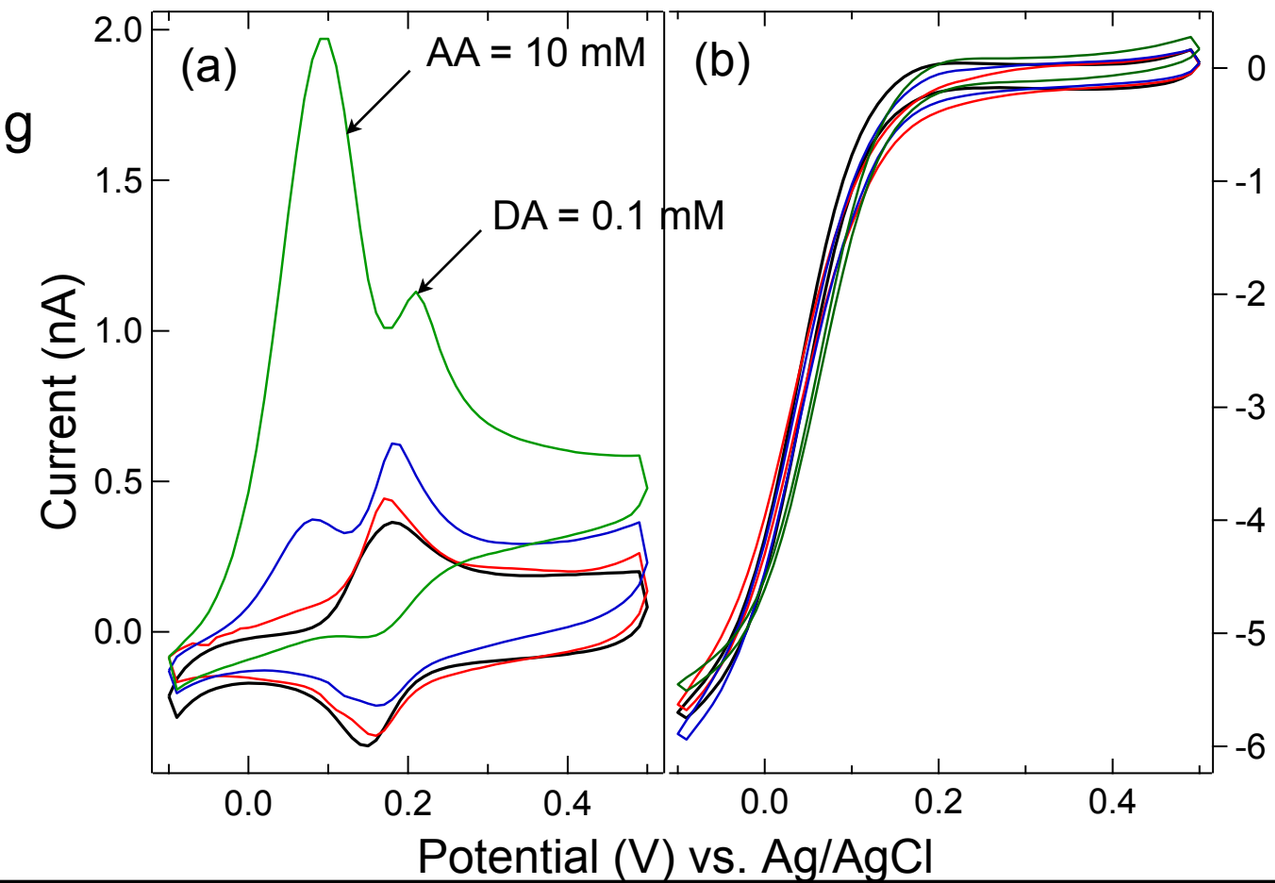
Ring floating

V_{ring} = 0.5 V, V_{ring} = -0.1 V



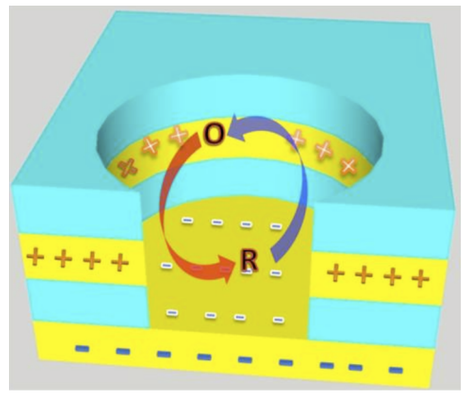


Ring floating



V_{ring} = +0.5V

Electrochemistry without Supporting Electrolyte



Electrochemistry without Supporting Electrolyte

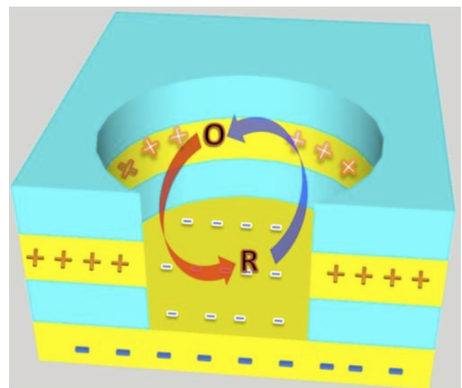
$Ru(NH_3)_6^{2/3+}$

Current (nA)

10^5
10^4
10^3
10^2
10^1
10^0

$1/\kappa_h$

3.0
2.5
2.0
1.5
1.0
0.5
0.0



10^{-1} 10^0 10^1 10^2 10^3 10^4 10^5

Concentration (μM)

Electrochemistry without Supporting Electrolyte

$Ru(NH_3)_6^{2/3+}$

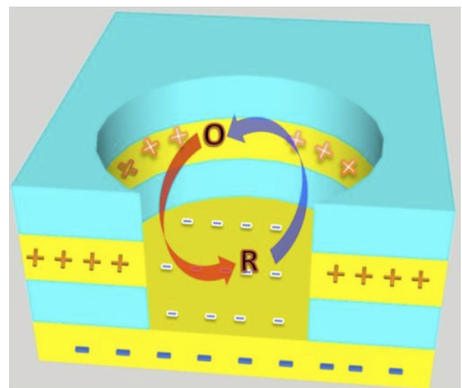
with SE

Current (nA)

10^5
10^4
10^3
10^2
10^1
10^0

$1/\kappa_h$

3.0
2.5
2.0
1.5
1.0
0.5
0.0



10^{-1} 10^0 10^1 10^2 10^3 10^4 10^5

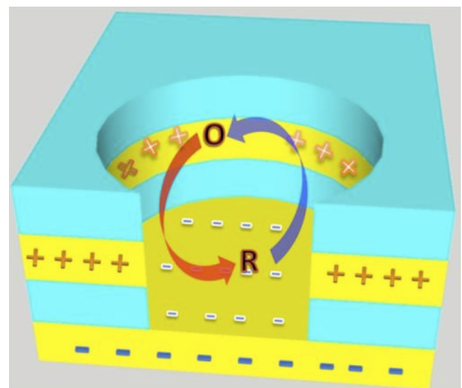
Concentration (μM)

Electrochemistry without Supporting Electrolyte

$Ru(NH_3)_6^{2/3+}$

without SE

with SE



Current (nA)

10^5
10^4
10^3
10^2
10^1
10^0

3.0
2.5
2.0
1.5
1.0
0.5
0.0

$1/\kappa_h$

10^{-1} 10^0 10^1 10^2 10^3 10^4 10^5

Concentration (μM)

Electrochemistry without Supporting Electrolyte

$Ru(NH_3)_6^{2/3+}$

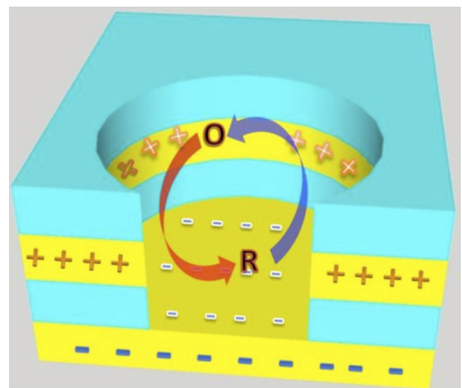
$h < \lambda_D$

$h \sim \lambda_D$

$h >> \lambda_D$

without SE

with SE



Current (nA)

10^5
10^4
10^3
10^2
10^1
10^0

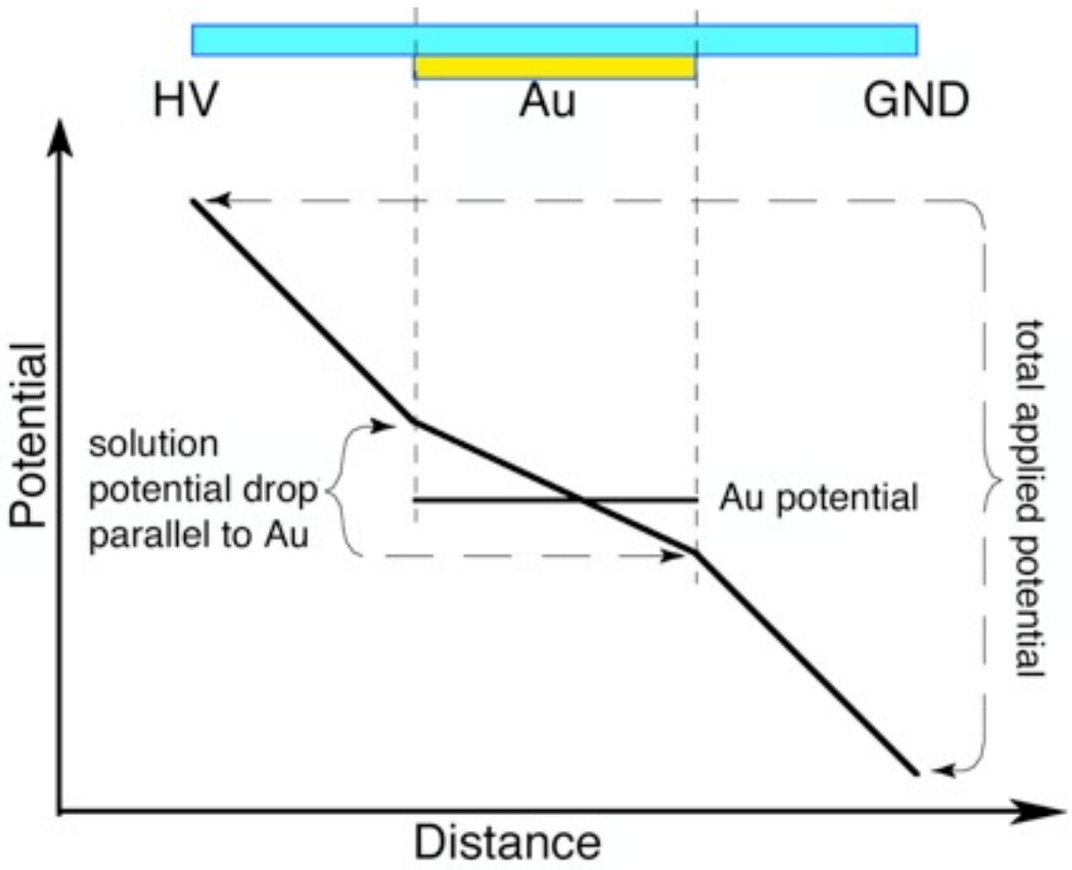
3.0
2.5
2.0
1.5
1.0
0.5
0.0

$1/\kappa h$

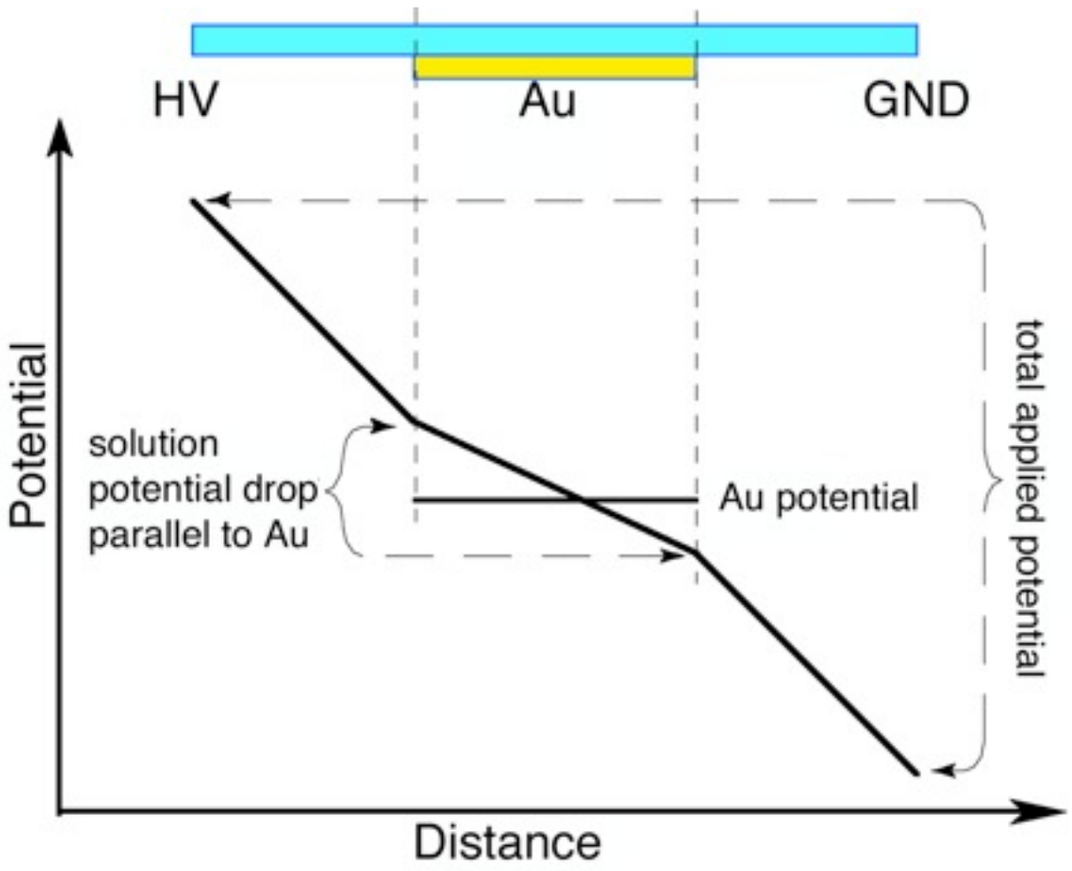
10^{-1} 10^0 10^1 10^2 10^3 10^4 10^5

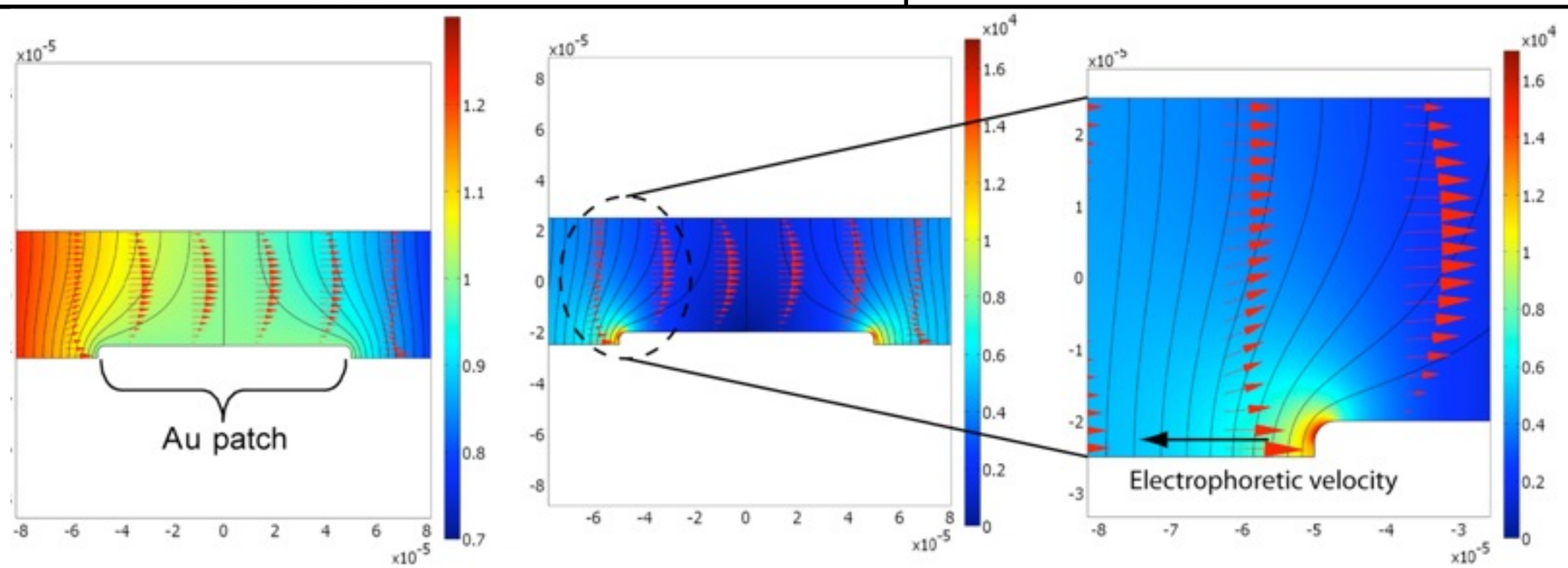
Concentration (μM)

Fundamental Problems using Metals with Electrokinetic Flow

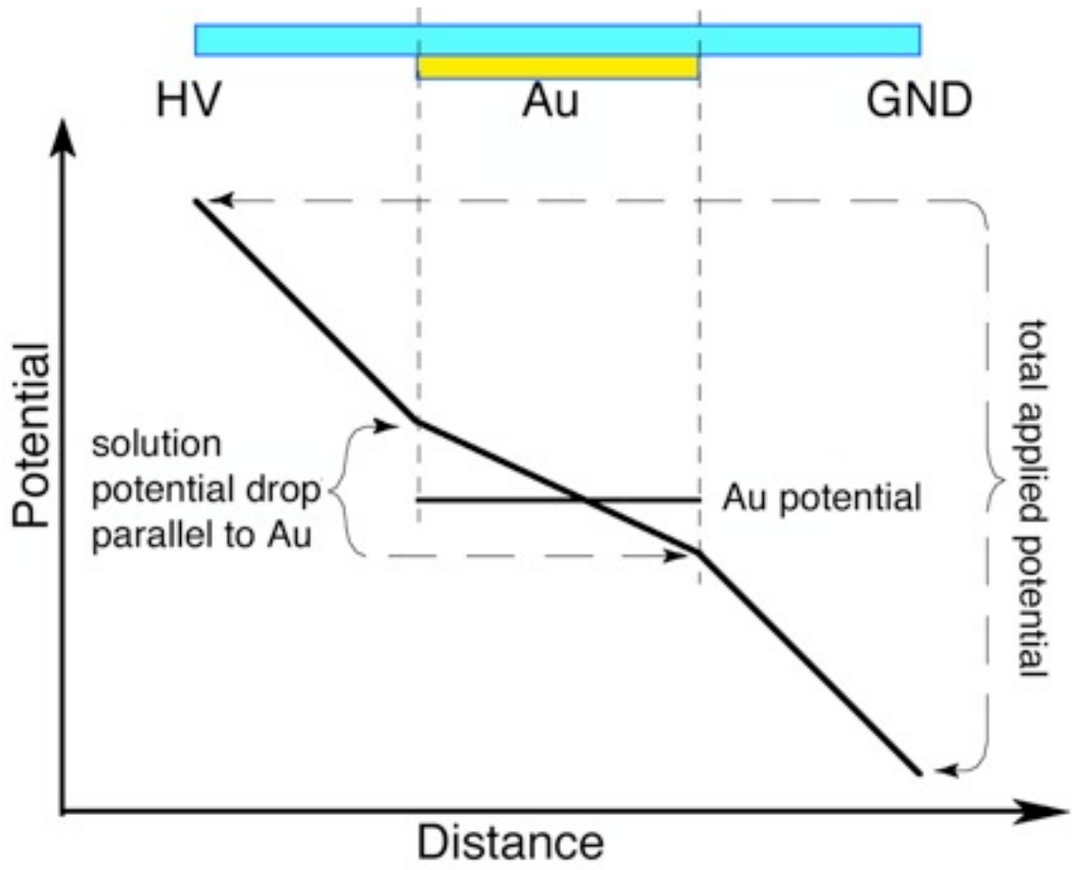


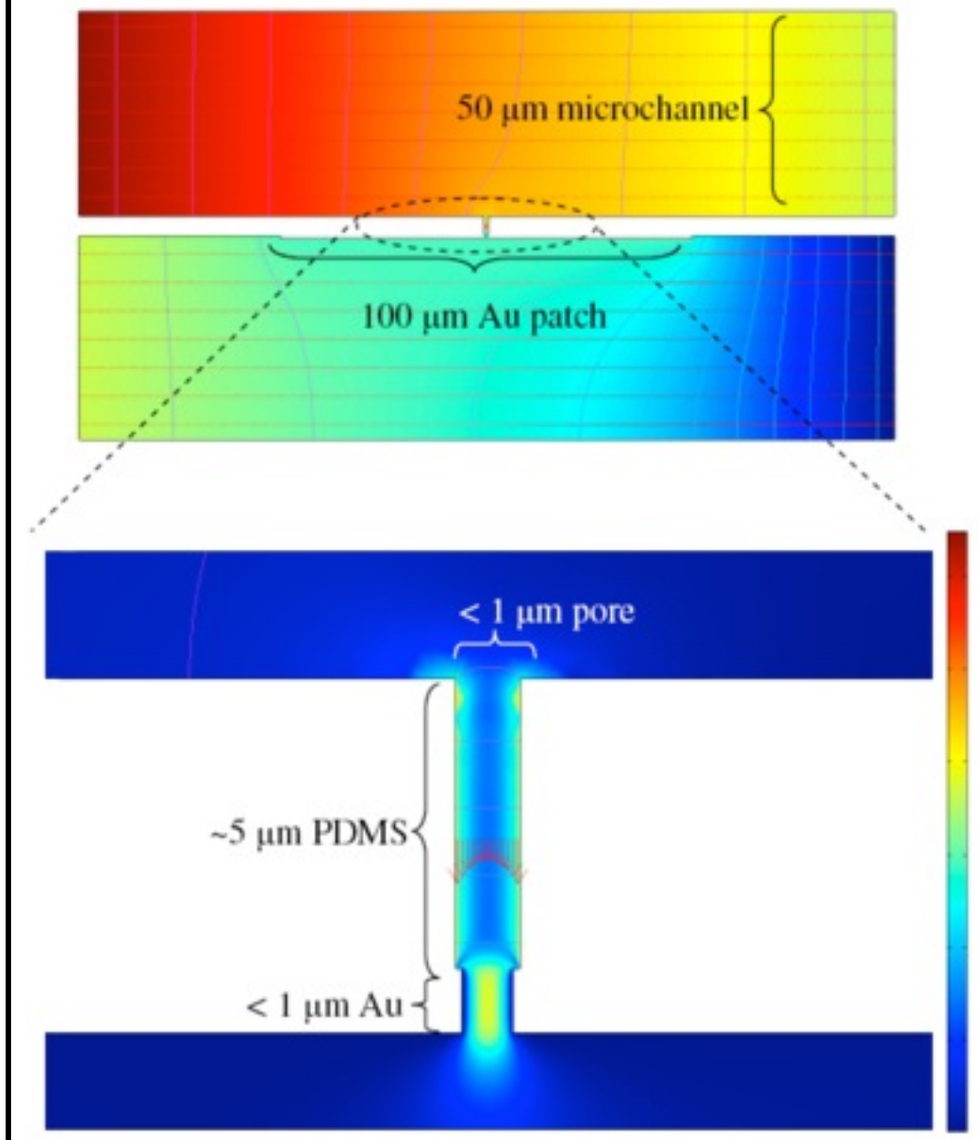
Fundamental Problems using Metals with Electrokinetic Flow

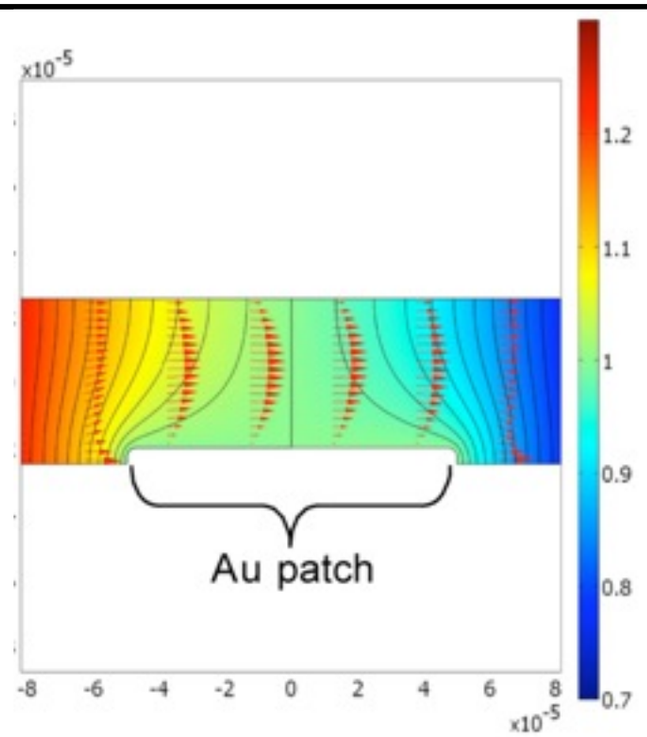


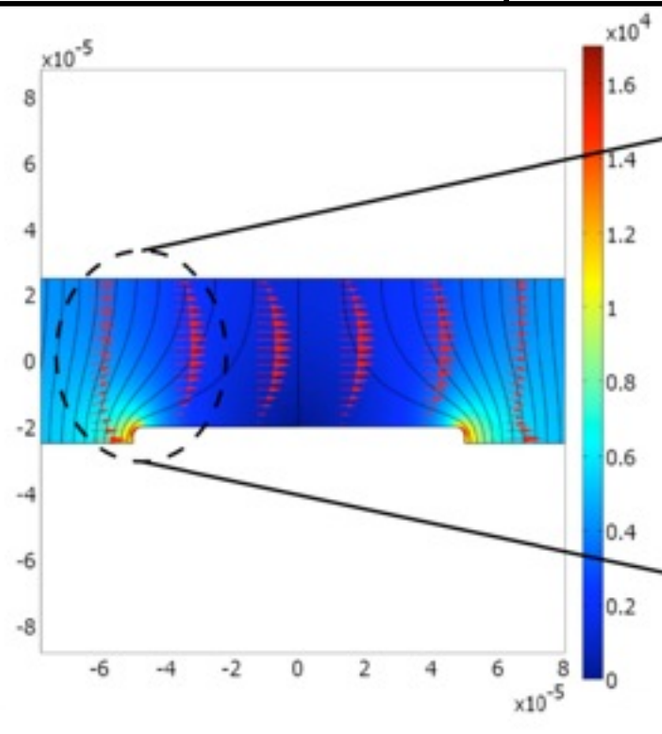


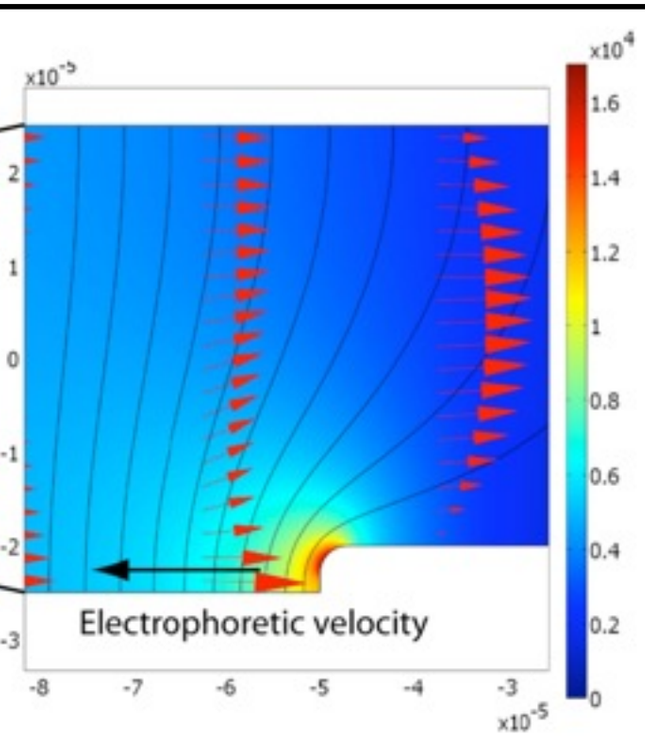
Fundamental Problems using Metals with Electrokinetic Flow



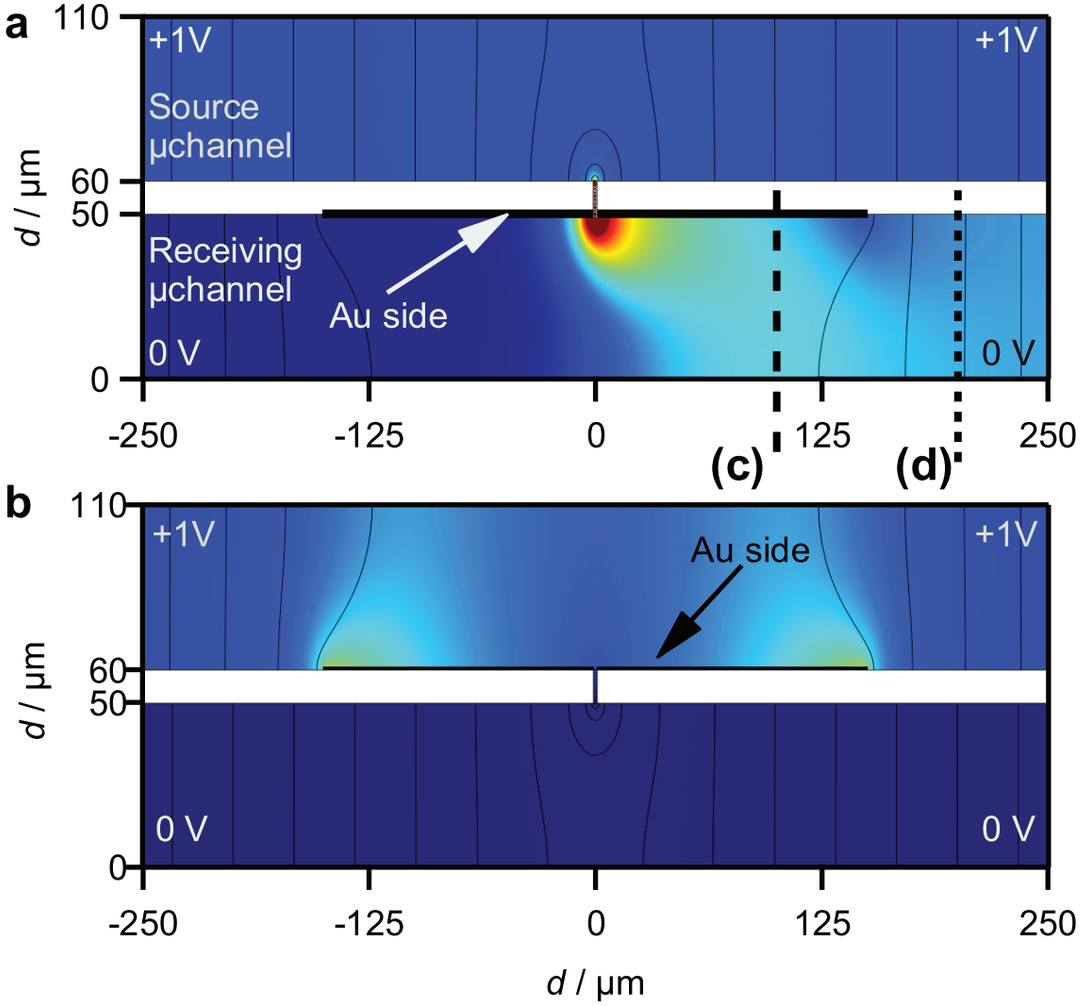


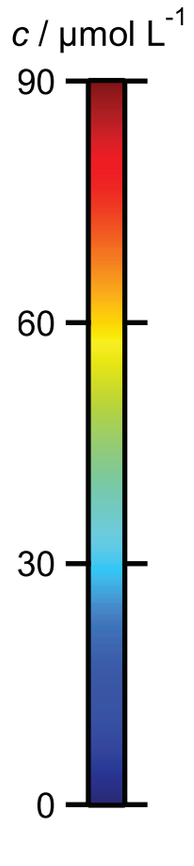


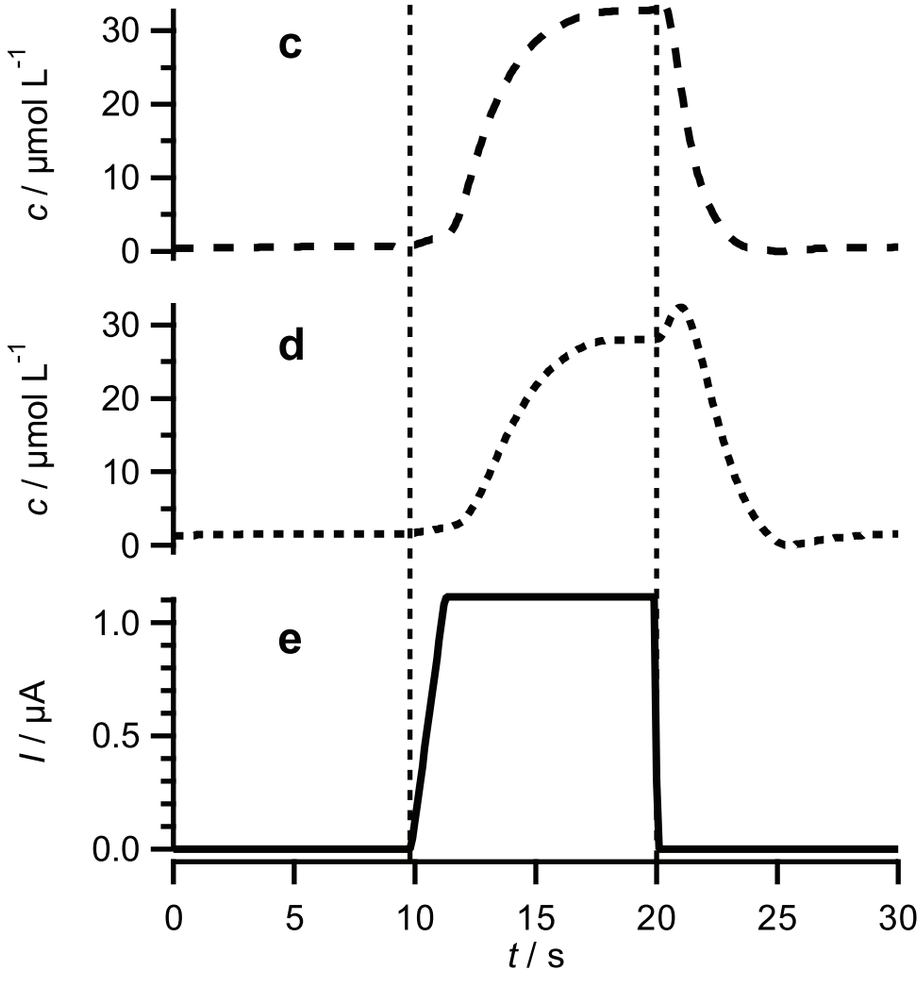




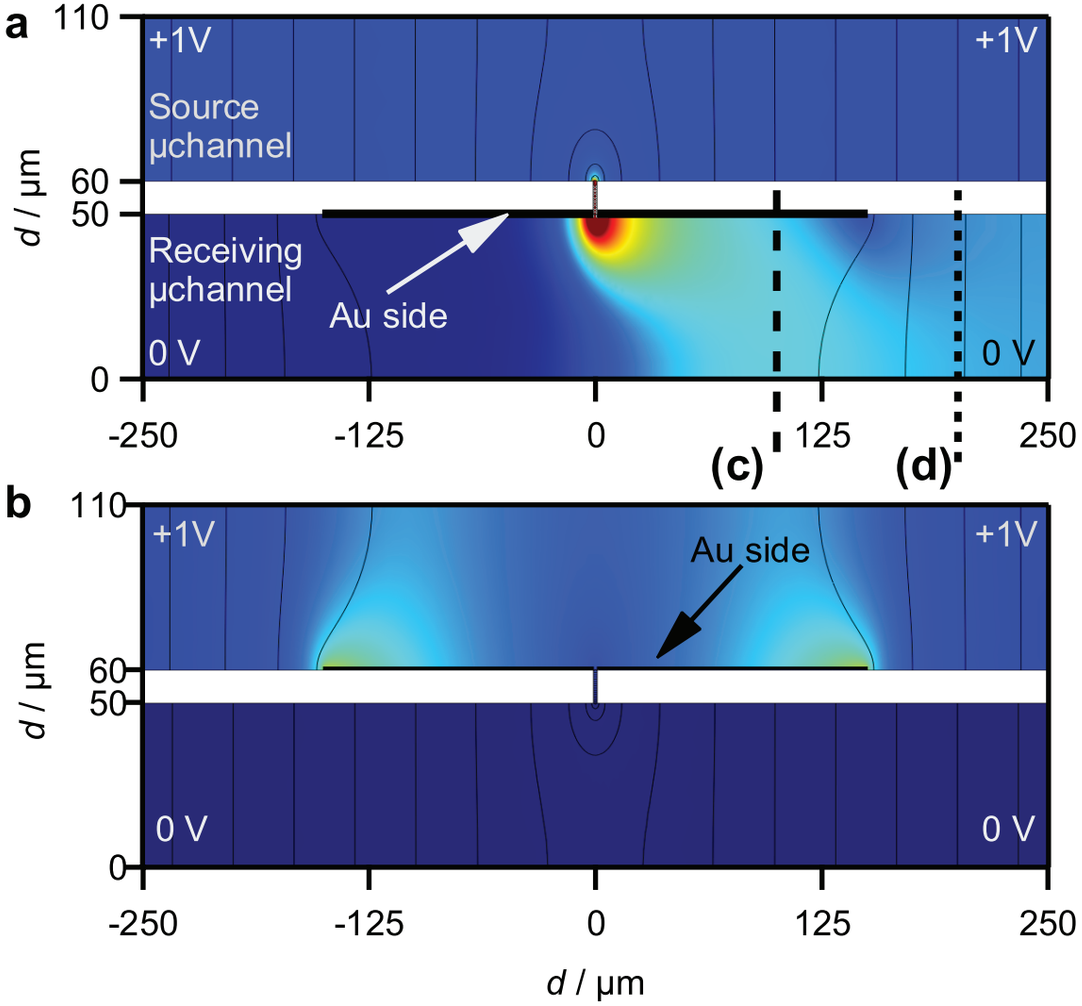
Simulation

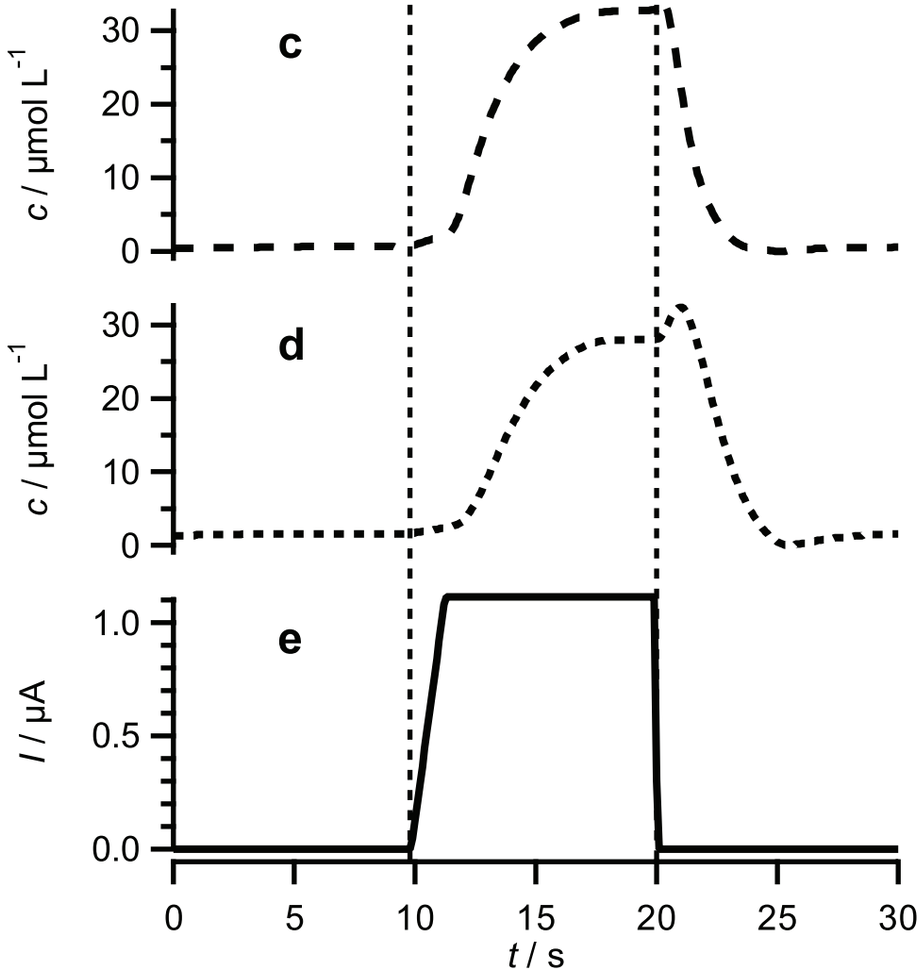

a
b
+1V
Source μchannel
Receiving μchannel
Au side
0 V
d / μm
110
60
50
0
-250
-125
0
125
250
(c)
(d)


c / μmol L-1
90
60
30
0


c
d
e
c / μmol L-1
I / μA
30
20
10
0
1.0
0.5
0.0
0
5
10
15
20
25
30
t / s

Simulation





Experiment