Optical Spectroscopy at Electrochemical and Biosensor Interfaces…

…Or how I got old with Prof. Hubert Girault.

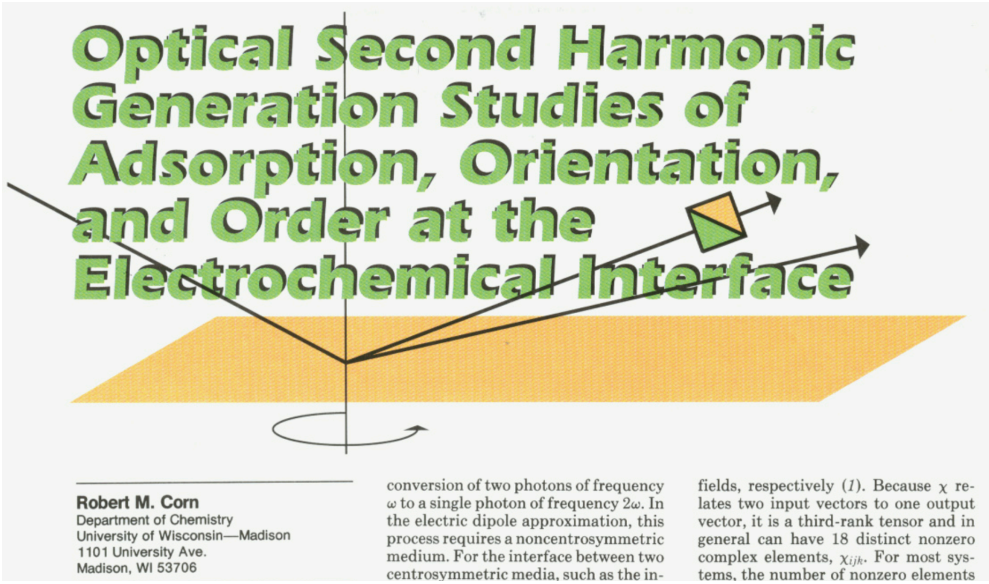
Robert M. Corn - UC Irvine, Dept. of Chemistry

UCIrvine
University of California, Irvine

Optical Second Harmonic Generation at Electrochemical Interfaces

August 1992 : Gordon Conference on Physical Electrochemistry

Organizer: Tito Abruña



Optical Second Harmonic Generation Studies of Adsorption, Orientation, and Order at the Electrochemical Interface

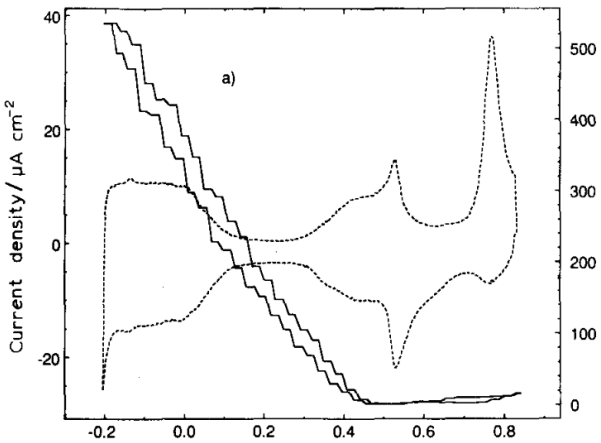
Robert M. Corn
Department of Chemistry
University of Wisconsin—Madison
1101 University Ave.
Madison, WI 53706

conversion of two photons of frequency ω to a single photon of frequency 2ω. In the electric dipole approximation, this process requires a noncentrosymmetric medium. For the interface between two centrosymmetric media, such as the in-

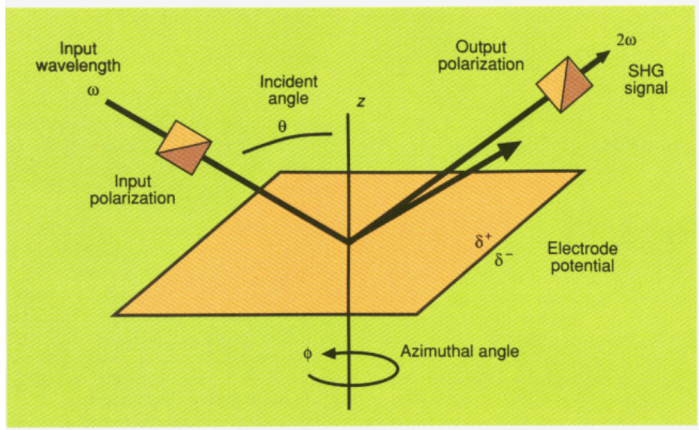
fields, respectively (*1*). Because χ relates two input vectors to one output vector, it is a third-rank tensor and in general can have 18 distinct nonzero complex elements, χ_{ijk}. For most systems, the number of nonzero elements

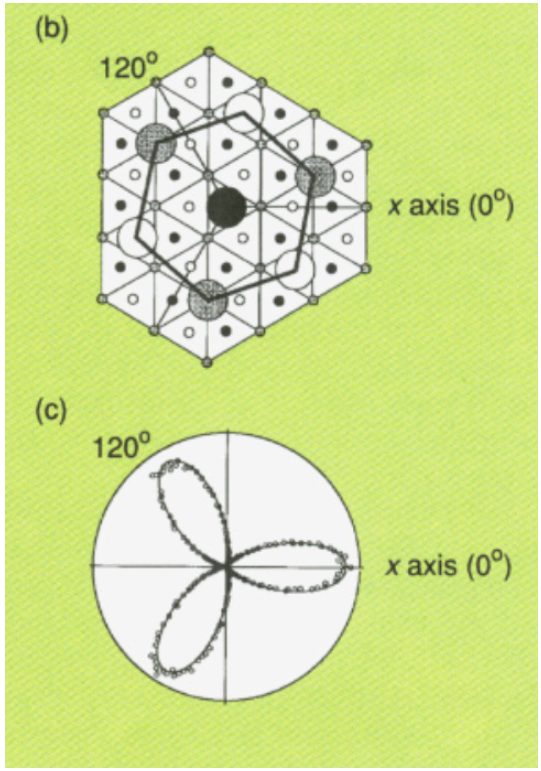
Surface Sensitive Spectroscopies:

Second Harmonic Generation (SHG)
Polarization-Modulation FTIR



Pt(111)





UCIrvine
University of California, Irvine

Electrochemistry at Liquid-Liquid Interfaces (ITIES)

August 1992 : Gordon Conference on Physical Electrochemistry

Prof. David Schiffrin
(Univ. Liverpool)

Prof. Hubert Girault (EPFL)

Prof. Takashi Kakiuchi (Kyoto Univ.)

UCIrvine
University of California, Irvine

Electrochemistry at Liquid-Liquid Interfaces (ITIES)

August 1992 : Gordon Conference on Physical Electrochemistry

Journal of Electroanalytical Chemistry and Interfacial Electrochemistry
Volume 170, Issues 1–2, 25 July 1984, Pages 127-141

Thermodynamics of a polarised interface between two immiscible electrolyte solutions

H.H.J. Girault, D.J. Schiffrin

Prof. Hubert Girault (EPFL)

Prof. Takashi Kakiuchi (Kyoto Univ.)

+ Schiffrin and Senda!

Bull. Chem. Soc. Jpn., **56**, 2912—2918 (1983)

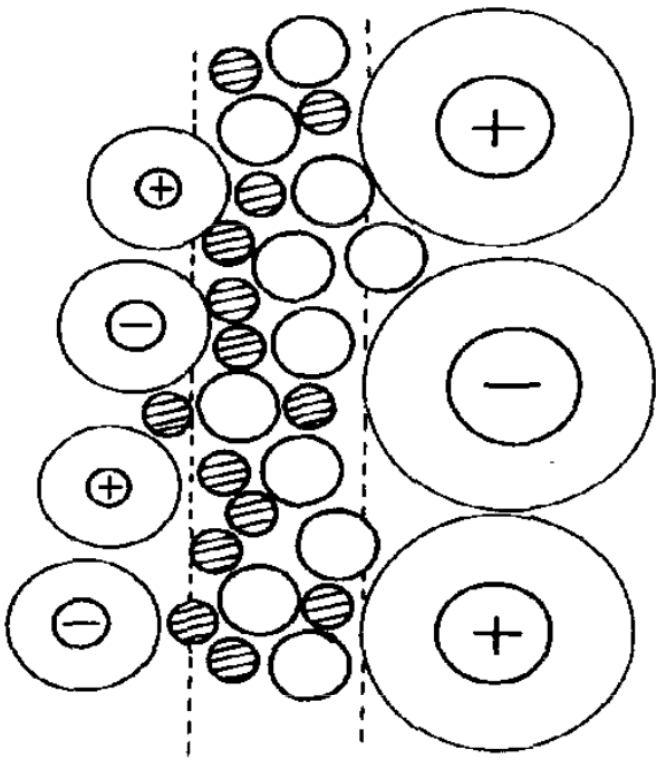
Thermodynamics of the Electrocapillarity of Oil-Water Interfaces

Takashi KAKIUCHI and Mitsugi SENDA*
Department of Agricultural Chemistry, Faculty of Agriculture, Kyoto University, Sakyo-ku, Kyoto 606
(Received March 26, 1983)

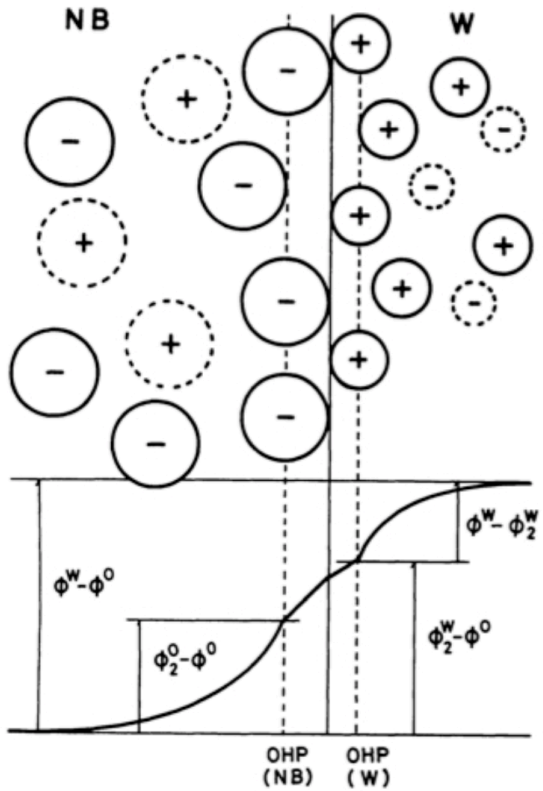
General electrocapillary equations for the interfaces between two immiscible or partially miscible electrolyte solutions have been derived. The theory includes both nonpolarized and ideal polarized interfaces. The electrocapillary equation for the latter has been derived from the equation for the former as a special case where no common ionic species are distributed between the two phases. Implications of the general electrocapillary equation for oil–water interfaces are indicated.

UCIrvine
University of California, Irvine

Electrochemistry at Liquid-Liquid Interfaces (ITIES)

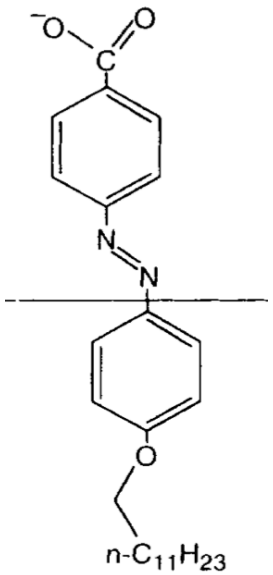


Girault and Schiffrin, 1984



Kakiuchi and Senda, 1983

100% Molecular Electrochemical Interface



DBA
730 nm

What is the true molecular interfacial structure?

What does phase potential mean on the molecular level?

Unique Molecular Environment

UCIrvine
University of California, Irvine

Electrochemistry at Liquid-Liquid Interfaces (ITIES)

Kakiuchi Me S. Kihara M. Senda Lasse Murtomaki Kopi Konturri

Girault T. Osakai D. Fermin A Volkov D. Schiffrin V. Cunnane

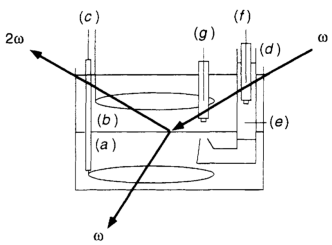
R. Dryfe Hiro Nagatani

Heyrovsky Discussion

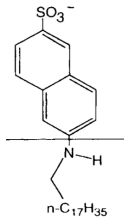
UCIrvine
University of California, Irvine

Optical Second Harmonic Generation at ITIES

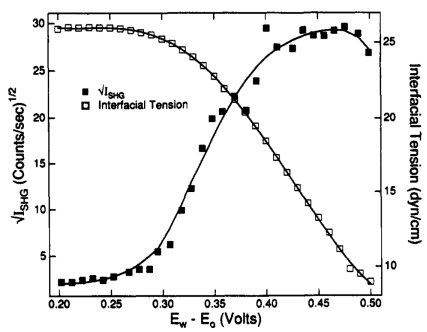
Potential Dependent Electrostatic Adsorption



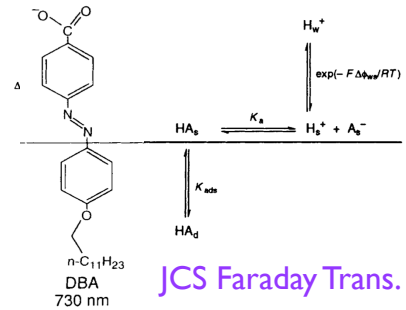
J. Phys. Chem. 1993



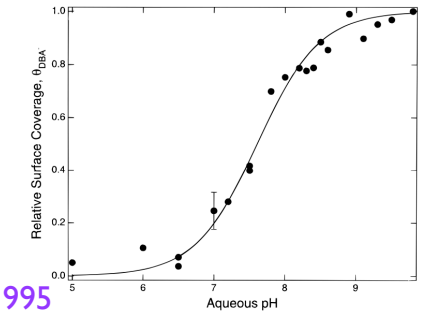
ONS
605 nm



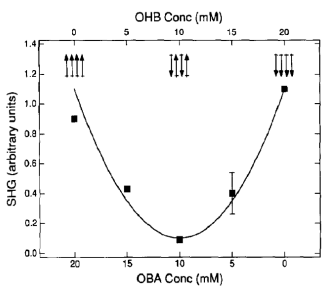
Surface Acid-Base Chemistry

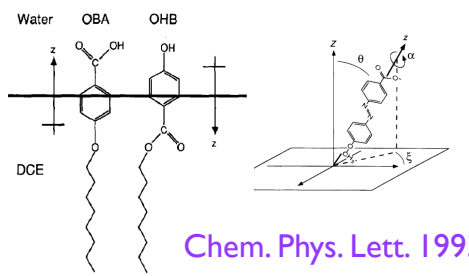


JCS Faraday Trans. 1995



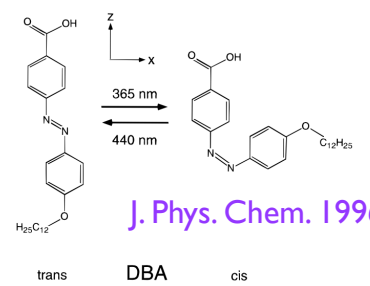
Absolute Surface Molecular Orientation





Chem. Phys. Lett. 1993

Surface Photoisomerization



J. Phys. Chem. 1996

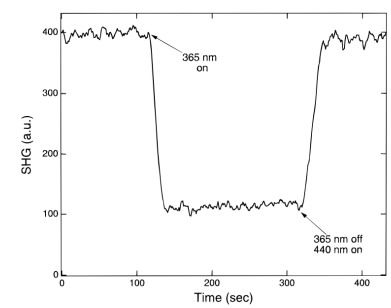
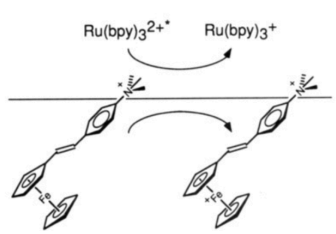
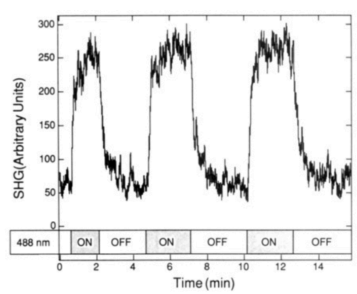


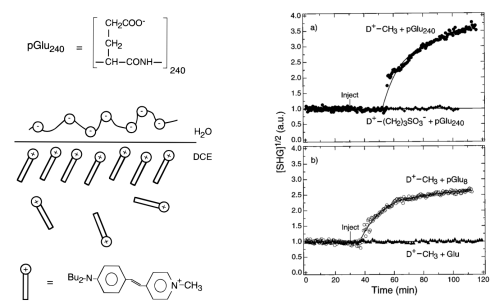
Photo-induced Interfacial Electron Transfer



JACS 1993



Interfacial Polymer Co-adsorption



J. Phys. Chem. 1997

R. N. Naujok, D.A. Higgins, D. G. Hanken and R. M. Corn, J. Chem. Soc., Faraday Trans., 91, 1411-1420 (1995).

UCIrvine
University of California, Irvine

SHG and Other Spectroscopic Measurements of ITIES

P. F. Brevet and Girault: SHG at ITIES

LANGMUIR

Surface Second Harmonic Generation of Cationic Water-Soluble Porphyrins at the Polarized Water|1,2-Dichloroethane Interface

Hirohisa Nagatani, Alexis Piron, Pierre-François Brevet, David J. Fermín, and Hubert H. Girault

Naoya Nishi and Kakiuchi: X-Ray Reflectivity Measurements

Ionic multilayers at the free surface of an ionic liquid, trioctylmethylammonium bis(nonafluorobutanesulfonyl)amide, probed by x-ray reflectivity measurements

J. Chem. Phys. **132**, 164705 (2010); https://doi.org/10.1063/1.3398029

Naoya Nishi[1], Yukinori Yasui[1], Tomoya Uruga[2], Hajime Tanida[2], Tasuku Yamada[3], Shun-ichi Nakayama[3], Hideki Matsuoka[3], *and* Takashi Kakiuchi[1, a)]

UCIrvine
University of California, Irvine

ITIES People: Young and Old!

M. Senda

Bob Samec Ana Baruzzi

Hiro Nagatani Hye Jin Lee

V. Maracek Kopi Konturri

Takashi Kakiuchi

Naoya Nishi

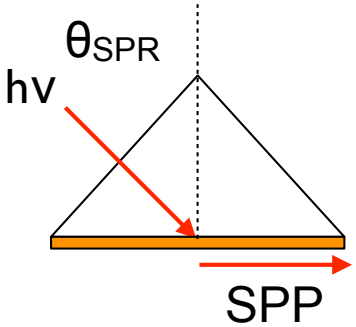
S. Kihara Bob Samec

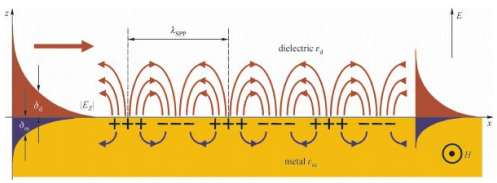
K. Maeda Yumi Yoshida

UCIrvine
University of California, Irvine

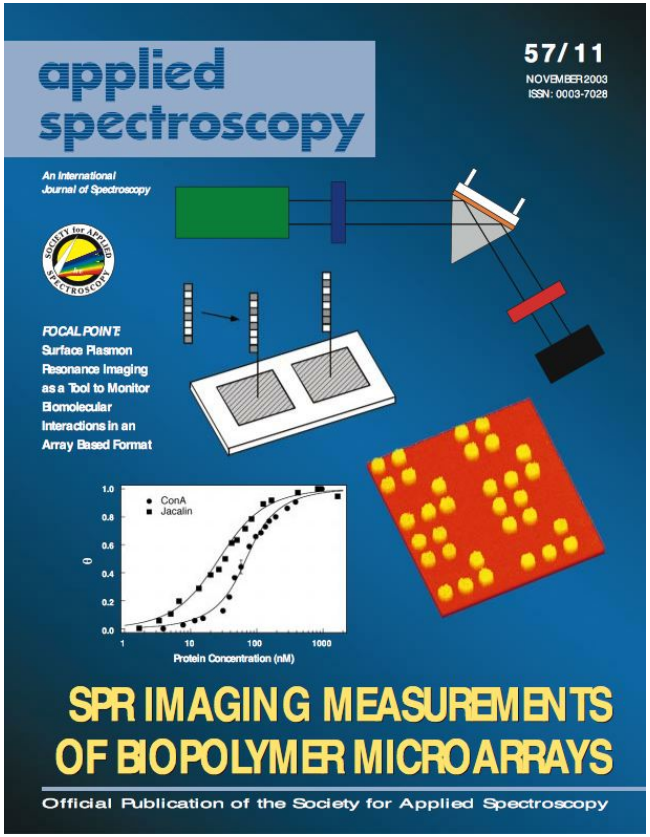
Surface Plasmon Resonance Imaging (SPRI) of Microarrays

Surface Plasmon Polaritons (SPPs)





Hye Jin Lee 🇰🇷
(Girault)



SPRI Microarrays:

DNA, RNA	*Carbohydrate*
Peptide	*Antibody*
Protein	*Aptamer*

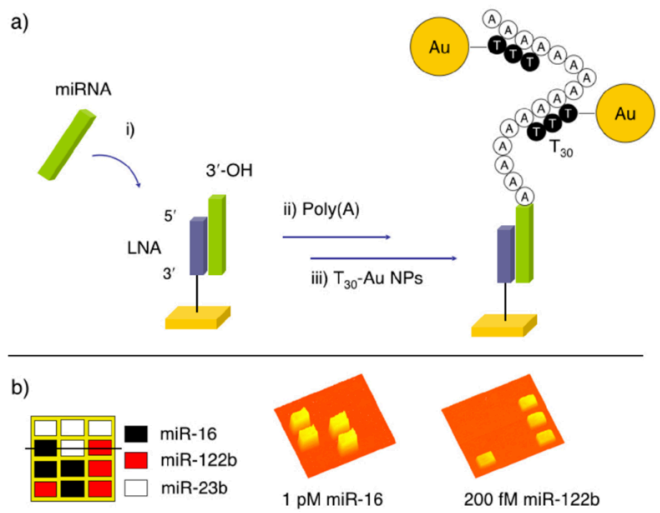
30 Publications
2001-2008

UCIrvine
University of California, Irvine

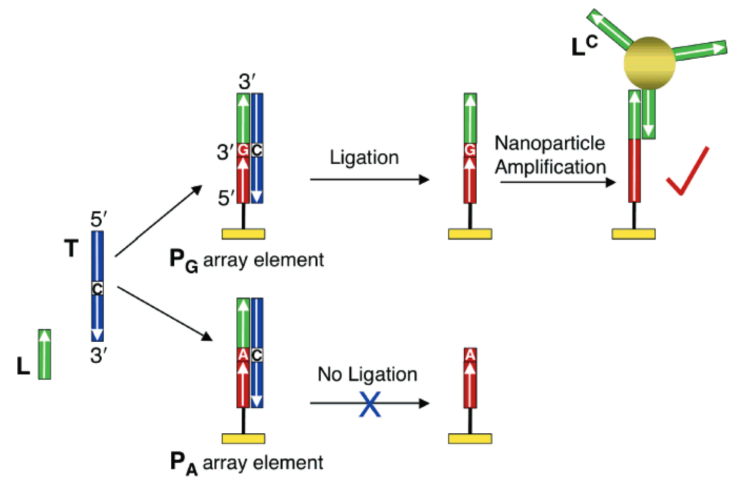
Surface Enzyme Chemistries for Ultrasensitive Biosensing

Hye Jin Lee

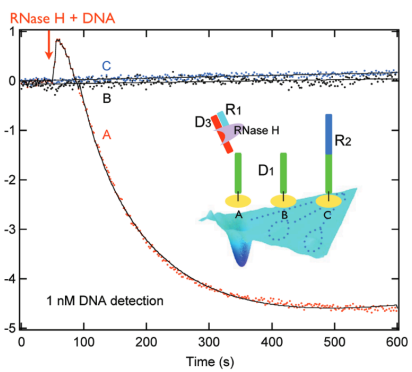
Poly-A Polymerase Amplification fM microRNA sensing

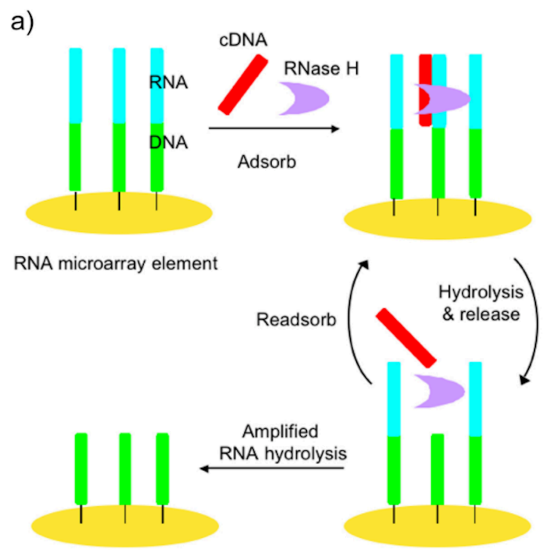


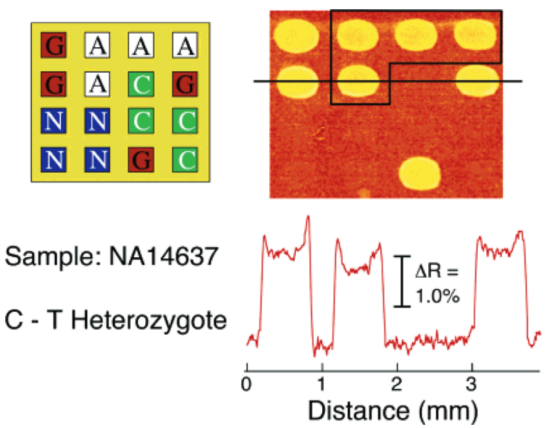
T4 Surface Ligation Chemistry Single Base Mismatch Identification SNP Genotyping



RNAse H Target Recycling genomic (fM) DNA biosensing







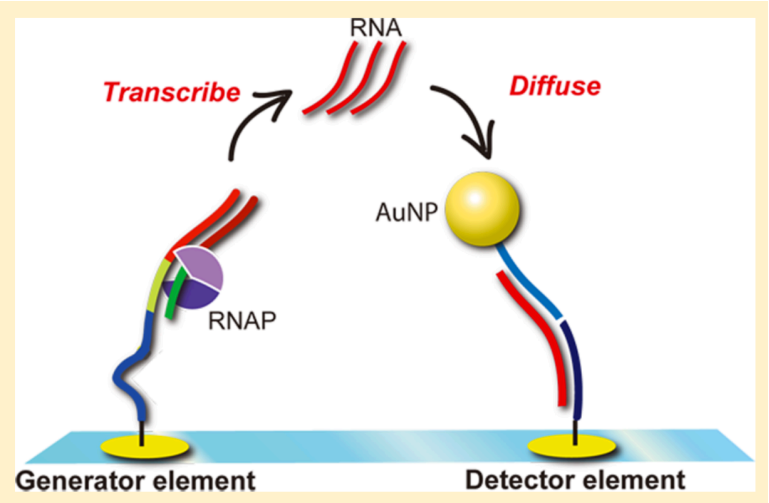
UCIrvine
University of California, Irvine

Surface Enzyme Chemistries for Ultrasensitive Biosensing

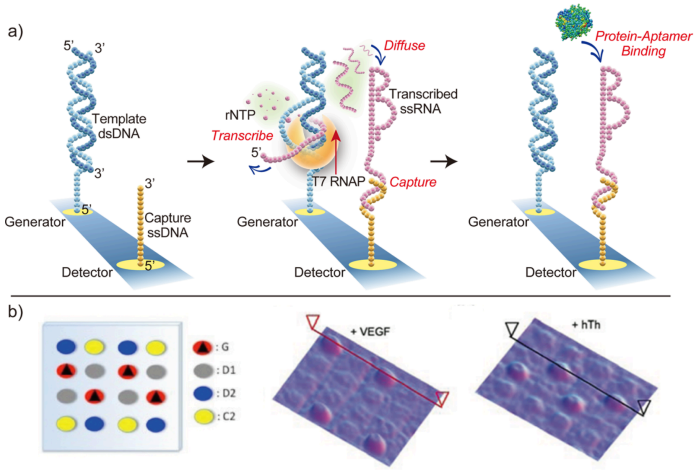
Iuliana Sendroiu
(Shiffrin)

Alastair Wark
(Berlouis)

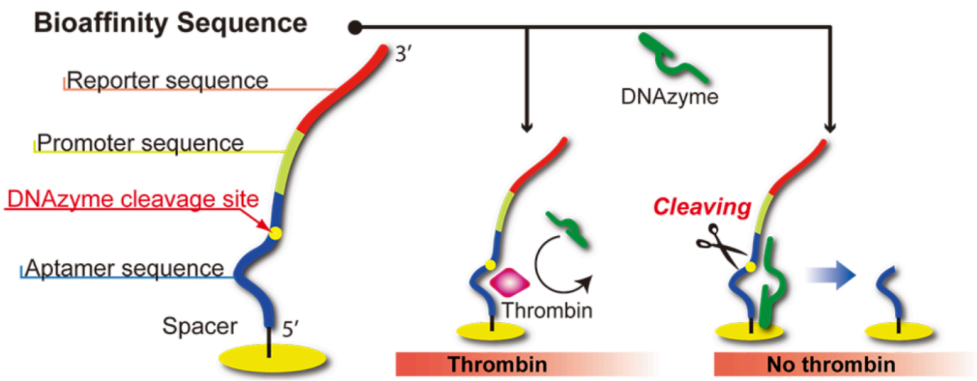
RNA Polymerase Amplification fM DNA biosensing



On Chip RNA Polymerase RNA & Protein Microarray Synthesis



DNAzyme Amplified Aptamer Protein Biosensing



UCIrvine
University of California, Irvine

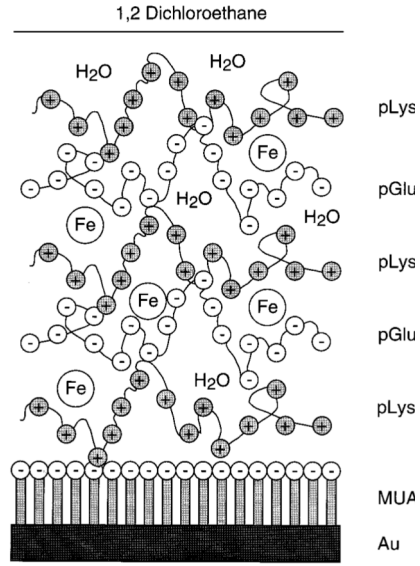
Ultrathin Electrostatic Multilayer L/L Interfaces

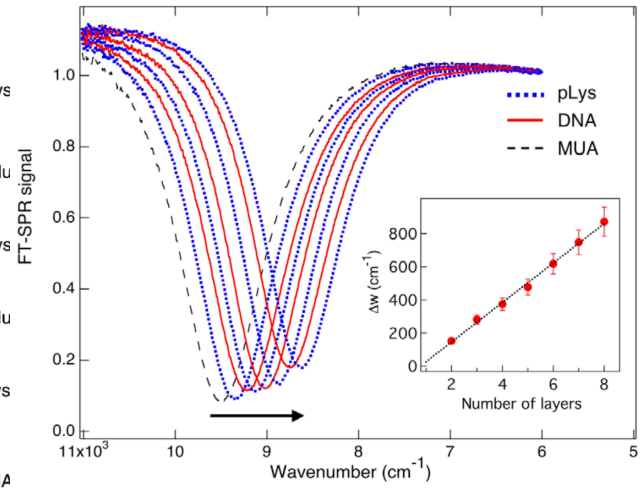
Yufei Cheng 🇨🇳

(Shiffrin)

Lasse Murtomäki 🇫🇮

(Konturri)





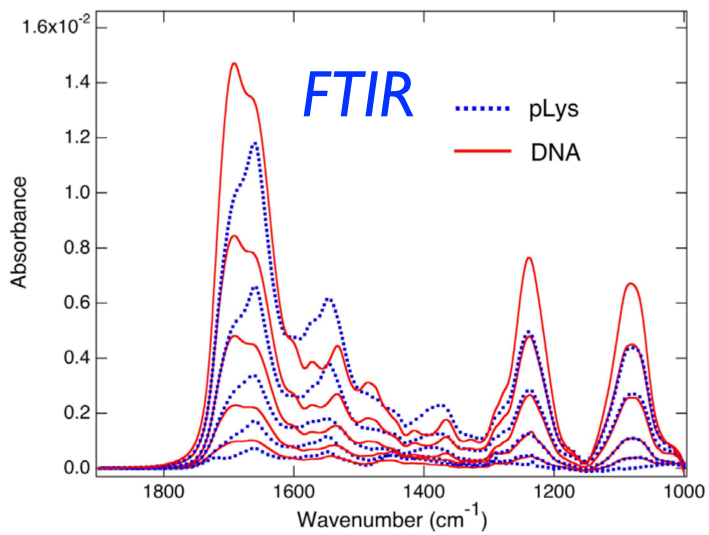
FT-SPR

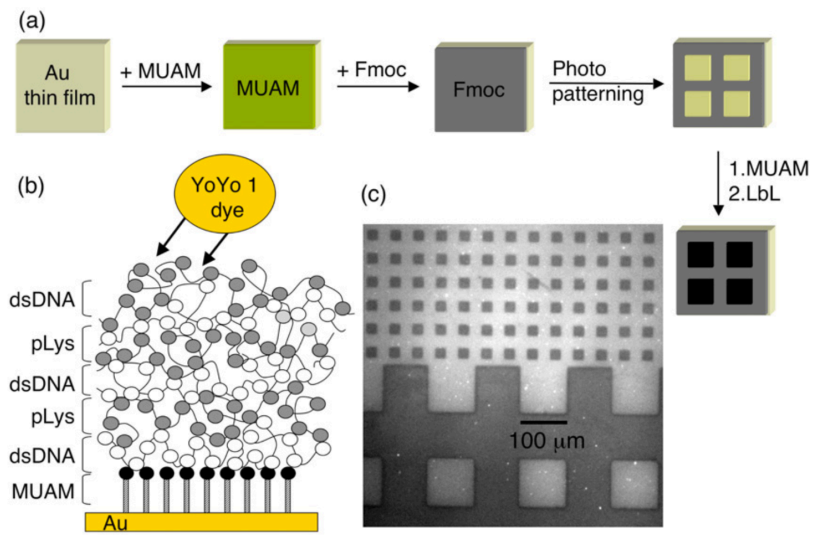
MUA = 11-mercaptoundecanoic acid

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

pLys = poly-L-lysine

pGlu = poly-L-glutamic acid

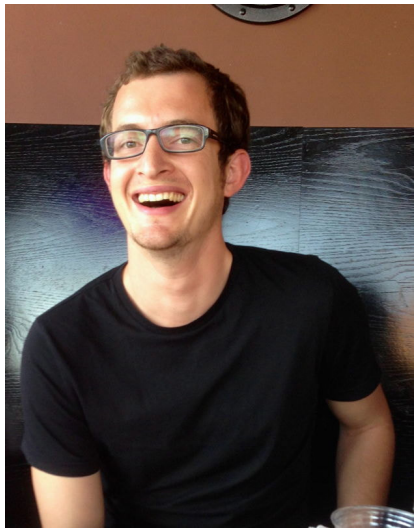




Mesoscale + Nanoscale

UCIrvine
University of California, Irvine

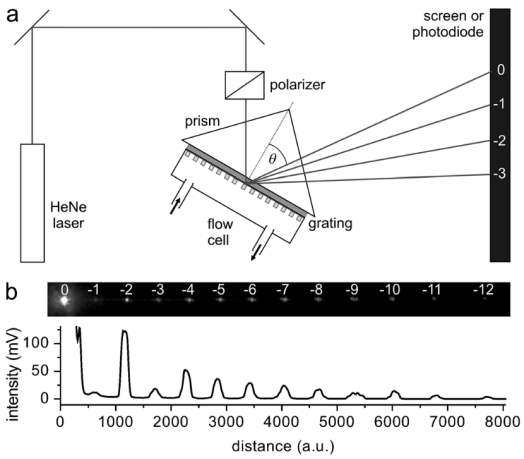
Electro-Optical Diffraction Biosensing: Nanowire and Nanocone Arrays

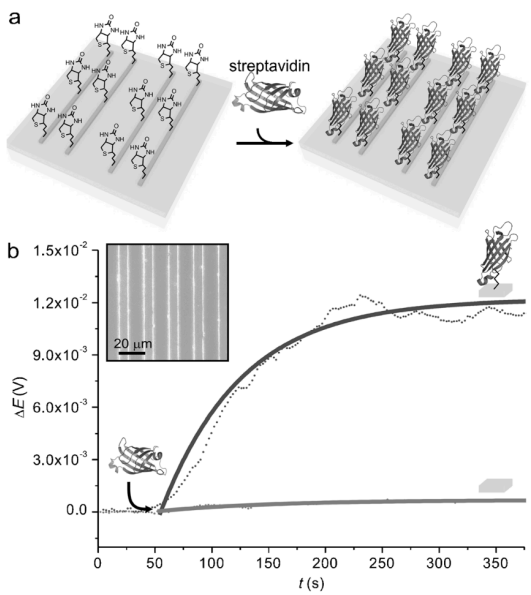


Naoya Nishi 🇯🇵
(Kakiuchi)

Gabriel Loget 🇫🇷
(Kuhn)

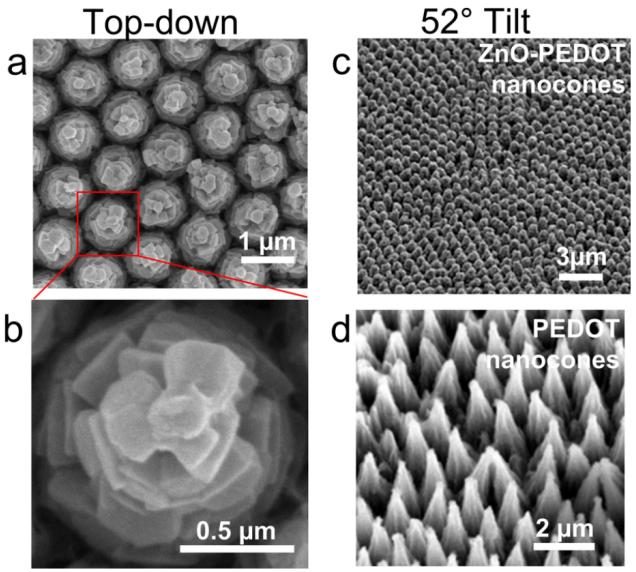
Seulgi So 🇰🇷
(Schmuki)

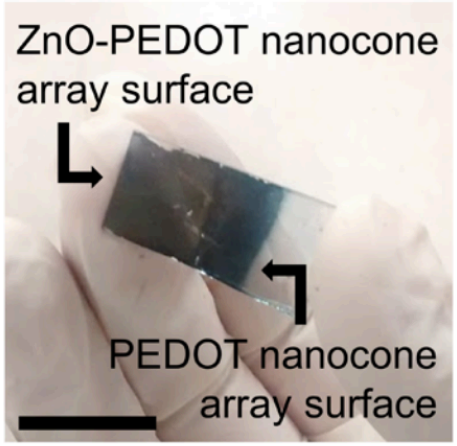




Silica Nanowires
EC Diffraction Biosensing

ZnO & PEDOT Nanocones
EC Anti-reflective Surfaces

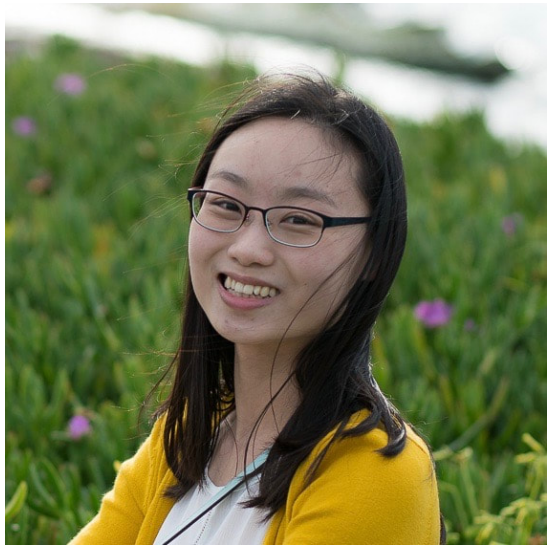




Mesoscale + Nanoscale

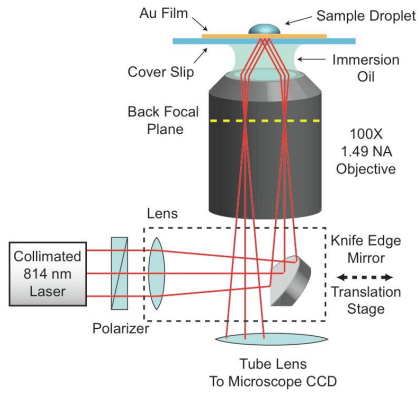
UCIrvine
University of California, Irvine

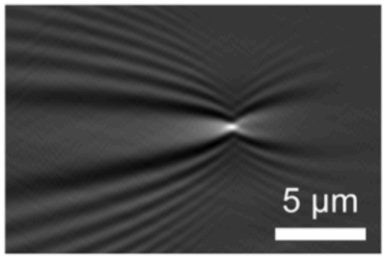
Latest Work: Single Gold Nanorod SPRI Microscopy

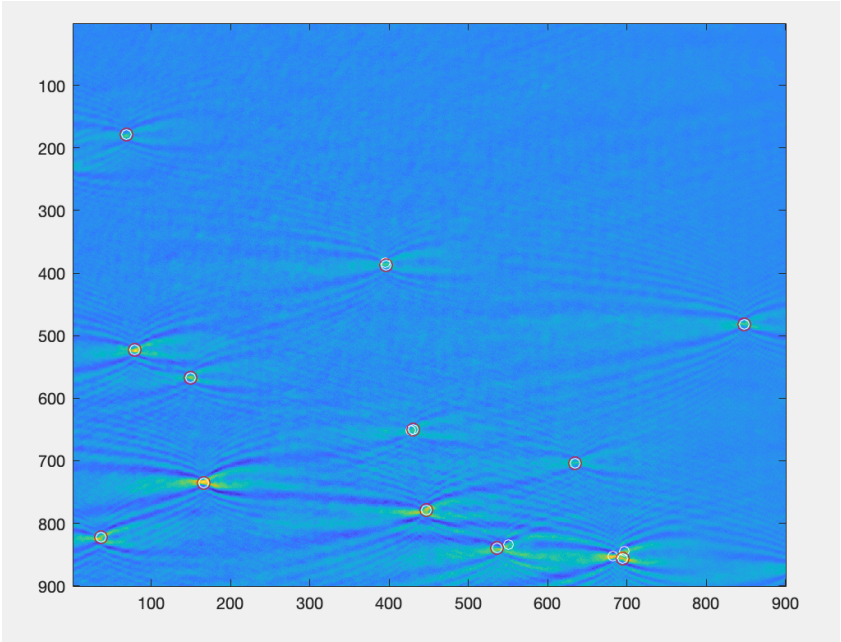


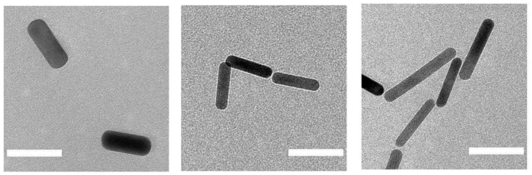
Yunshan Fan 🇨🇳

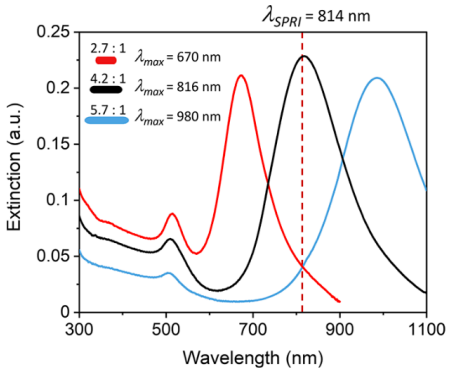
(Bo Zhang UW)

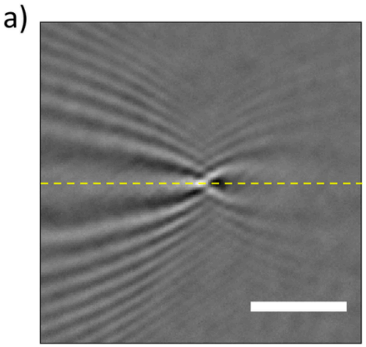


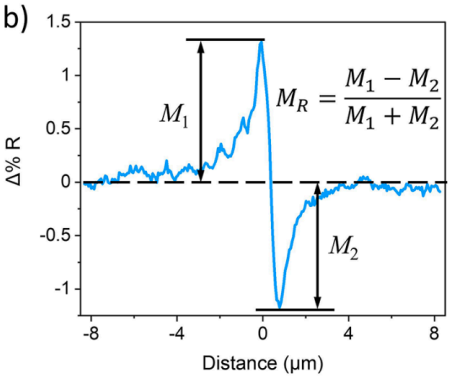


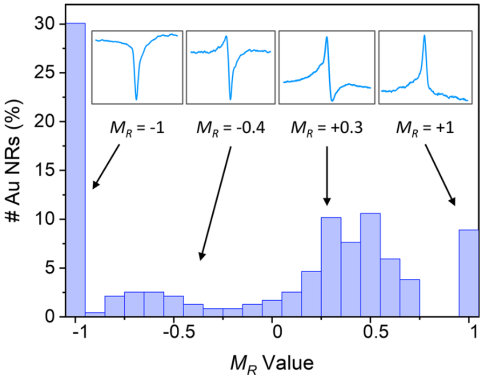








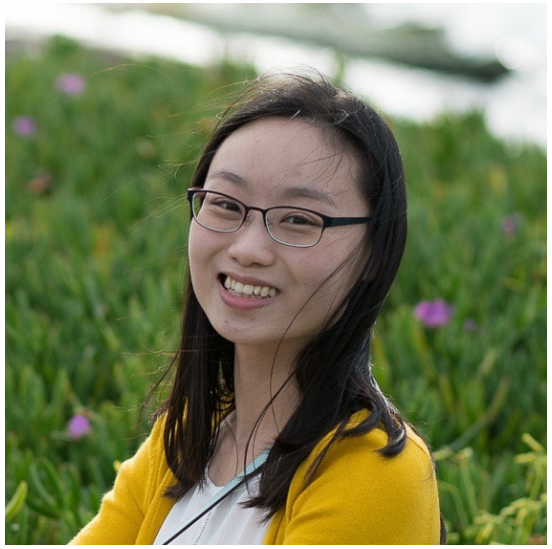




*Yunshan Fan et. al., "Complex Resonant Scattering Behavior in the Surface Plasmon Resonance Imaging Microscopy of Single Gold Nanorods," J. Chem. Phys. Lett., **12** 2004-2010 (2021).*

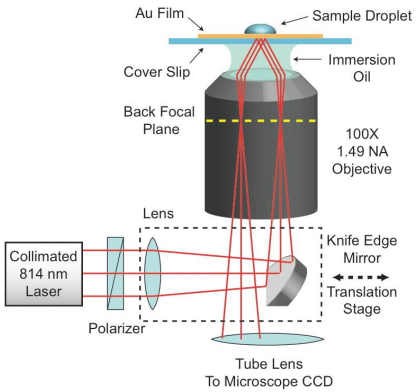
UCIrvine
University of California, Irvine

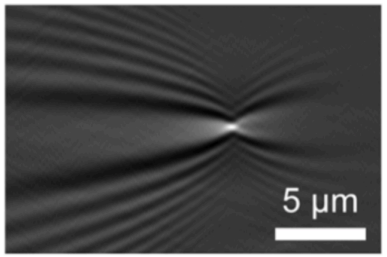
Latest Work: Single Gold Nanorod SPRI Microscopy

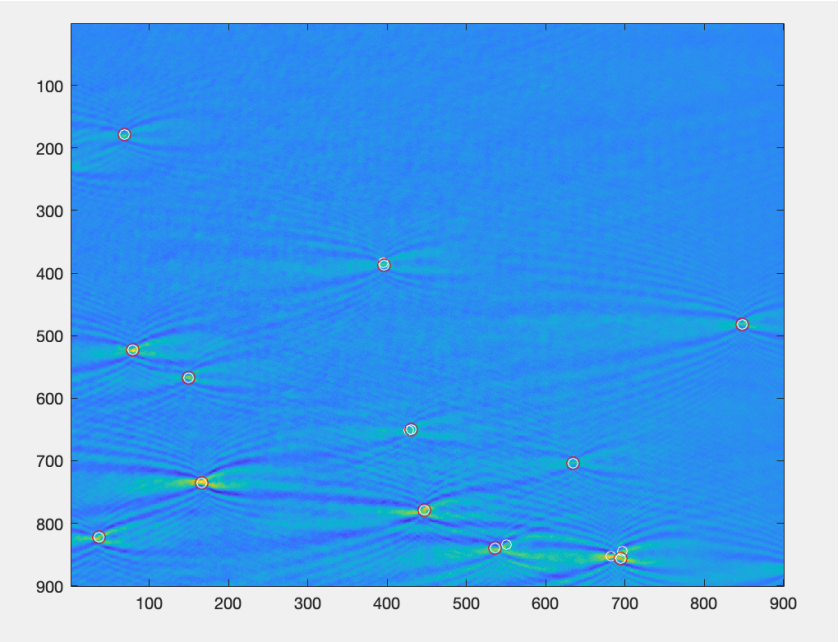


Yunshan Fan 🇨🇳

(Bo Zhang UW)







Pacifichem 2021 - Symposium on Nanostructured Interfaces for Biosensing
Honolulu, Hawaii - December 18-20, 2021.

PACIFICHEM

The International Chemical Congress of

Pacific Basin Societies 2021

Co-Organizers:

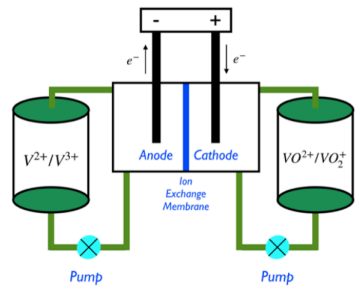
Alexandre Brolo (U.Victoria),
Hye Jin Lee (Kyungpook National Univ)
Kaoru Tamada (Kyushu Univ)
Reg Penner (UCI)
Hiroshi Aoki (AIST)
Meikun Fan (SW Jiantong Univ)
Jian-Feng Li (Xiamen)

Robert M. Corn - UC Irvine, Dept. of Chemistry

UCIrvine
University of California, Irvine

H. Girault: Vanadium Redox Flow Batteries in Martigny

Vanadium Redox Flow Battery



Cathode Half Cell Potential: E^0_{red} = 1.00V

$$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$$

Anode Half Cell Potential: E^0_{ox} = -.26V

$$V^{3+} + e^- \rightleftharpoons V^{2+}$$

$$E_{cell} = E_{red} - E_{ox}$$

$$E^0_{cell} = 1.00V - (-0.26V) - = +1.26V$$

Congratulations, Hubert!

https://www.chem.uci.edu/~unicorn/reprints/JejudoISE

UCIrvine
University of California, Irvine