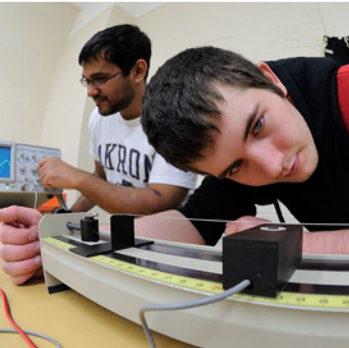


Aliaksei (Alex) Boika

Assistant Professor, Department of Chemistry, UA

Hot Microelectrodes: Fundamentals and Applications

01/27/2020
Akron Physics Club



The University of Akron

Buchtel College of Arts and Sciences

Acknowledgements

Group members:

Zhiling (Linda) Zhao

Jason Bonezzi

Ariana Frkonja-Kuczyn

Tulashi Luitel

Syed Rafiquddin

<http://www.hotelectrochemistry.org>

Collaborators:

Prof. Michael Konopka (UA)

Prof. Kevin Leonard (KU)

Prof. Dmitry Matyushov (ASU)

Funding provided by The University
of Akron

The
University
of Akron



Outline

What are Microelectrodes?

What are Hot Electrodes?

Electrokinetic Manipulation and Electrochemical
Detection of Analytes

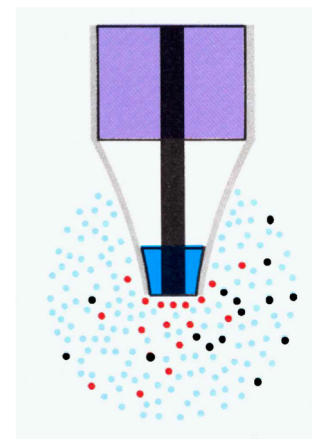
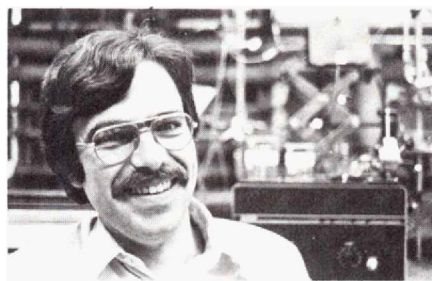
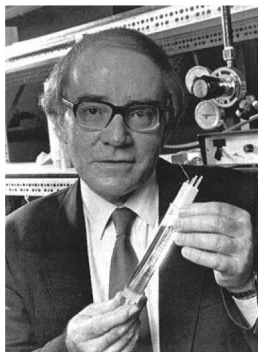


The University of Akron
Buchtel College of Arts and Sciences

Elephant in the Room - UME

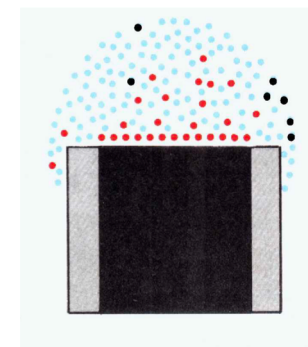
Developed ca. 1980 by:

- Martin Fleischmann (U. Southampton, UK)
- Mark Wightman (Indiana U., USA)



Advantages:

- size
- measurement of steady-state currents
- measurements in highly resistive media

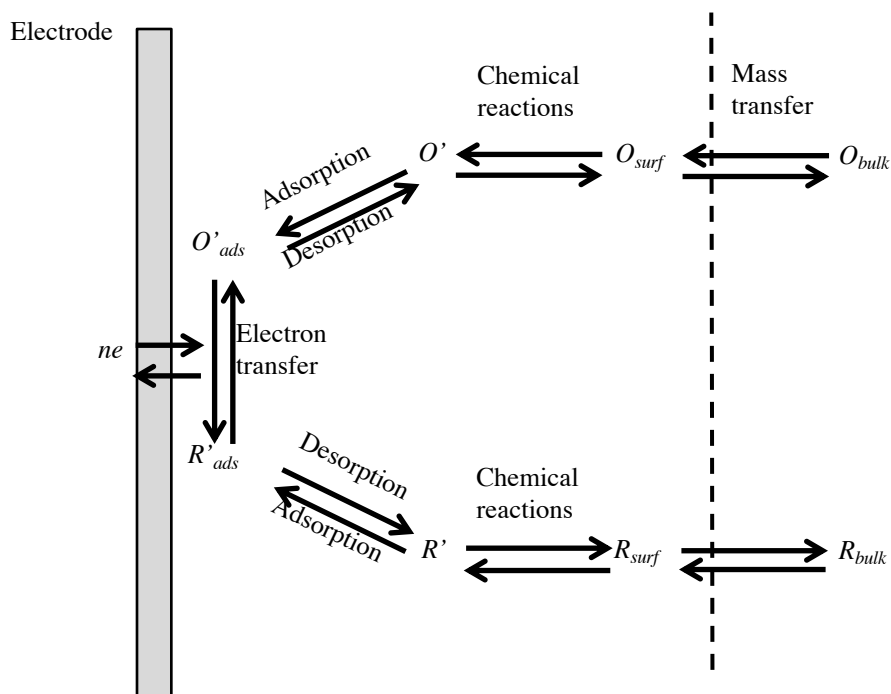
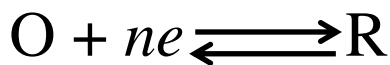
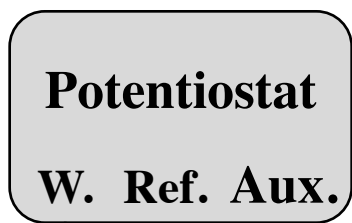


By Source, Fair use, <https://en.wikipedia.org/w/index.php?curid=24939952>

Heinze, J. *Angewandte Chemie* **1993**, *105*, 1327-1349

Wightman, R. M. *Analytical Chemistry* **1981**, *53*, 1125A-1134A

Faradaic Electrochemistry



What are Hot UMEs ?

Baranski, 2002:

Hot Microelectrodes

Andrzej S. Baranski*

Department of Chemistry, University of Saskatchewan, 110

Heat generation at disk microelectrodes by a high-amplitude (few volt) and high-frequency (0.1–2 GHz) alternating voltage is described. This method allows changing electrode temperature very rapidly and maintaining it well above the boiling point of solution for a very long time without any indication of boiling. The size of the hot zone in solution is determined by the radius of the electrode. There is no obvious limit in regard to the electrode size, so theoretically, by this method, it should be possible to create hot spots that are much smaller than those created with laser beams. That could lead to potential applications in medicine and biology. The heat-generating waveform does not electrically interfere with normal electroanalytical measurements. The noise level at hot microelectrodes is only slightly higher, as compared to normal microelectrodes, but diffusion-controlled currents at hot microelectrodes may be up to 7 times higher, and an enhancement of kinetically controlled currents may be even larger. Hot microelectrodes can be used for end-column detection in capillary electrophoresis and for in-line or in vivo analyses. Temperature gradients at hot microelectrodes may exceed 1.5×10^5 K/cm, which

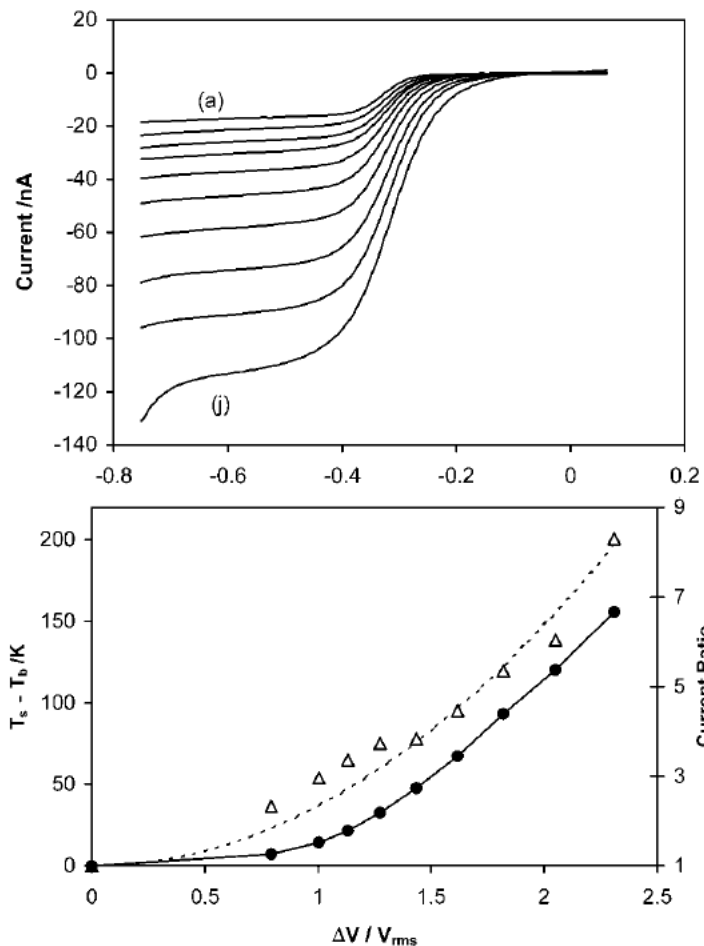


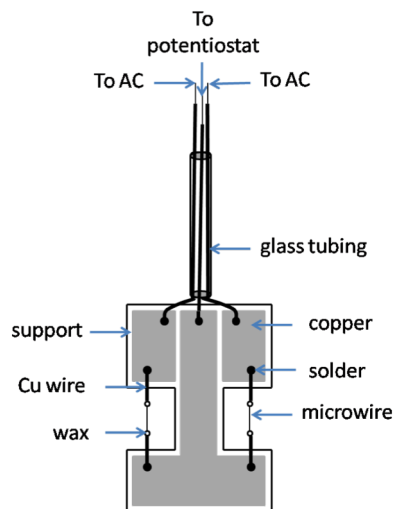
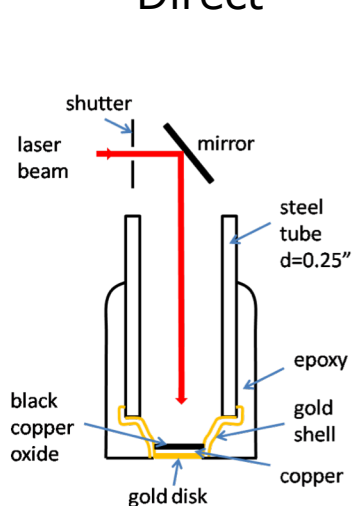
Figure 5. Temperature change (Δ) and the limiting current ratio (\bullet) calculated from experimental results in Figure 4. Dashed line shows the temperature change predicted by eq 16 for $\rho = 2.4 \Omega\text{cm}$ and $\kappa = 5.64 \times 10^{-3} \text{ Wcm}^{-1} \text{ K}^{-1}$.

Baranski, A. S. *Anal. Chem.* **2002**, *74*, 1294-1301.

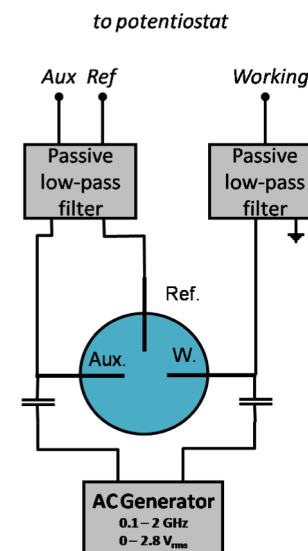
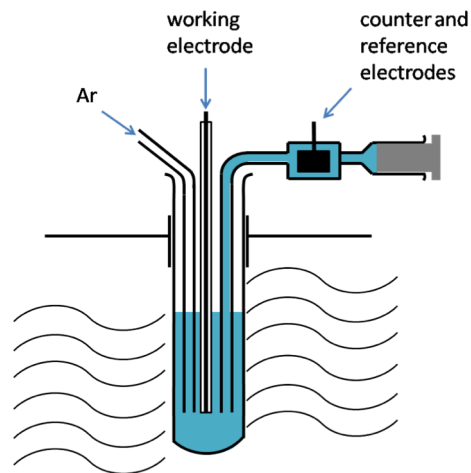
What are Hot Electrodes?

Methods of heating

- Direct



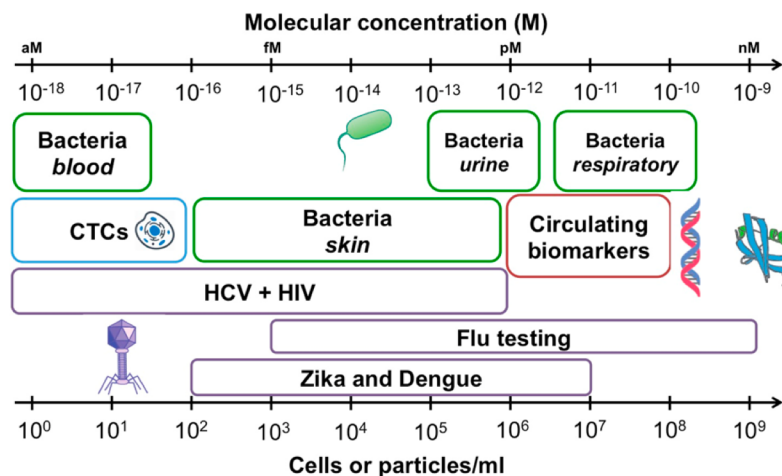
- Indirect



1. Miller, B. J. *Electrochem. Soc.* **1983**, *130*, 1639-1640.
2. Zerihun, T.; Gründler, P. J. *Electroanal. Chem.* **1996**, *404*, 243-248.
3. Compton, R. G.; Coles, B. A.; Marken, F. *Chem. Commun.* **1998**, 2595-2596.
4. Baranski, A. S. *Anal. Chem.* **2002**, *74*, 1294-1301.

Grand Challenges

- Detection of ultra-low concentrations of analytes (bioparticles, ions)



Kelley, S. O. *ACS Sens.* **2017**, *2*, 193-197.

- Better understanding of electron transfer
 - Butler – Volmer vs. Marcus theory
 - Energy, catalysis, life



Solution: Electrochemistry + AC Electrokinetics

- Electrochemical measurements are most suitable for sensing applications
 - success of electronics industry
- Electrokinetic phenomena control the behavior of analytes in solution

Electrokinetic phenomenon	Origin of charge	Typical frequency range
Electroosmotic flow	Ionic charge in the electrical double layer	10 – 100 kHz, can be dc
Electrothermal flow	Unbalanced ionic charge in non-isothermal solution	100 kHz – 1 GHz
Dielectrophoresis	Electric polarization charge (dipole)	10 kHz – 1 GHz, can be dc
Electrophoresis	Permanent charge (ions, colloids)	dc (ac does not lead to migration)

The Big Picture

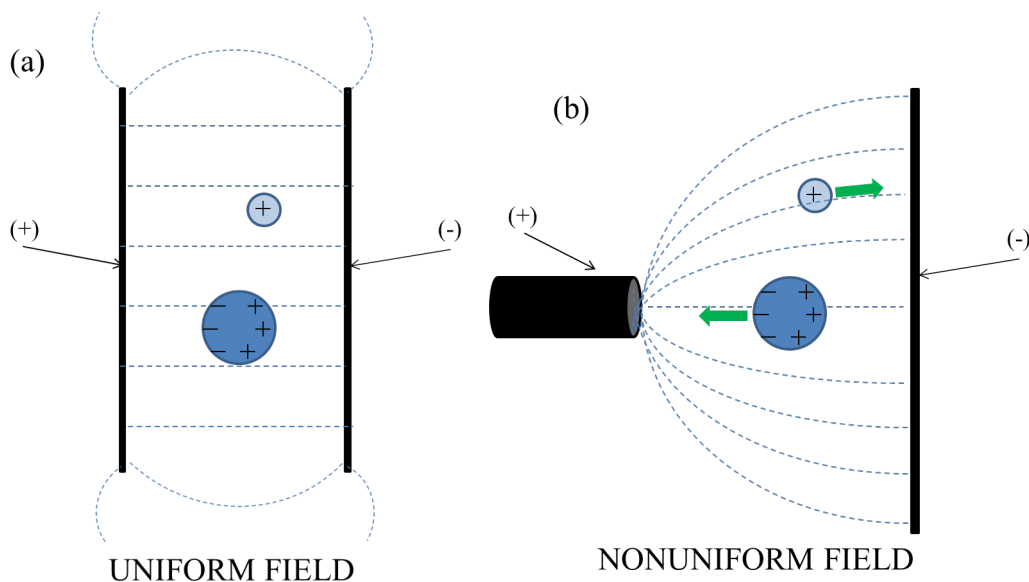


Fig. 1. Behavior of particles

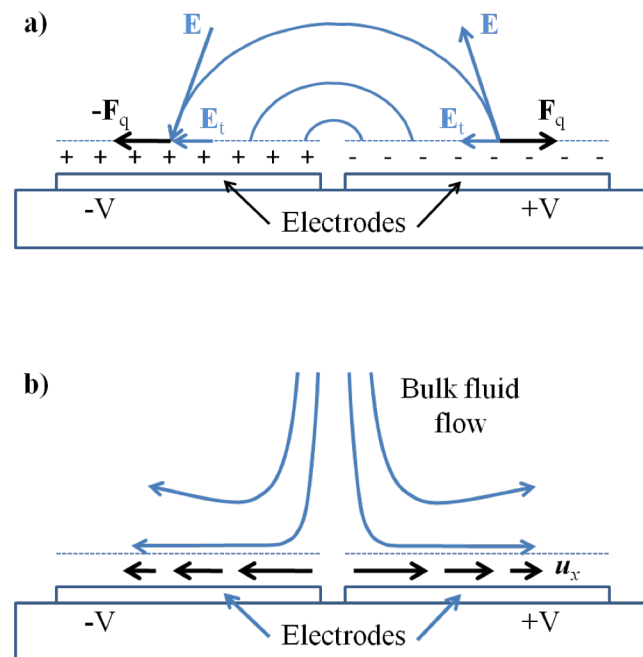


Fig. 2. Mechanism of EO (ET) flow

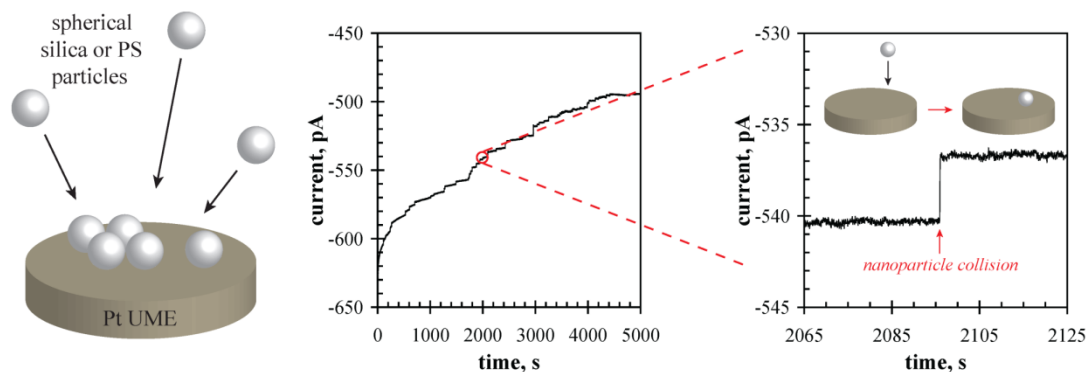
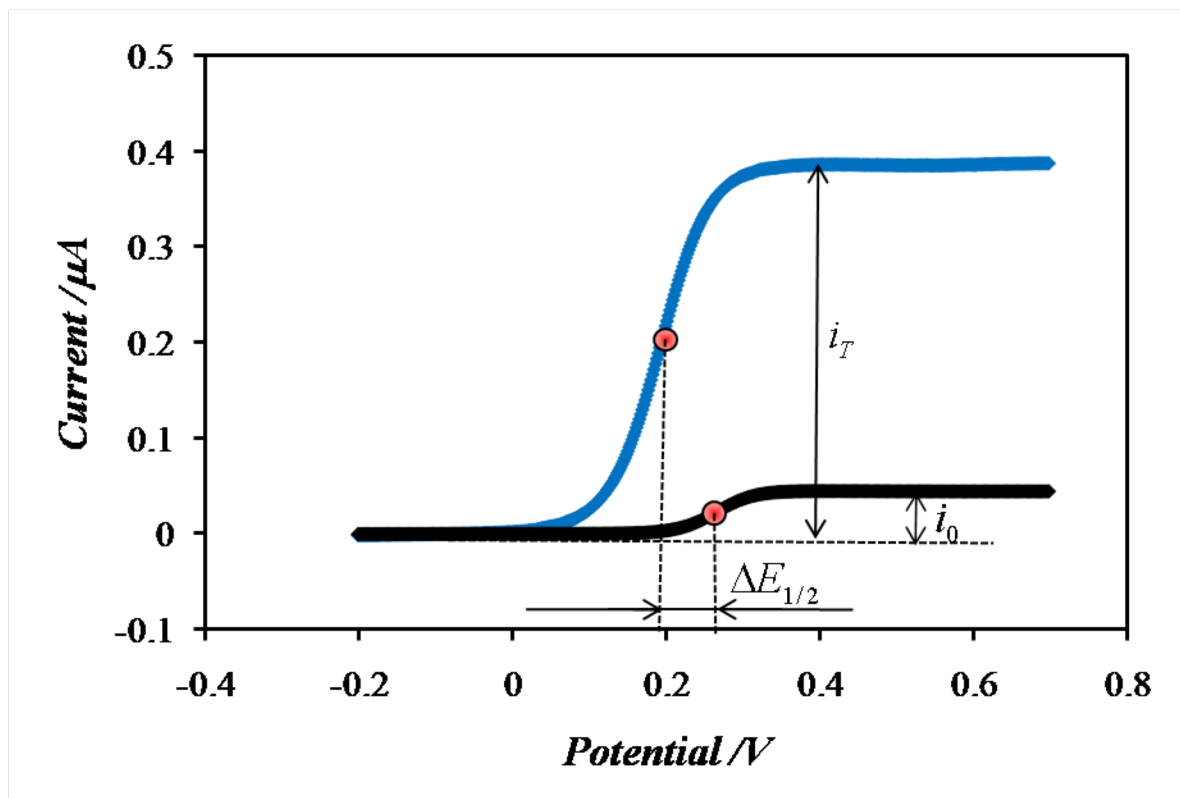


Fig. 3. Detection of particles (analytes)

Temperature Determination



$$\frac{\Delta E^0}{\Delta T}$$

Solution: 12.5 mM $\text{K}_4\text{Fe}(\text{CN})_6$, 20 mM KCN and 0.5 M KCl.

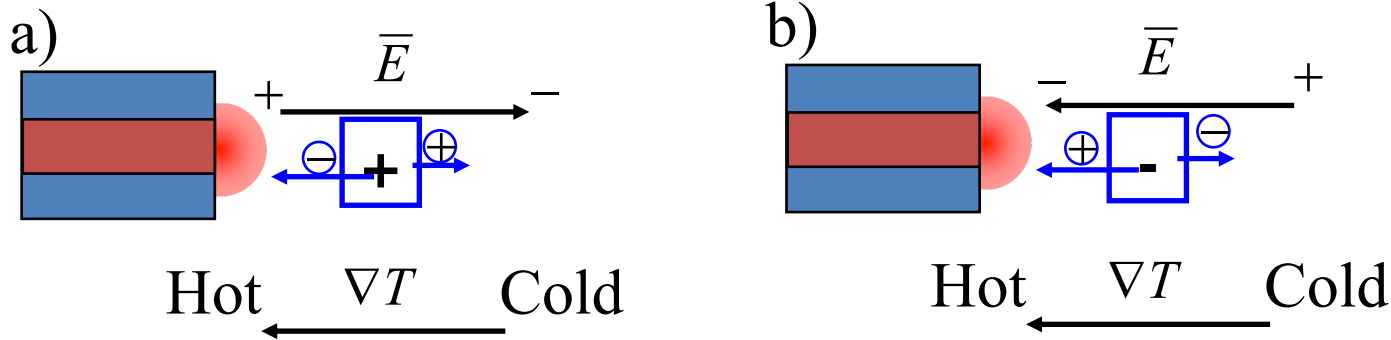
W. el.: 25 μm Pt disk; scan rate: 0.015 V/s; heating: 100 MHz, 2.8 V_{rms}

Boika, A.; Baranski, A. S. *Anal. Chem.* **2008**, *80*, 7392-7400.

Effect of AC Heating

Electrothermal flow (ETF)

$$\bar{f}_E = -\frac{1}{2} \left[\left(\frac{d\sigma}{\sigma dT} - \frac{d\varepsilon}{\varepsilon dT} \right) \frac{\varepsilon}{1 + (\omega\tau)^2} (\nabla T \cdot \nabla \phi_{ac}) \nabla \phi_{ac} + \frac{1}{2} |\nabla \phi_{ac}|^2 \frac{d\varepsilon}{dT} \nabla T \right]$$



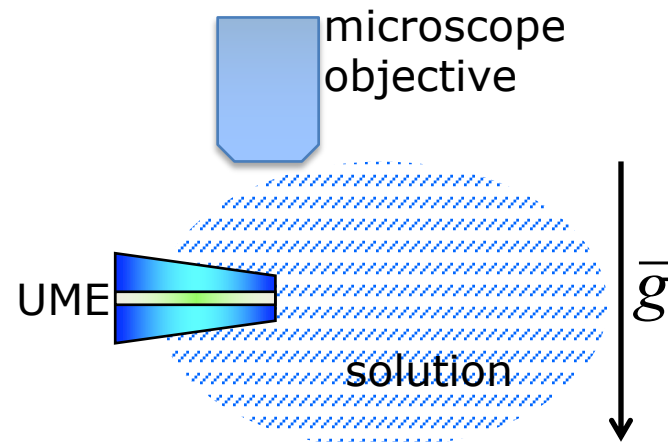
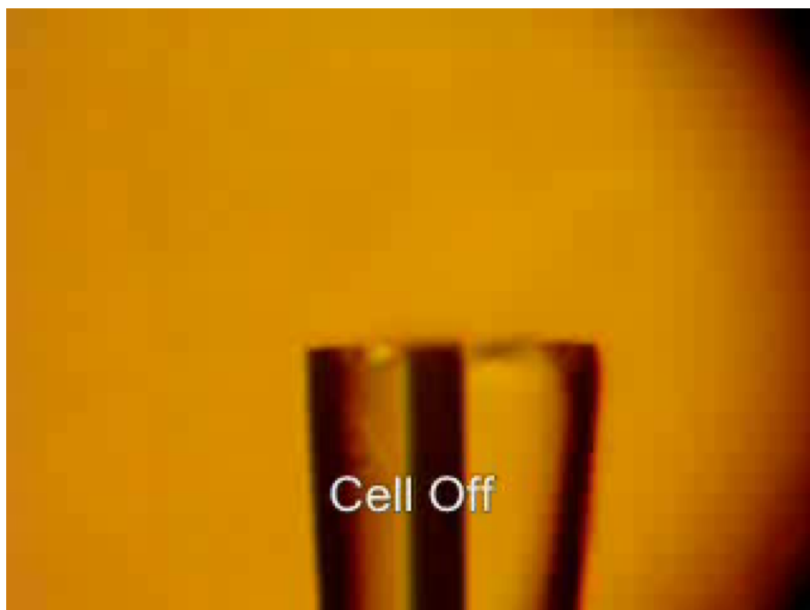
Coulomb force directed away from electrode
 Dielectric force – towards electrode

Ramos et al. *J. Phys. D: Appl. Phys.* **1998**, 31, 2338-2353.

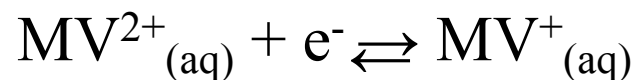
Morgan, H.; Green, N.G. *AC electrokinetics: colloids and nanoparticles*; Research Studies Press: Baldock, Eng.; Philadelphia, Pa.; 2003

Example of ETF

Microscopic observations of hot UMEs



Cell On:



50 mM methyl viologen in 0.5 M NaCl at a $25 \mu\text{m}$ Pt disk; heating 160 MHz, $2.8 \text{ V}_{\text{rms}}$

Boika, A.; Baranski, A. S. *Anal. Chem.* **2008**, *80*, 7392-7400.

Dielectrophoresis



$$F_{DEF} = 2\pi a^3 \epsilon_0 \epsilon_m K \nabla(\nabla \phi)^2$$

$$K = \frac{\epsilon_p - \epsilon_m}{\epsilon_p + 2\epsilon_m} \quad \text{Clausius - Mossotti factor}$$

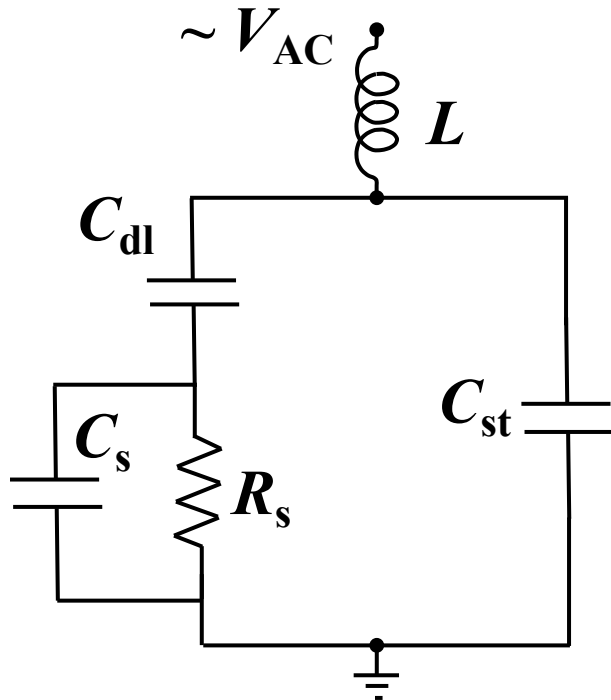
m-medium; p-particle

For metal particles $K=1$,
positive dielectrophoresis

Au particles (0.4 to 0.8 μm dia.) in 0.6 M H_2SO_4 at 25 μm Pt disk; heating by 160 MHz, 2.0 V_{rms}

Boika, A.; Baranski, A. S. *Anal. Chem.* **2008**, *80*, 7392-7400.

High Frequency AC heating



$$Z_L = jL\omega$$

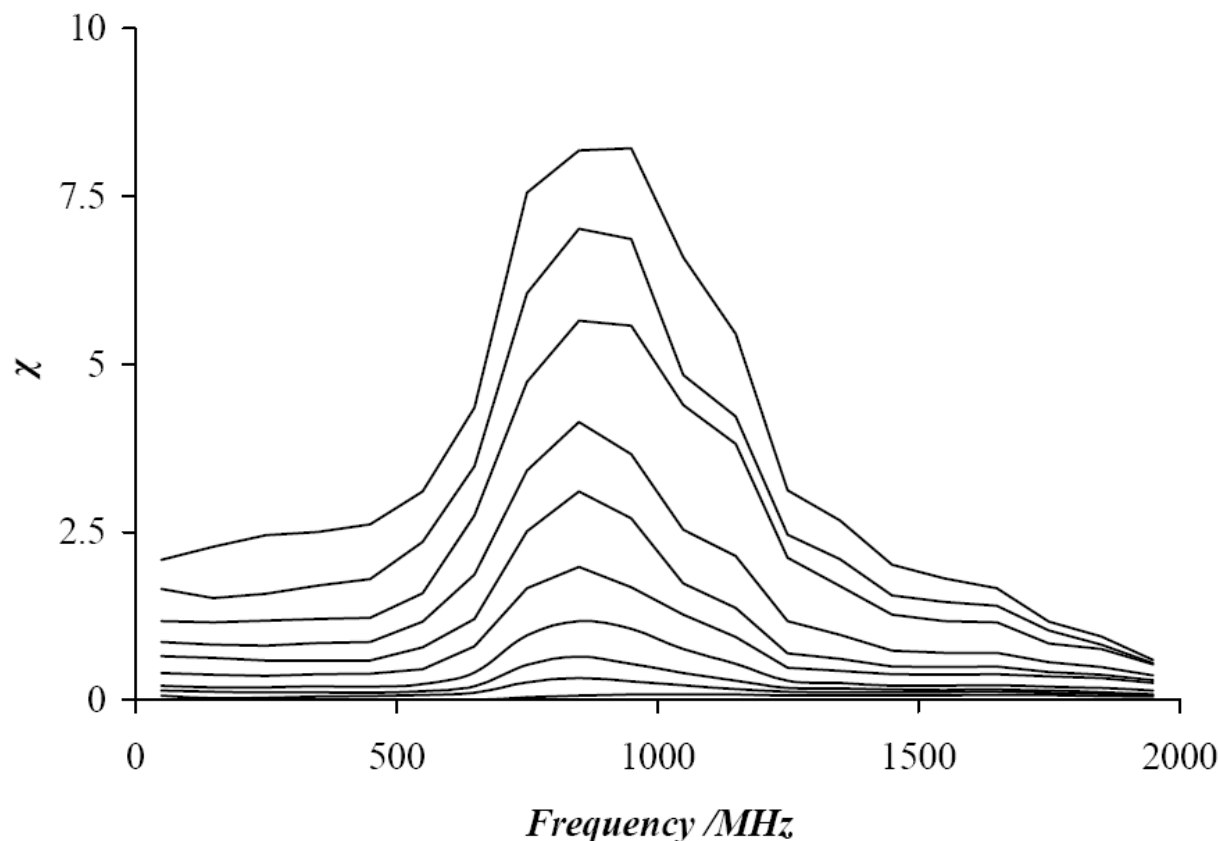
$$Z_C = -\frac{j}{\omega C}$$

$$P = \frac{(\Delta V_{R_s})^2}{R_s}$$

- Heating due to electrical energy dissipation on R_s
- Effectiveness depends on electrode construction

Boika, A.; Baranski, A.S. *Anal. Chem.* **2008**, *80*, 7392-7400.

Frequency Dependence Shows Maximum



12.5 mM $\text{K}_4\text{Fe}(\text{CN})_6$ in 0.5 M KCl(aq.) at a 25 μm Pt disk, dc potential kept at 500 mV, ac amplitude varied.

Boika, A.; Baranski, A.S. *Anal. Chem.* **2008**, *80*, 7392-7400.

Addressing low LOD by measuring collisions

- Electrochemical Collisions or Single-Entity Electrochemistry
 - *Ultimate sensitivity* amenable to analytical chemists

analytical
chemistry

Feature

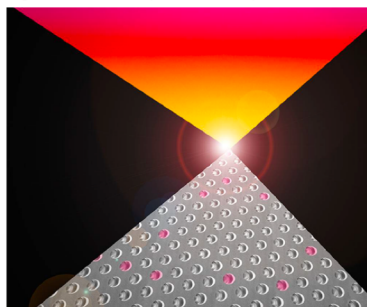
pubs.acs.org/ac

Optical Methods for Single Molecule Detection and Analysis

As analytical chemists, the highest resolution measurement one can make is at the single molecule level; it just does not get any better than that. To determine the concentration of a molecule in solution, the best way is to count the number of molecules in a given volume. As long as the volume contains a statistically large enough number of molecules and is above the Poisson noise limit, molecular counting is the most accurate way to make a measurement. Molecular counting is the method of the future and is beginning to be performed today.

David R. Walt

Department of Chemistry, Tufts University, Medford, Massachusetts 02155, United States



■ **INTRODUCTION: COUNTING MOLECULES IS AS GOOD AS IT GETS**

Single molecule analysis provides a resolution that cannot be obtained with ensemble measurements. Ensemble measurements are averages; small or rare differences between ostensibly

example, if these protein molecules are enzymes, each molecule may have a slightly different rate or specificity. Even small proteins, where some molecules will have identical primary sequences, will exhibit different conformations. Naturally occurring isotopes give the same molecular heterogeneity, which can result in different rates of reactions of different molecules in the population. Only by detecting and analyzing these single molecules will we be able to fully characterize a population of molecules and thereby understand their behavior.

This Feature describes single molecule detection and analysis methods but focuses on optical methods. Moerner² is credited with performing the first spectroscopic measurements of single molecules. Much of his seminal work and of others is in the realm of basic biophysics and will not be discussed in this Feature.

■ **HISTORICAL: ROTMAN WINS BY A MILE**

The first single molecule measurement was performed in 1961 by Boris Rotman at Stanford Medical School.³ Rotman sprayed a solution containing β -galactosidase and a fluorogenic substrate over a silicone oil preparation to create droplets in oil. By waiting for several hours, Rotman was able to detect and measure the presence of individual enzyme molecules by observing which droplets became fluorescent.

J | A | C | S
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Cite This: *J. Am. Chem. Soc.* 2018, 140, 15549–15559

Perspective

pubs.acs.org/JACS

Perspective and Prospectus on Single-Entity Electrochemistry

Lane A. Baker*¹

Department of Chemistry, Indiana University, 800 E. Kirkwood Avenue, Bloomington, Indiana 47405, United States

ABSTRACT: Single-entity electrochemistry (SEE) describes a recent trend in state-of-the-art electrochemistry applied to the study of individual “things.” Conceptually, SEE covers fundamentals and applications of SEE, as well as methods and tools to make SEE measurements. SEE is especially appealing, as it unifies different branches of electrochemistry and combines diverse approaches and techniques toward similar goals. In this Perspective, motivations and advantages of SEE are considered. A brief historical perspective and overview of recent ideas and directions in research in SEE are considered. In closing, future challenges, opportunities, and destinations related to SEE are discussed.

becoming more prevalent with the advent of microelectrodes in the 1980s, SEE has sought to push the limits of electrochemical measurement to ever shrinking size scales.

A 2016 Faraday Discussion (organized by Unwin, Bartlett, Fermin, Gooding, Koper, and Vincent) coined the name “single-entity electrochemistry”,¹ and prompted electrochemists to codify the concept of SEE as a special area of inquiry.^{2–4} Thus, SEE has begun to take corporeal form as an organizing or a unifying theme in electrochemical measurement, and has been the subject of additional recent meetings, editorials^{5–7} and reviews, and original research.

This perspective considers why we should make SEE measurements, pioneering experiments of the concept, recent triumphs, and a prospectus of the future for SEE measurements.

■ **WHY SHOULD WE STRIVE TO MEASURE SINGLE ENTITIES VIA ELECTROCHEMISTRY?**

There are two layers to this question. First, why should we measure single entities? Second, if we postulate such measurements are important, why use electrochemistry to do so?

1. **To Separate Individual Responses from the Bulk.** The most obvious reason is to determine what individual

At the most basic level, single-entity electrochemistry (SEE) refers to the study of one “thing” at a time by electrochemical means. SEE is an overarching concept in measurement. The “thing” measured could be anything (a cell, a molecule, a reaction) that represents a unit of interest. A diversity of topics, which includes entities from fields such as cellular biology, catalysis, and organic chemistry, means SEE is inherently interdisciplinary, seeking to answer questions from all corners of science. Length scales for SEE measurements can

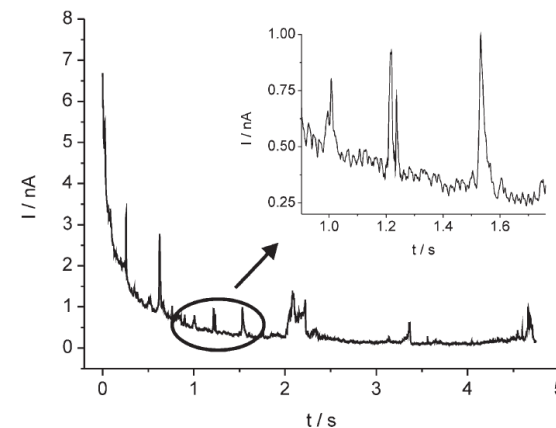
NP Collisions with Electrode

- R. Compton – direct oxidation

 - Ag NP oxidation in citrate solution

 - Zhou, Y. G. *et al. Angew. Chem., Int. Ed.*, **2011**, *50*, 4219.

 - Review: Rees, N.V. *et al. RSC Advances*, **2012**, *2*, 379

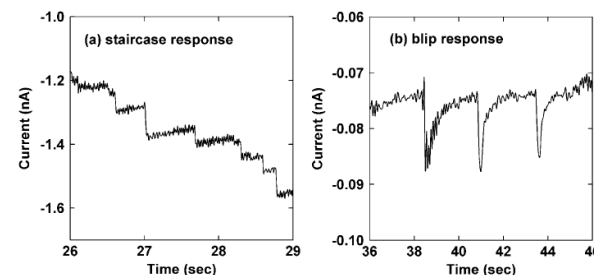


- A. Bard - electrocatalytic voltammetry

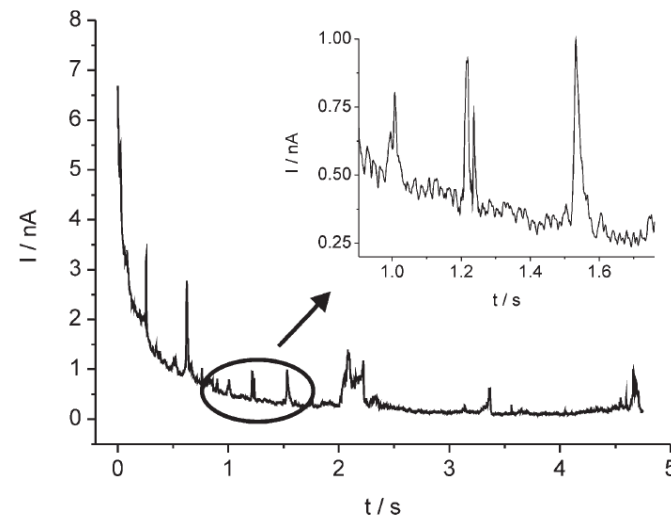
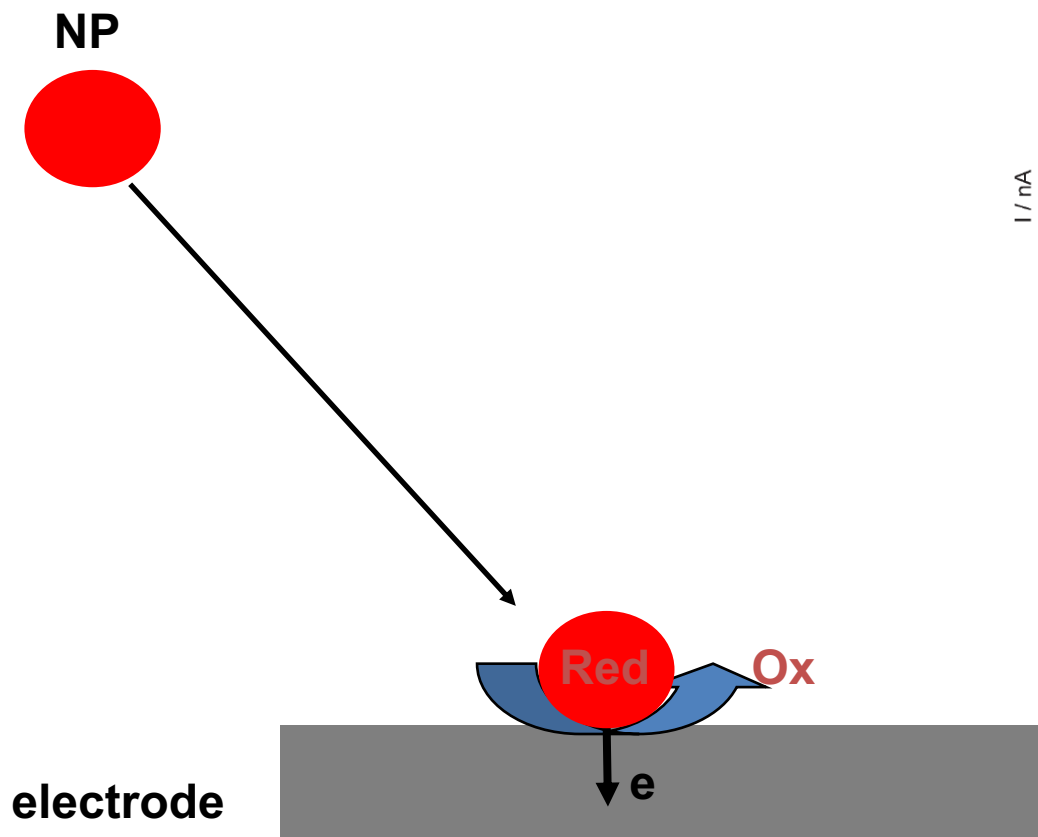
 - Stochastic Electrochemistry

 - Kwon, S.J. *et al. Phys. Chem. Chem. Phys.*, **2011**, *13*, 539

 - Review: Bard, A.J. *et al. Isr. J. Chem.*, **2010**, *50*, 267



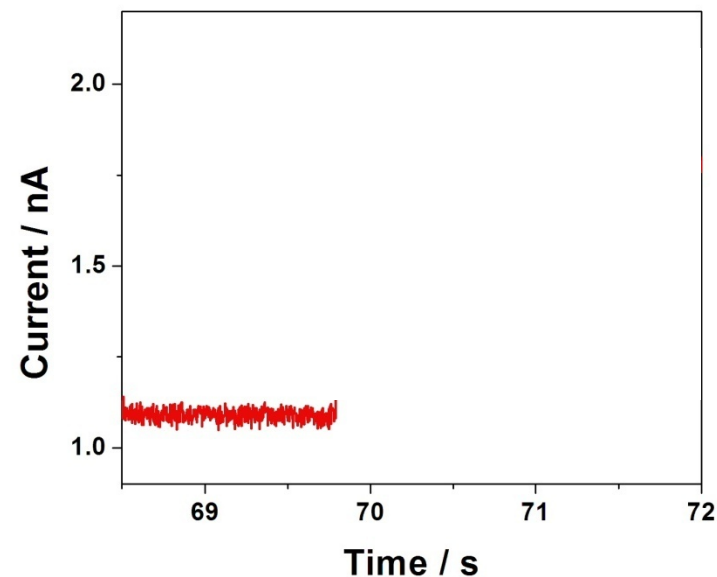
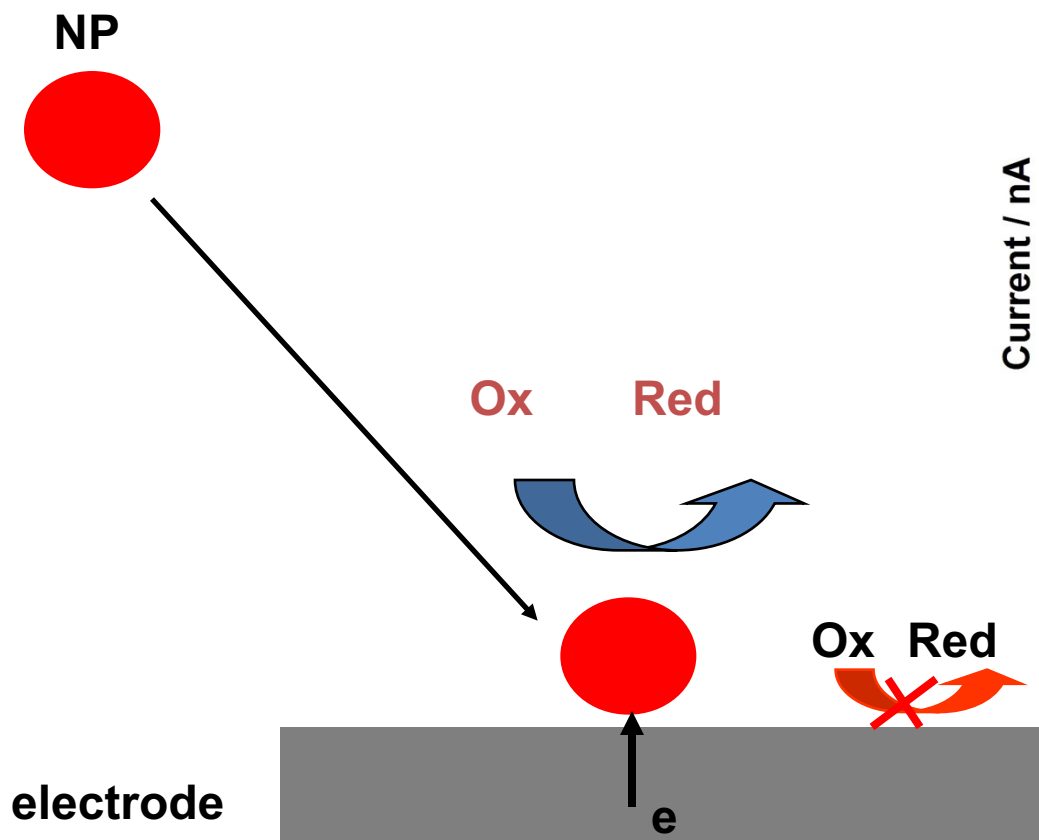
Direct Detection – Redox



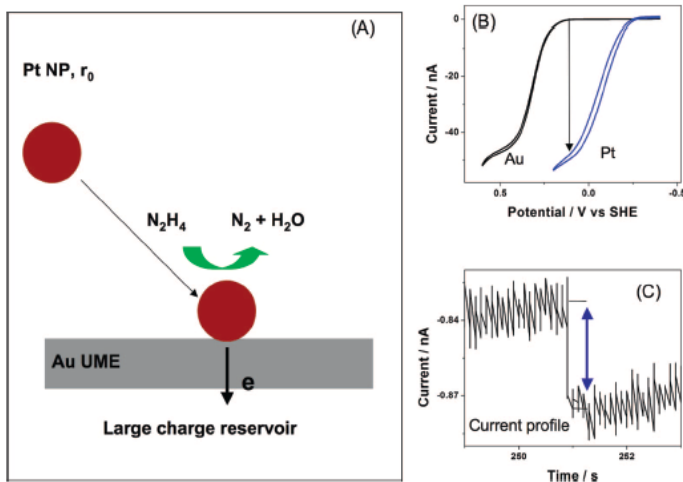
C electrode
Ag nanoparticles
Direct Oxidation

Indirect Detection – Catalytic

Electrocatalytic amplification

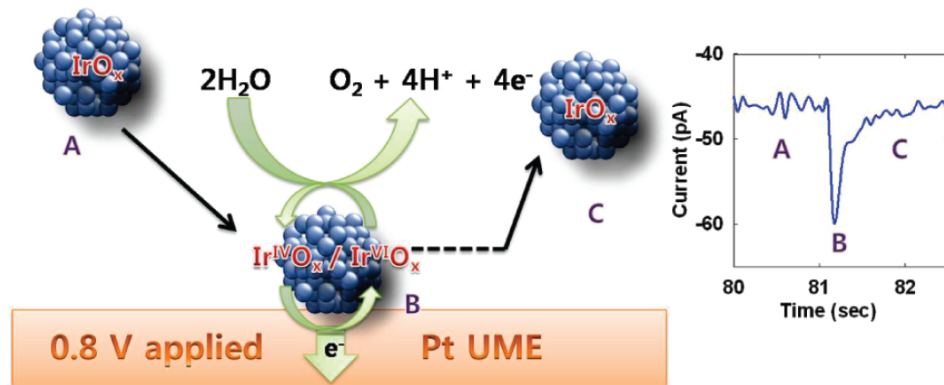


NP Collisions – Catalytic



C/Au electrode
Pt nanoparticles
Hydrazine Oxidation

Xiao, X. and Bard, A.J. *J. Am. Chem. Soc.* **2007**, *129*, 9610.



Pt electrode
IrOx nanoparticles
Water Oxidation

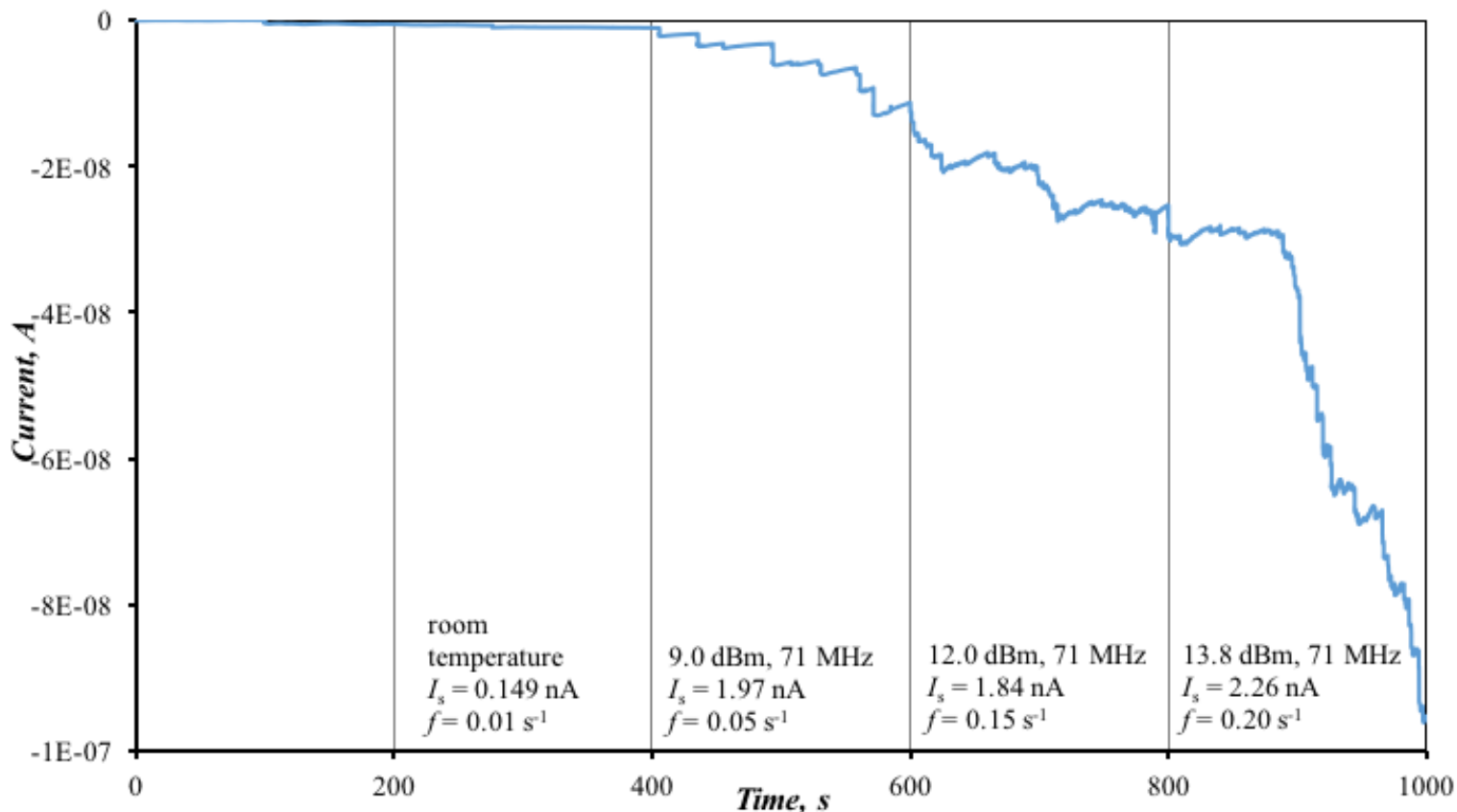
Kwon, S.J.; Fan, F.-R.F.; Bard, A.J. *J. Am. Chem. Soc.* **2010**, *132*, 13165.

Understanding Frequency of Collisions

- Particles can be transferred by:
 - Diffusion (T, viscosity)
 - Convection (microfluidics, forced convection)
 - Migration (electrophoresis)
- No prior reports on using electrokinetic phenomena
- Nernst-Planck equation:

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x)$$

Electrokinetic Manipulation of Pt NPs



15 mM hydrazine in 50 mM PBS (pH 7) at a 9- μ m Au disk; Pt NP (32 nm diam.) 1 pM; ac waveform 71 MHz, 9 – 13.8 dBm.

Bonezzi, J.; Luitel, T.; Boika, A. *Anal. Chem.* **2017**, *89*, 8614-8619.

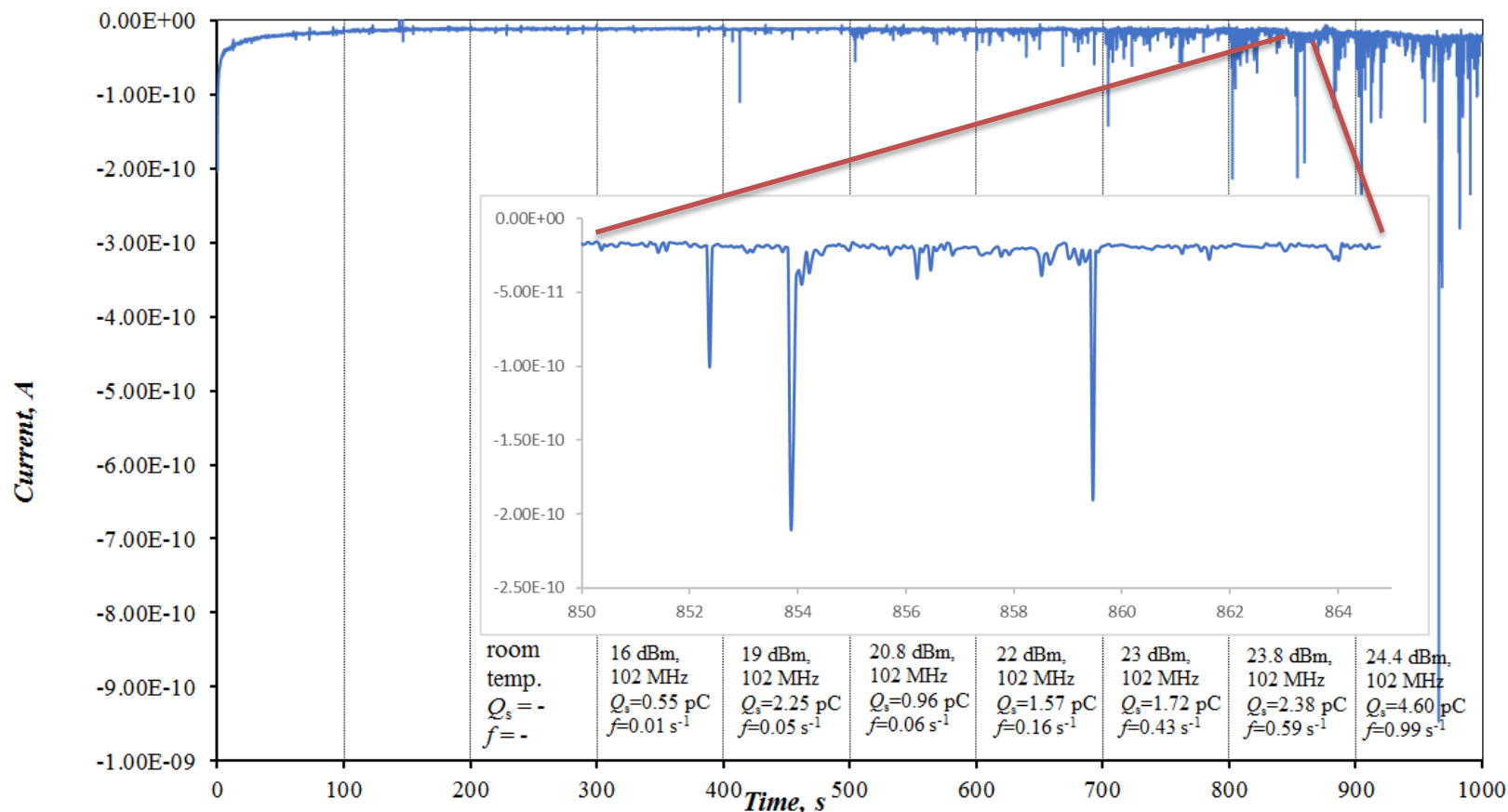
What is dBm?

- Power ratio in dB of the measured power referenced to 1 mW
- To convert x dBm to mW:

$$P = 1\text{mW} \cdot 10^{x/10}$$

dBm	mW	Notes
0	1	Bluetooth standard radio (Class 3), 1 m
15	32	Wireless LAN transmission power in laptops
27	500	Cellular phone transmission power

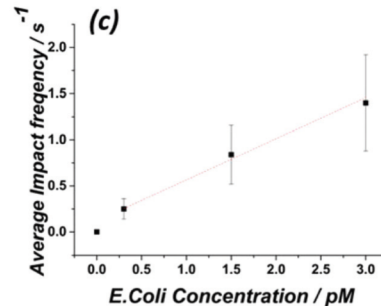
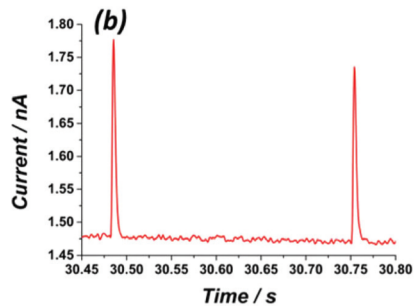
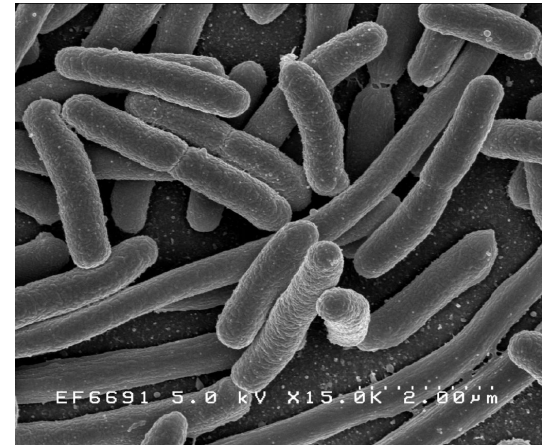
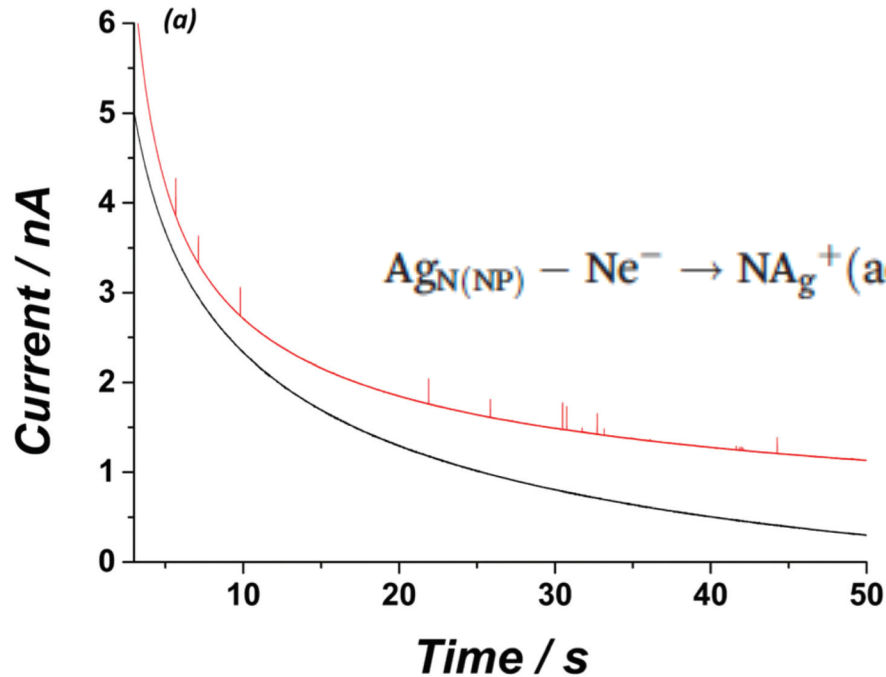
Electrokinetic Manipulation of Ag NPs



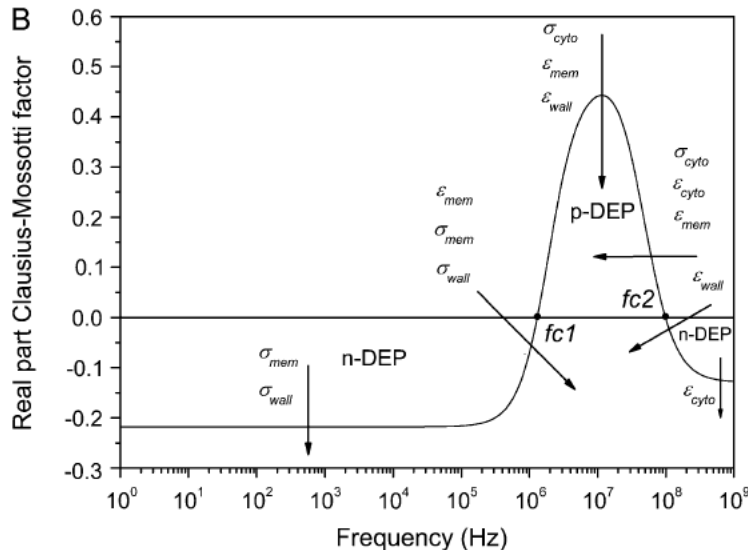
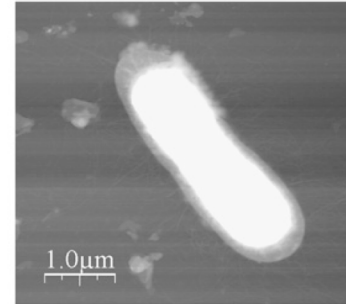
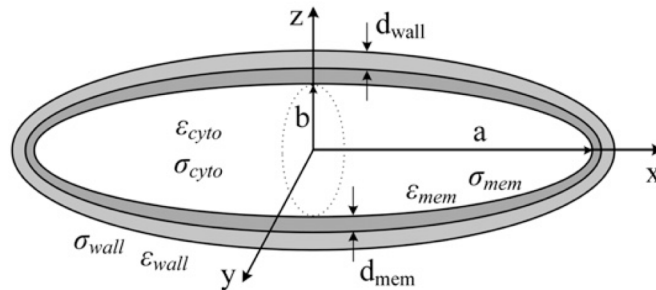
100 mM citrate buffer (pH 3.8), 11- μ m C fiber disk; Ag NP (110 nm diam.) 50 fM; ac waveform 102 MHz, 16 – 24.4 dBm.

Bonezzi, J.; Luitel, T.; Boika, A. *Anal. Chem.* **2017**, *89*, 8614-8619.

Detection of *E. coli*



Dielectrophoresis – *E. coli* Model



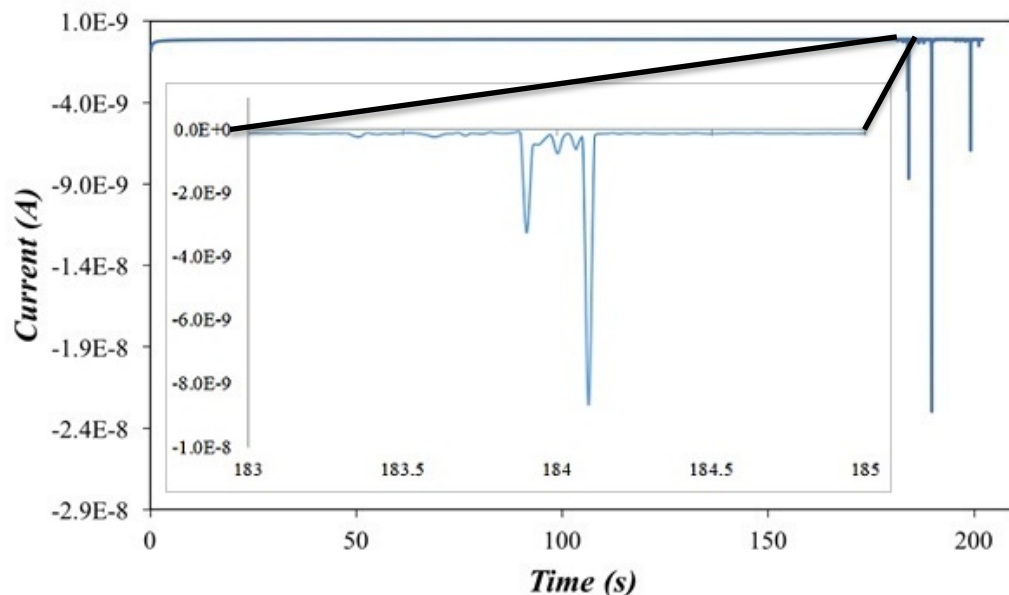
$$K_i(\omega) = \frac{1}{3} \frac{(\epsilon_p^* - \epsilon_m^*)}{\epsilon_m^* + A_i(\epsilon_p^* - \epsilon_m^*)} \quad \text{Re}[K(\omega)] = \frac{1}{3} \sum_{i=x,y,z} \text{Re}[K_i(\omega)]$$

$$A_x = \frac{1 - e^2}{2e^3} \left[\log \left(\frac{1 + e}{1 - e} \right) - 2e \right] \quad A_z = A_y = (1 - A_x)/2.$$

$$e = \sqrt{1 - \left(\frac{b}{a} \right)^2}$$

Sensitivity study of the two-shell model parameters on the real part of the Clausius-Mossotti factor

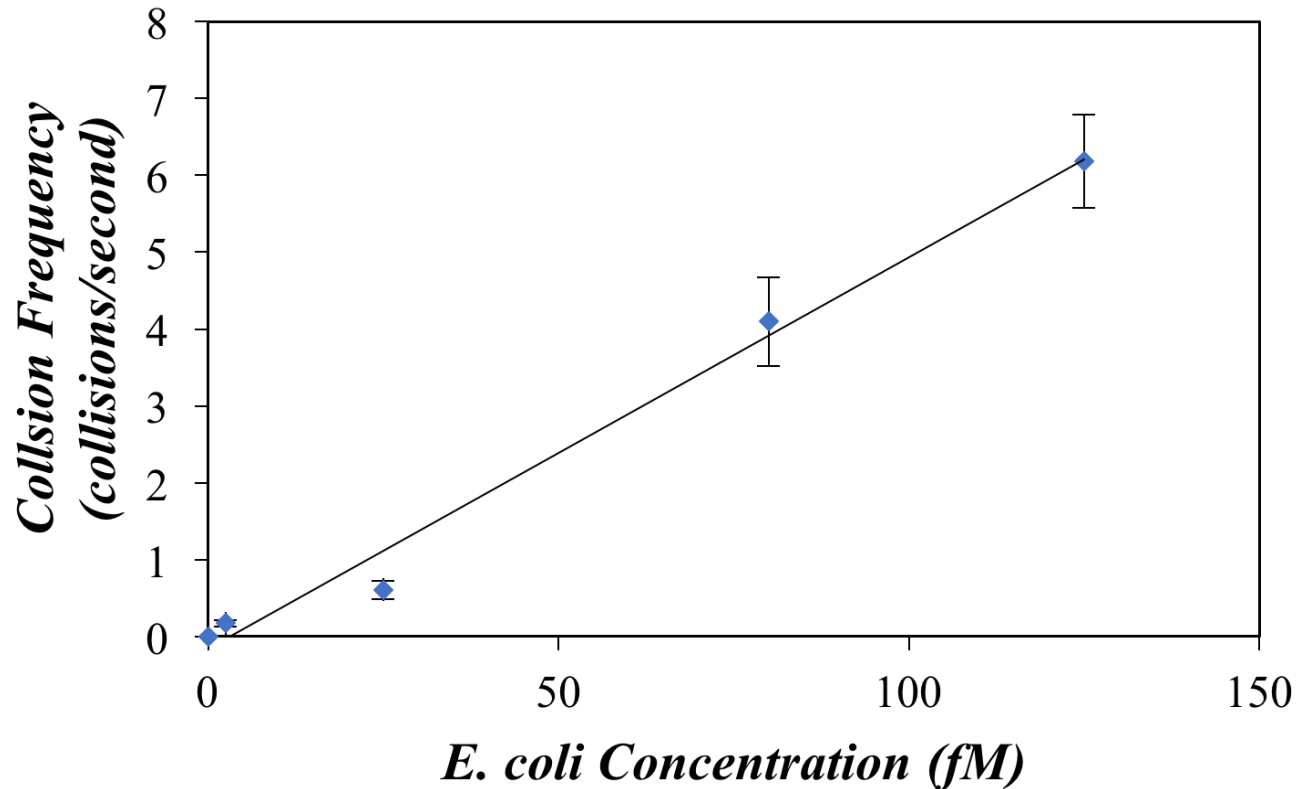
Detection of *E. coli* – AC Electrokinetics



Number	Time (s)	Charge (C)	No. of Ag NPs
1	183.88	-3.6E-11	358
2	183.96	-1.3E-11	127
3	184.04	-1.2E-11	122
4	184.08	-9.9E-11	991
5	186.52	-7.8E-12	78
6	186.78	-5.8E-12	58
7	187.72	-9.3E-12	94
8	187.94	-5.7E-12	58
9	189.52	-1.3E-11	127
10	189.58	-2.1E-11	208
11	189.64	-5.9E-10	5942
12	197.79	-1.6E-11	158
13	199.03	-6.9E-12	70
14	199.11	-2.7E-10	2673
15	199.19	-9.6E-12	96
16	201.09	-2E-11	204

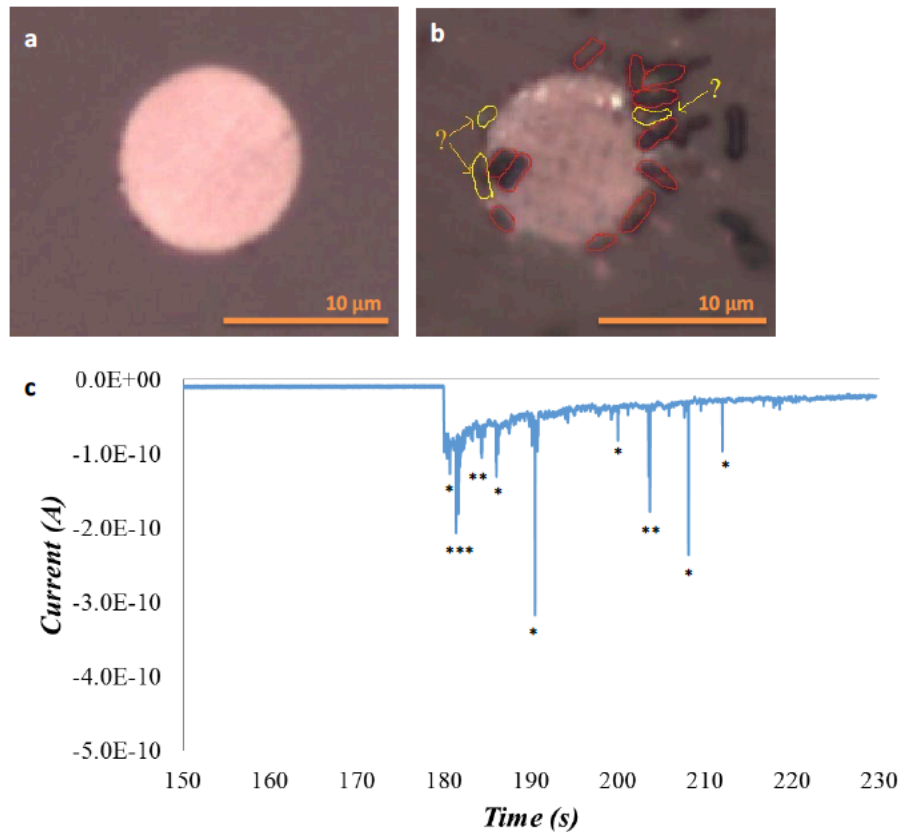
100 mM KNO₃ containing 2.42×10^{11} 27 nm Ag NPs per mL and 25 fM *E. coli*. At 180 seconds, ac waveform (19.80 dBm, 93.4 MHz) was applied.

Detection of *E. coli* – AC Electrokinetics



100 mM KNO₃ containing Ag NPs and *E. coli* (2.5 – 125 fM).

Microscopy of *E. coli* at Hot UME



Conclusions

Hot Electroanalysis:

- Collisions: most sensitive electroanalytical approach
- Electrokinetic manipulation of analytes leads to over 10^3 preconcentration
- Developing quantitative understanding
- Making collisions more specific
- Future applications in the detection of:
 - Bacteria
 - Viruses
 - Toxic ions