

Controlling Interfacial Symmetry Breaking: Electrodeposited Antireflective Nanocone Arrays and Diffraction Gratings

Cones



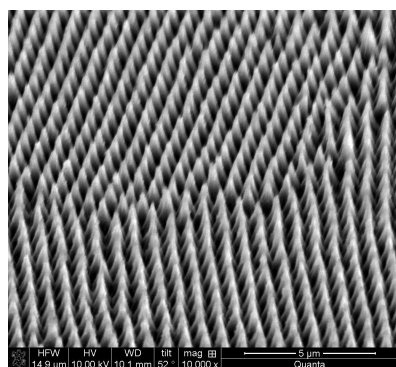
Gratings



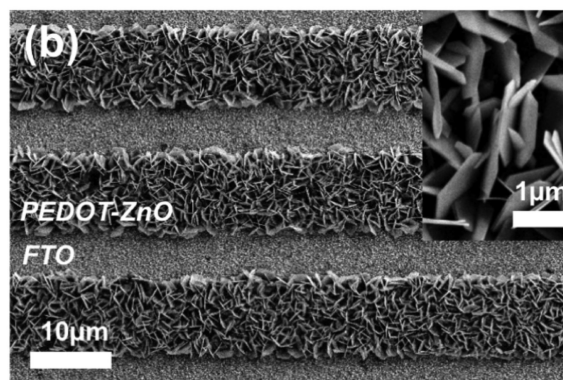
Rings



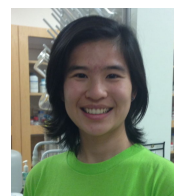
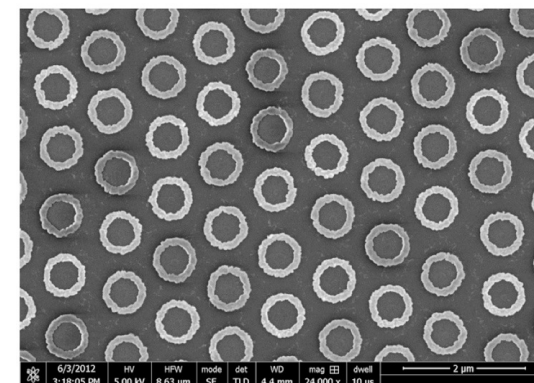
Nanocones



Nanogratings



Nanorings

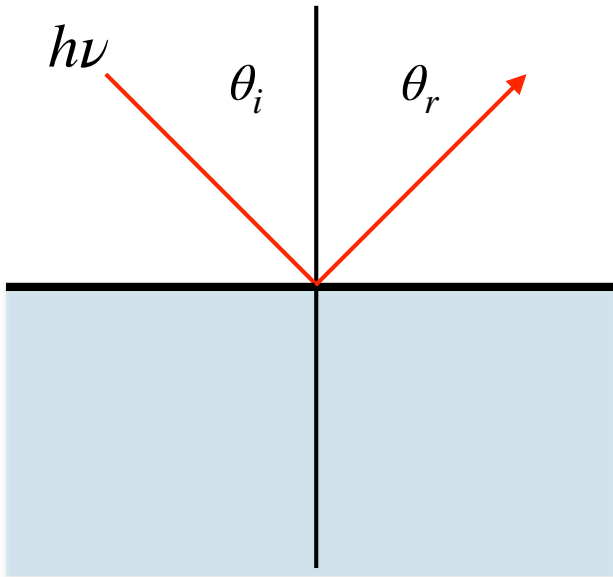


Prof. Robert M. Corn
Department of Chemistry, UC Irvine

UCIrvine
University of California, Irvine



Optical Symmetry Breaking at Interfaces



$$\theta_i = \theta_r$$

Specular Reflection



*Hero of Alexandria
10 A.D. - 70 A.D.*

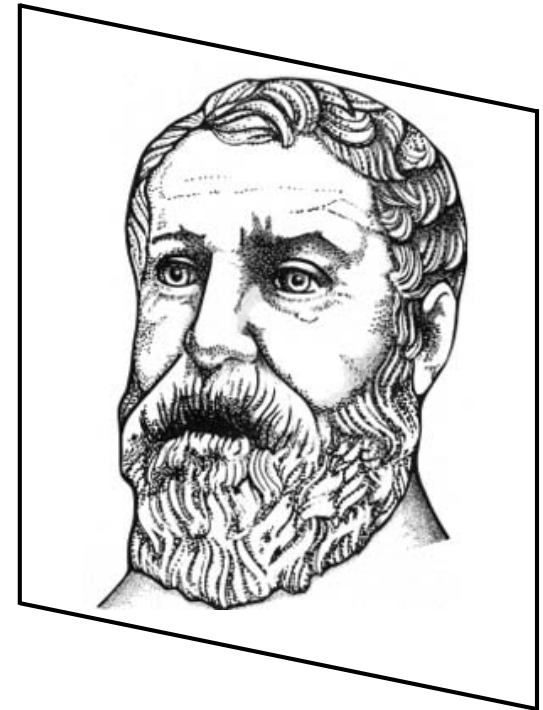
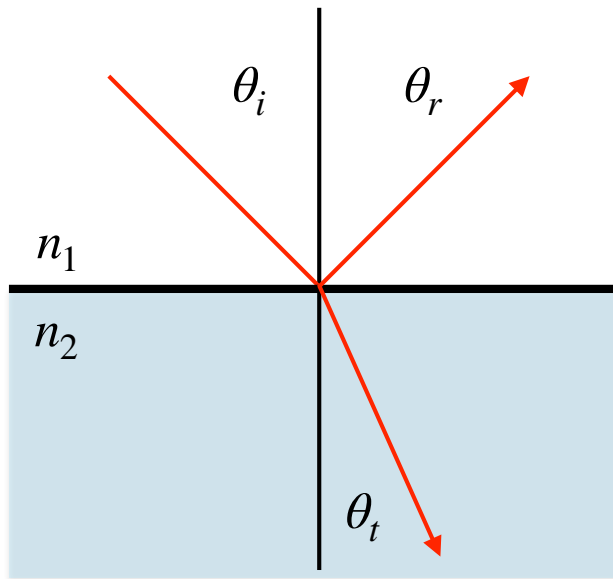


Image Source: Wikipedia

Optical Symmetry Breaking at Interfaces



Refractive Indices n_1 & n_2

$$n_1 \sin \theta_i = n_2 \sin \theta_t$$

Snell's Law

$$\theta_i = \theta_r$$

Specular Reflection

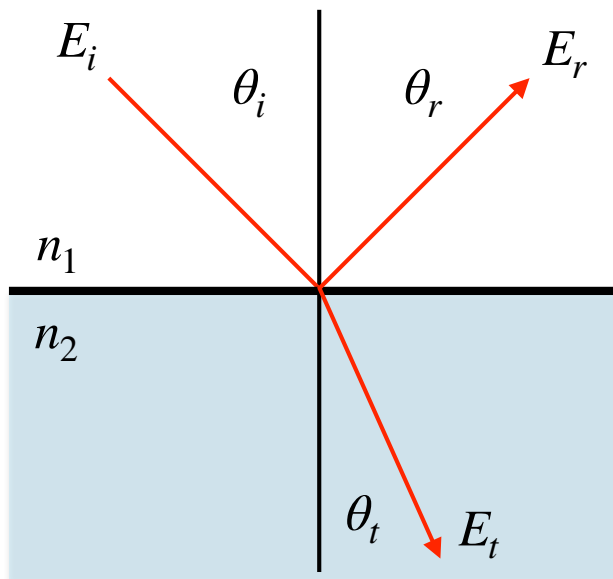


Willebrord Snellius
1580-1626



Image Source: Wikipedia

Optical Symmetry Breaking at Interfaces



$$E_r = rE_i$$

$$E_t = tE_i$$

r & t

Fresnel Coefficients

$$R = |r|^2$$

Reflectance

$$T \propto |t|^2$$

Transmittance

$$R + T = 1$$

$$\theta_i = \theta_r$$

Specular Reflection

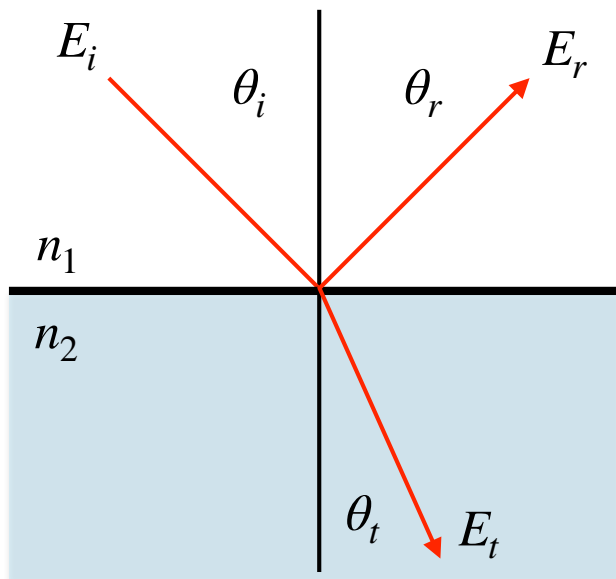
$$n_1 \sin \theta_i = n_2 \sin \theta_t$$

Snell's Law



Augustin-Jean Fresnel
1788-1827

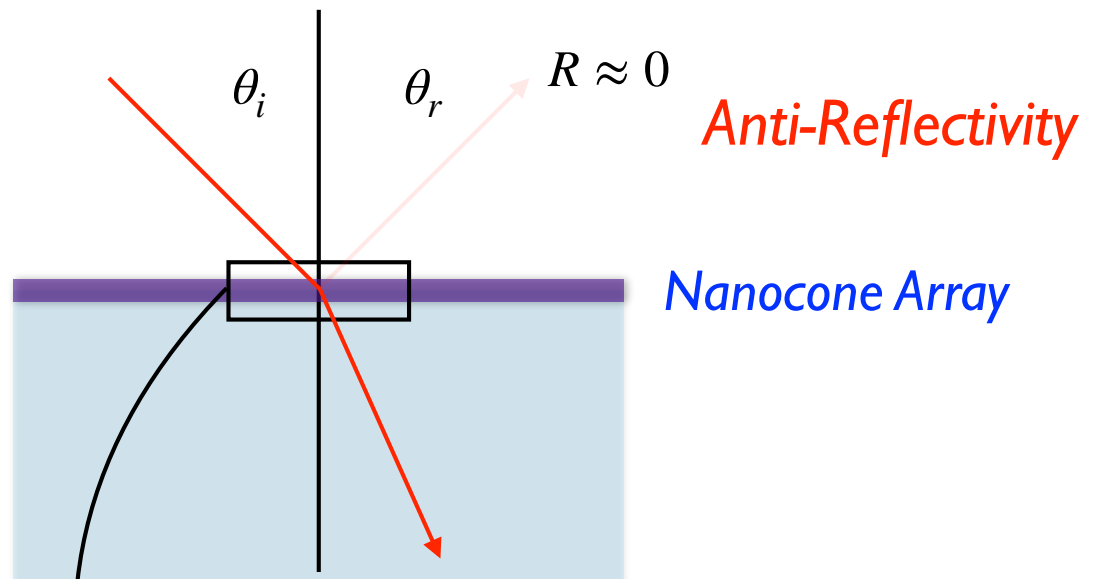
Optical Symmetry Breaking at Interfaces



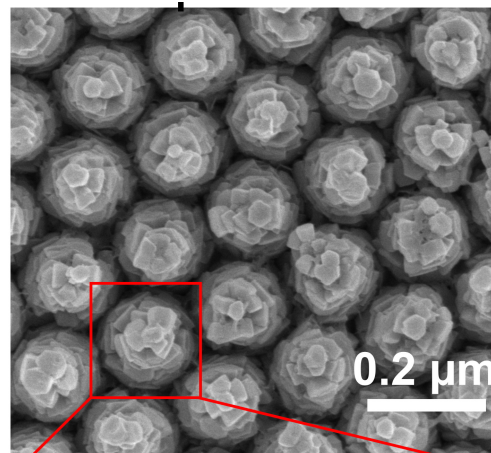
$\theta_i = \theta_r$
Specular Reflection

$n_1 \sin \theta_i = n_2 \sin \theta_t$
Snell's Law

$E_r = rE_i \quad E_t = tE_i \quad R = |r|^2$
Fresnel Coefficients

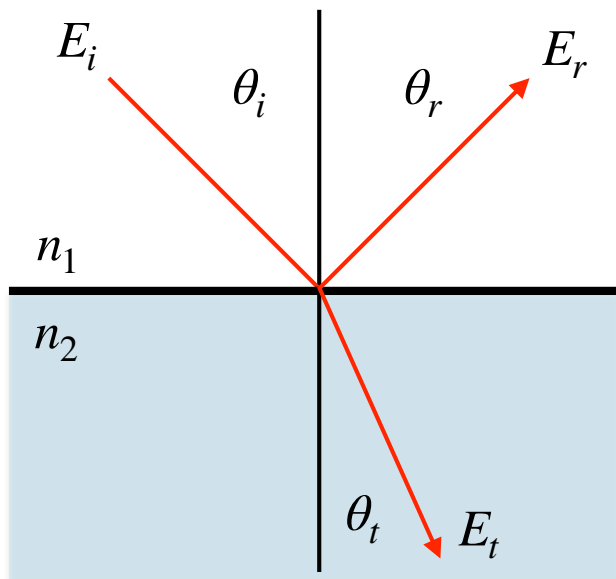


Electrodeposited Nanostructured Film



Nanocone Arrays

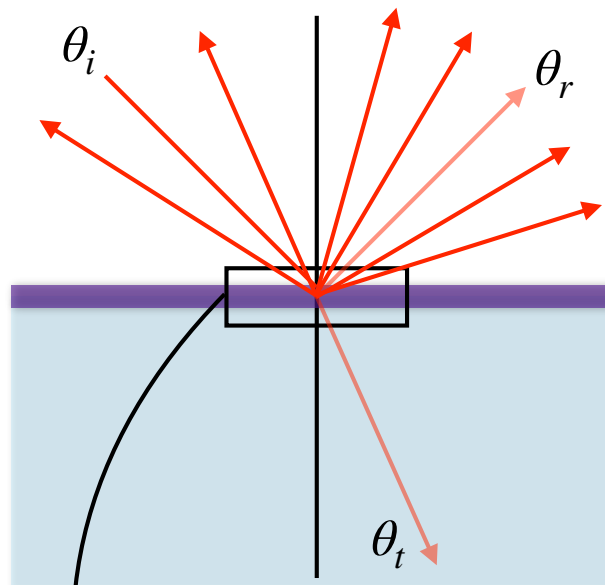
Optical Symmetry Breaking at Interfaces



$\theta_i = \theta_r$
Specular Reflection

$n_1 \sin \theta_i = n_2 \sin \theta_t$
Snell's Law

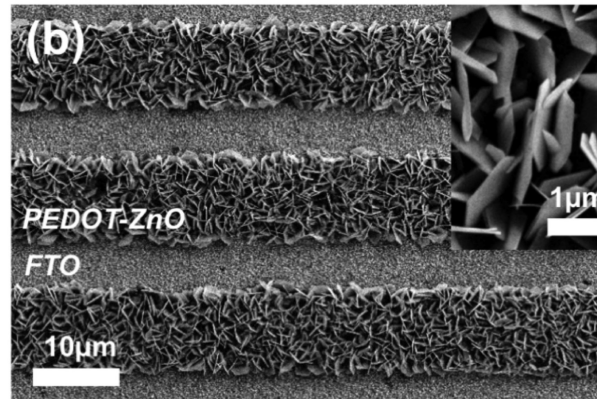
$E_r = rE_i \quad E_t = tE_i \quad R = |r|^2$
Fresnel Coefficients



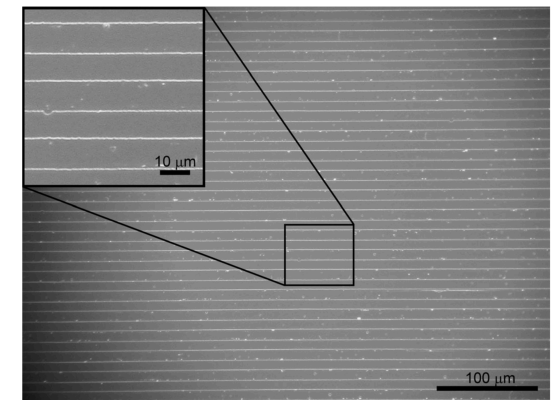
Diffraction

Nanostructured Grating

Electrodeposited Periodic Nanostructures



Gratings



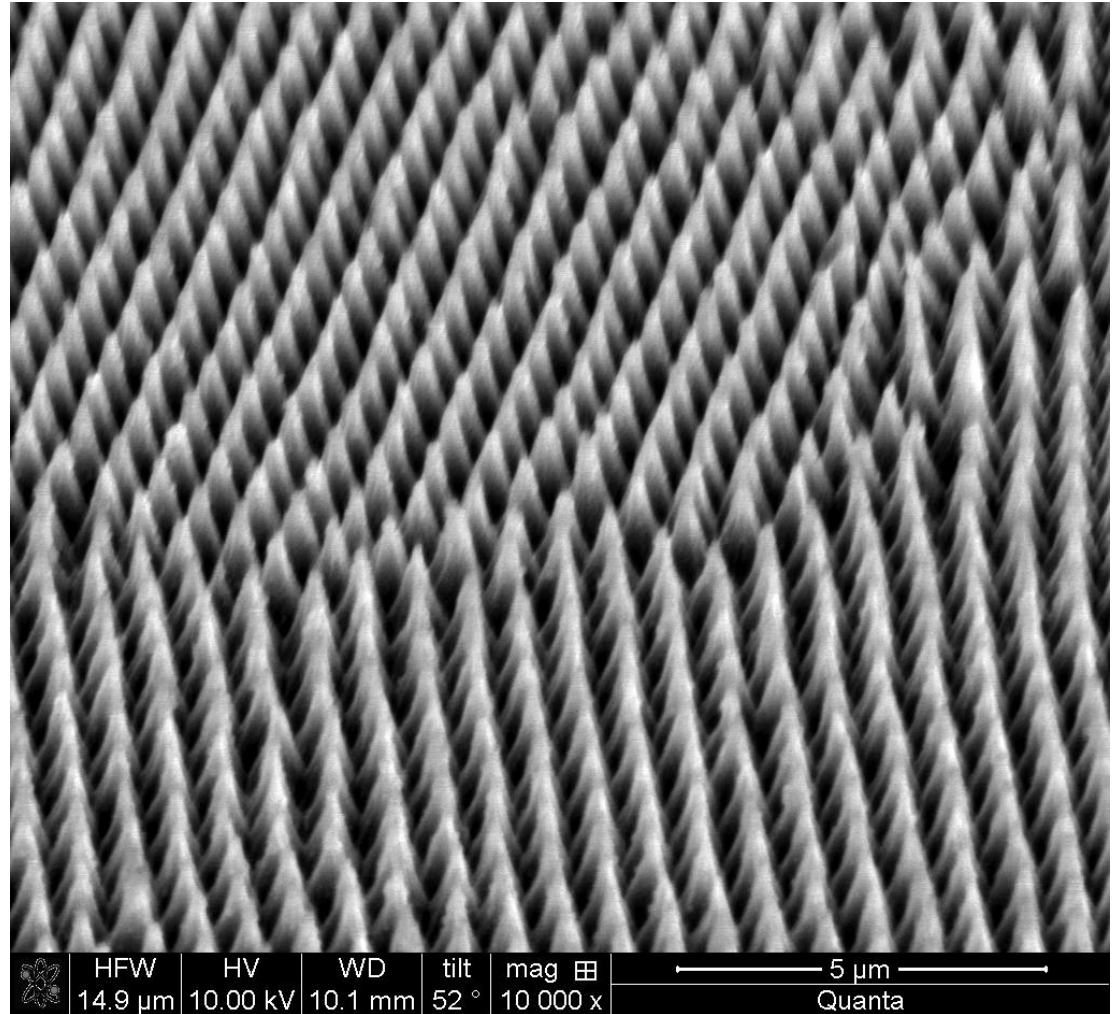
Nanowires



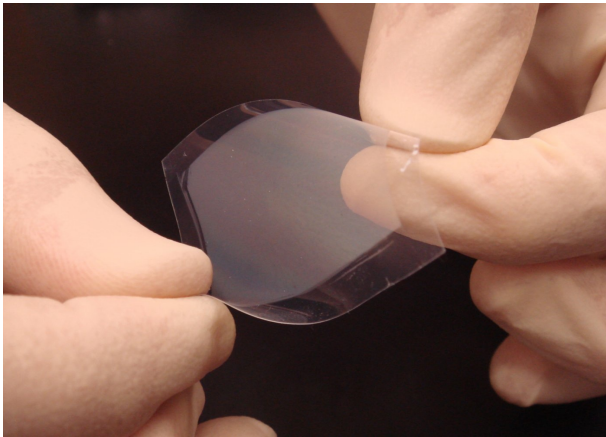
Nanostructured Mesoscale Optical Materials

Nanocones

Cones



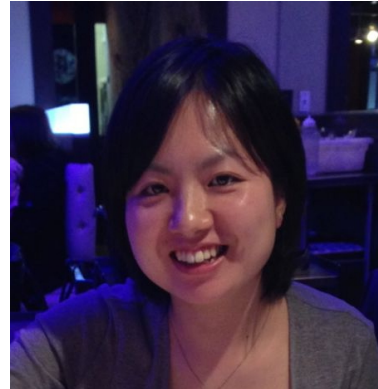
Anti-Reflective Nanocone Arrays



Plastic nanocone array



Gold-coated plastic nanocone array



Dr. Mana Toma

Tokyo Institute of Technology



Dr. Gabriel Loget

CNRS Rennes

Gabe and Mana were actually trying to make a flexible nanohole array. But...

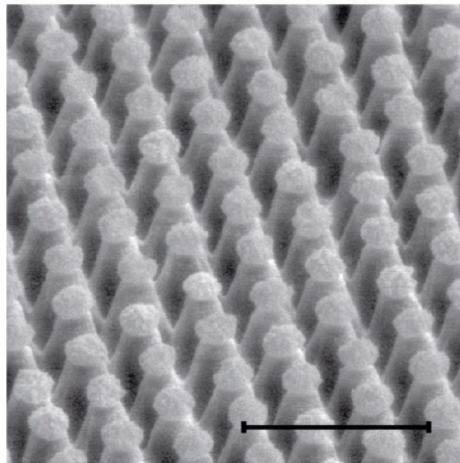
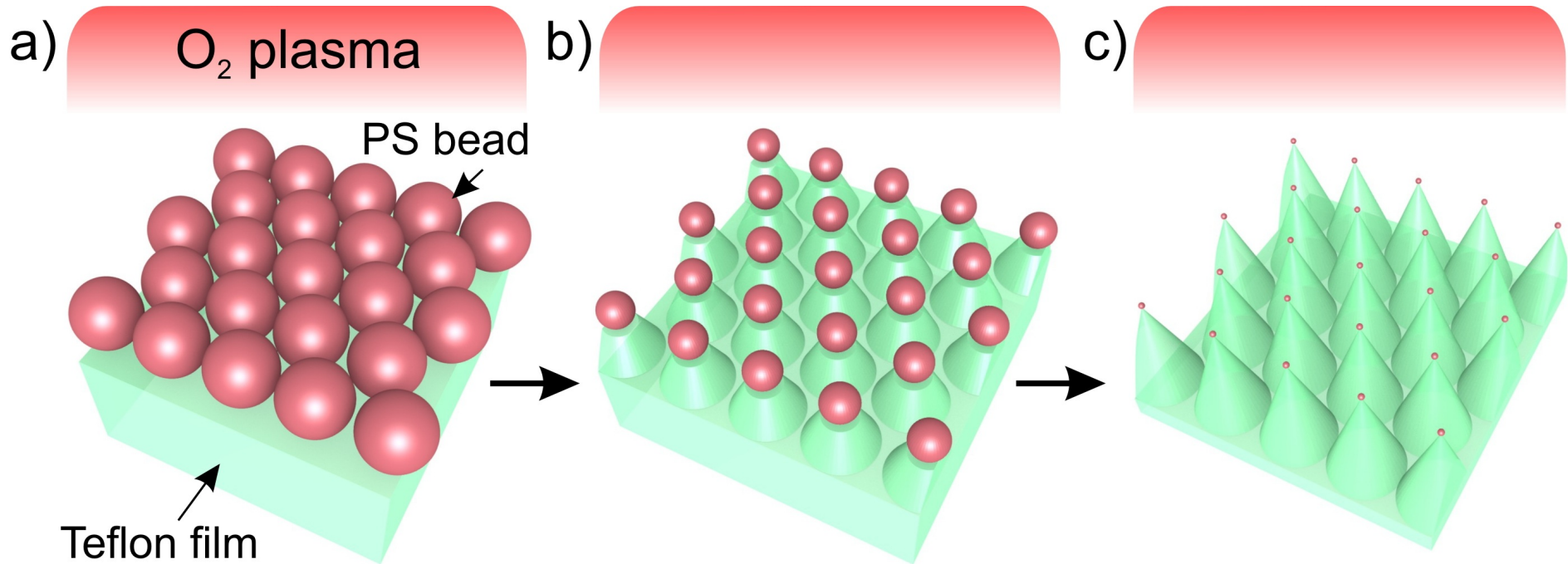
Why did this film turn jet black?

*“Chance favors only the prepared mind”
- Louis Pasteur*

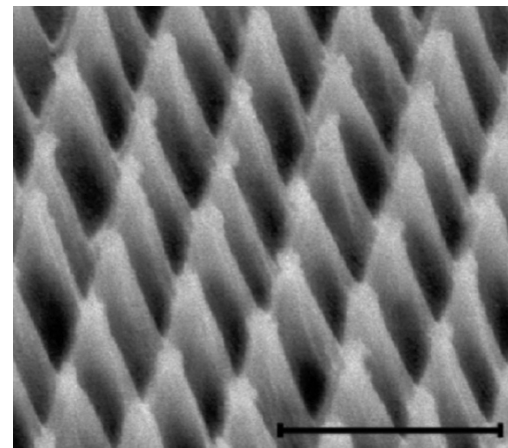


Electrochromic and Anti-Reflective Oxide Nanocone Arrays

Formed by the differential etching of polystyrene beads and Teflon



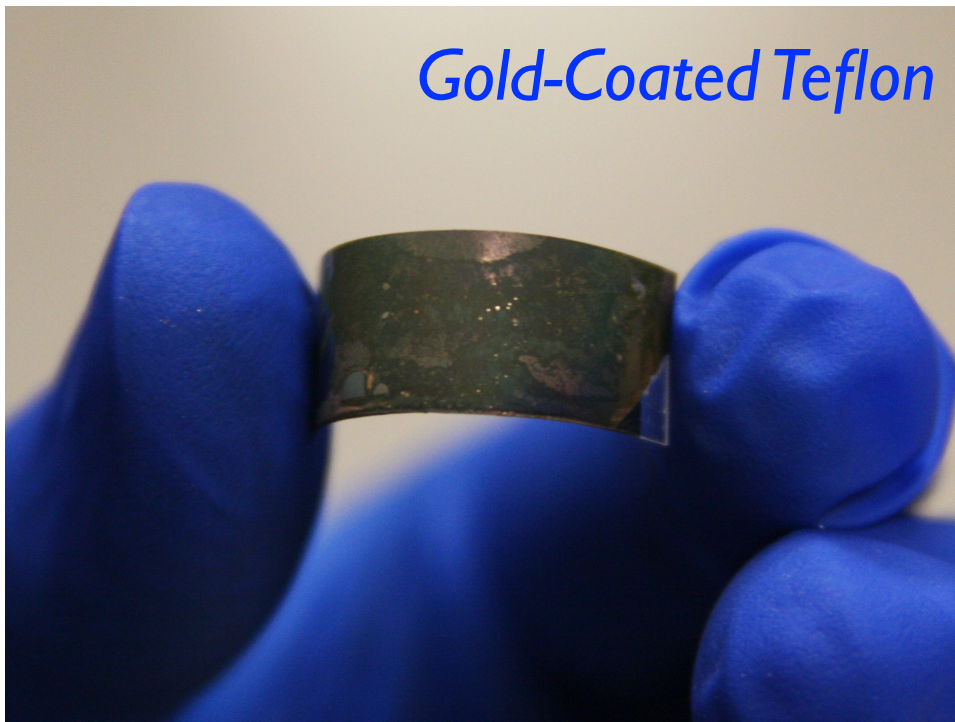
2 μm



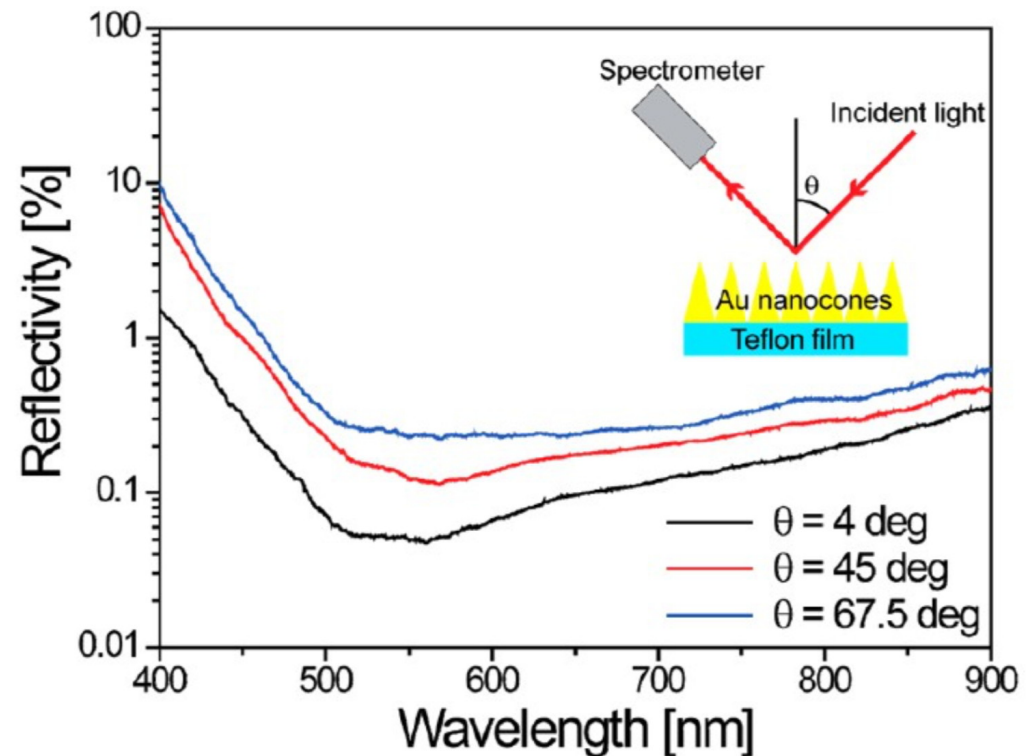
2 μm



Broadband Plasmonic Nanocone Anti-Reflection Surface

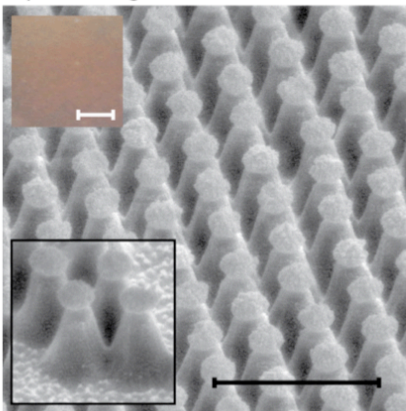


Gold-Coated Teflon

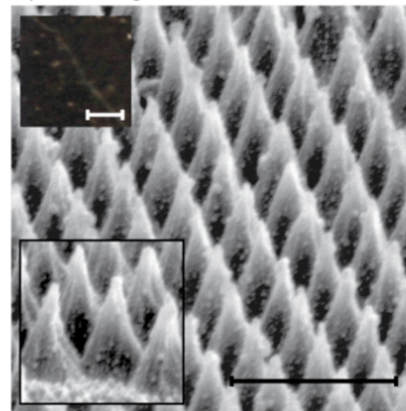


30 nm Au deposition

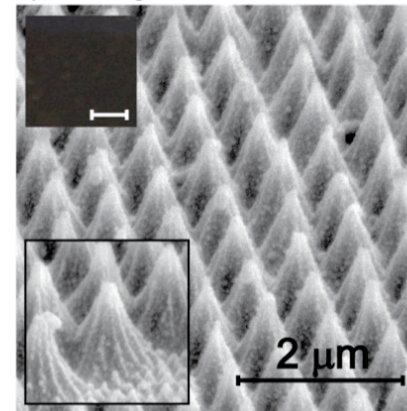
a) Etching time: 3 min



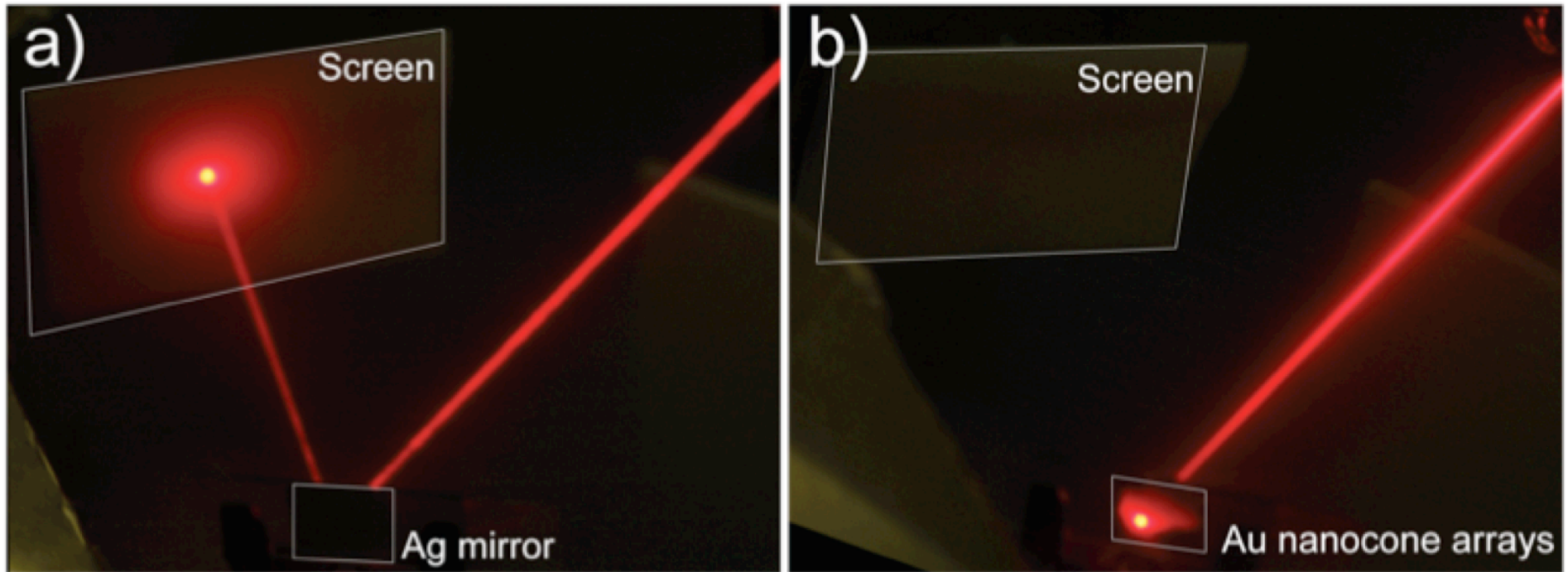
b) Etching time: 6 min



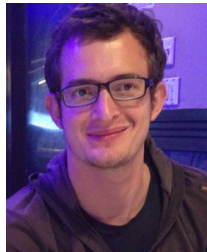
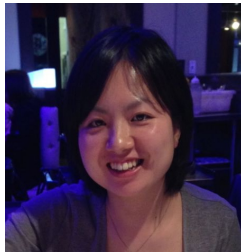
c) Etching time: 12 min



Broadband Plasmonic Nanocone Anti-Reflection Surface



Beam dissipation by a combination of diffraction, scattering and absorption



*flexible
anti-reflective films*

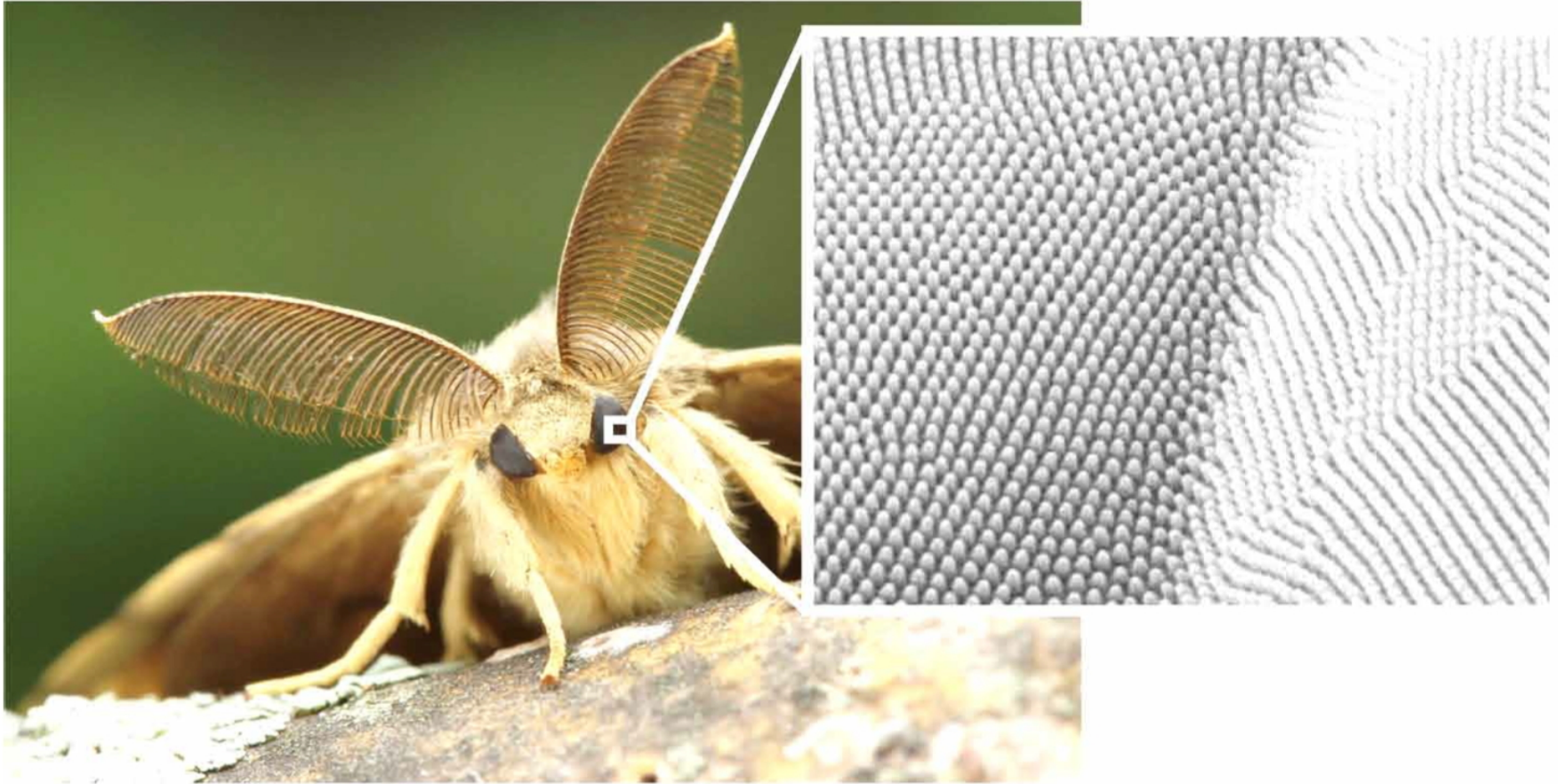


Mana Toma, Gabriel Loget and Robert M. Corn,
"Fabrication of Broadband Antireflective Plasmonic Gold
Nanocone Arrays on Flexible Polymer Films"
Nano Lett., **13** 6164-6169 (2013).



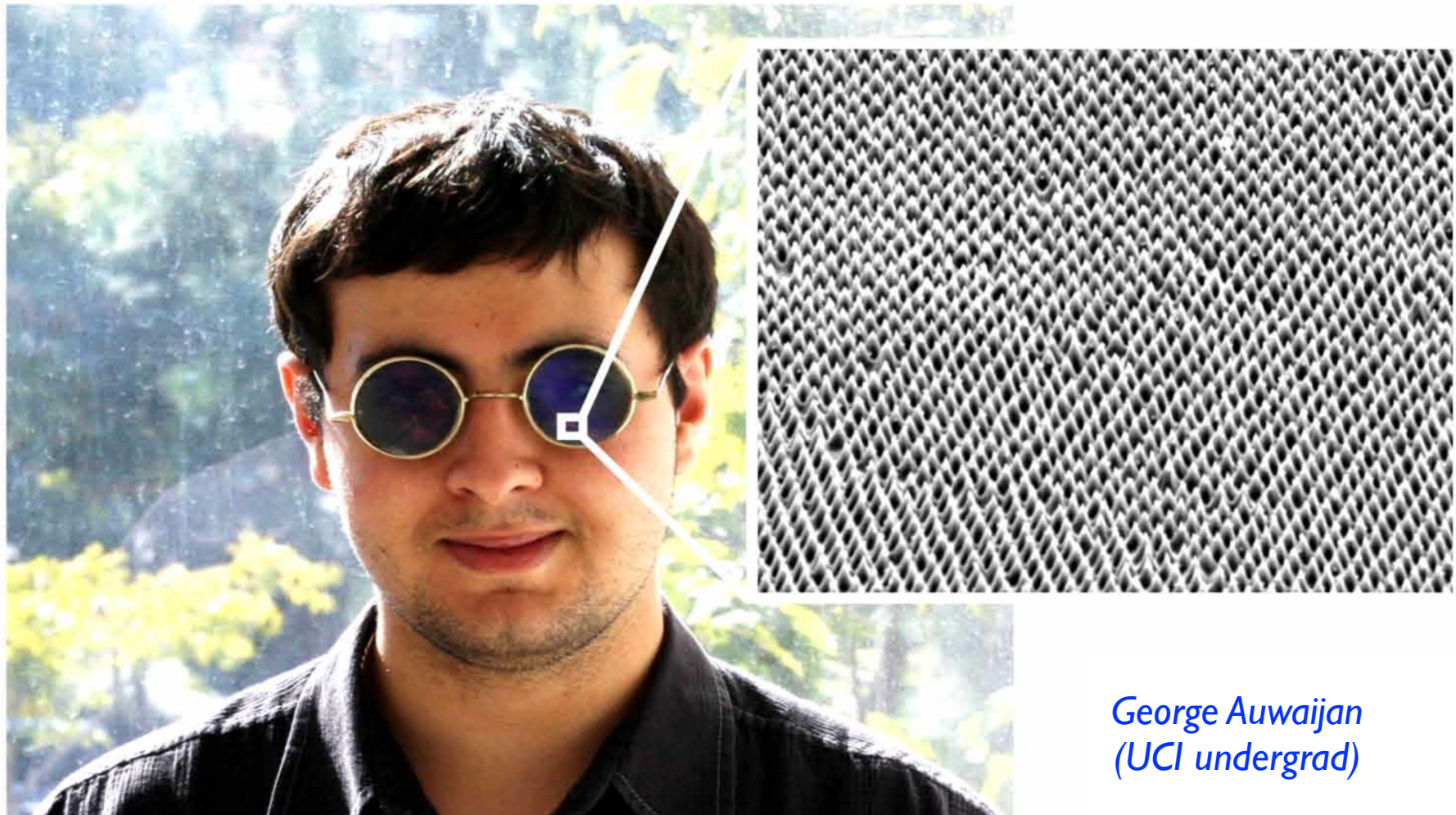
Nanocone Array Surfaces are Biomimetic

Moth eye



Nanocone Array Surfaces are Biomimetic

George eye



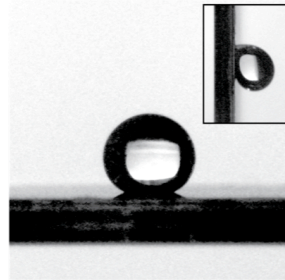
George Auwaijan
(UCI undergrad)



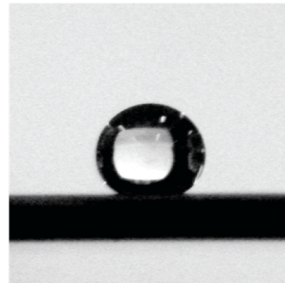
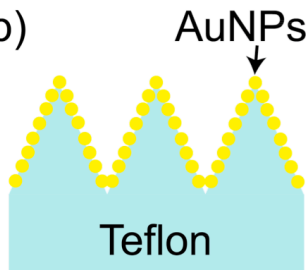
Superhydrophobic Nanocone Array Surfaces

Superhydrophobic Surfaces

a)



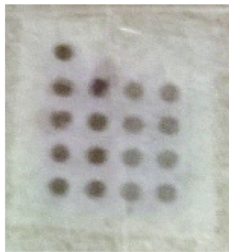
b)



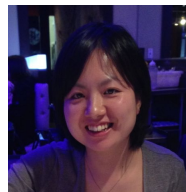
Teflon (Gecko Style)

or

Gold-Coated Teflon (Lotus Style)



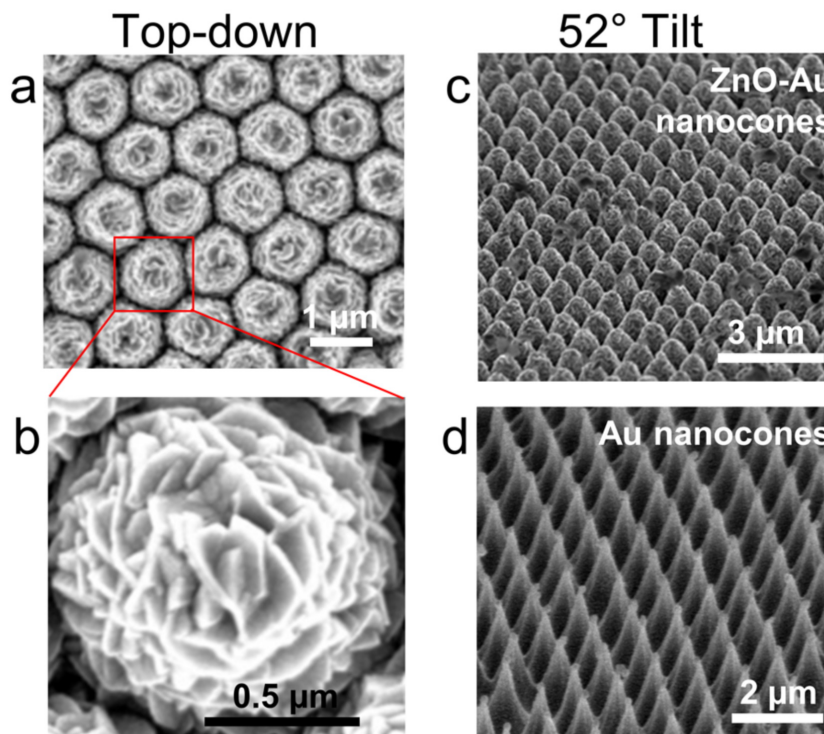
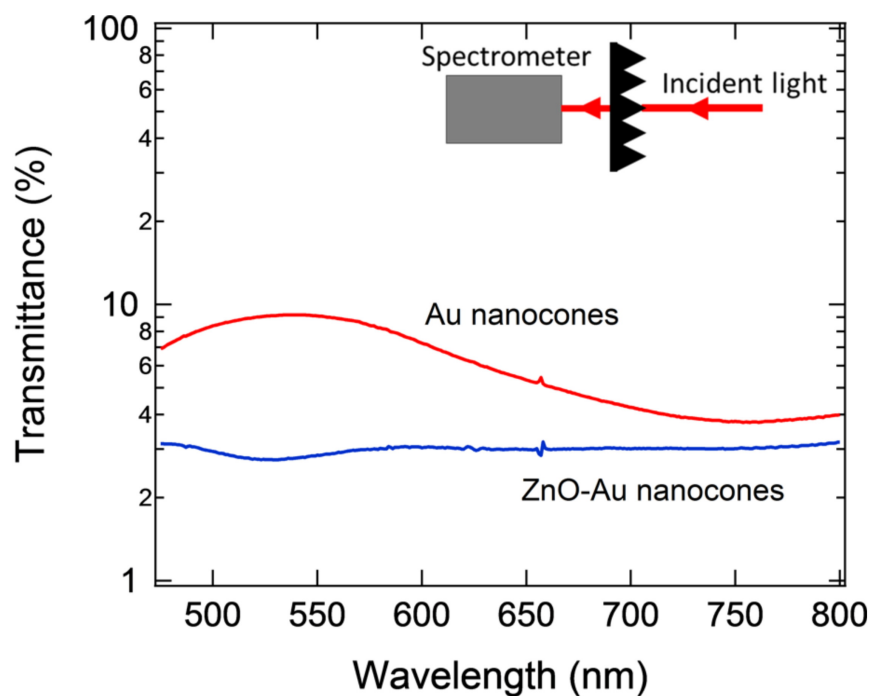
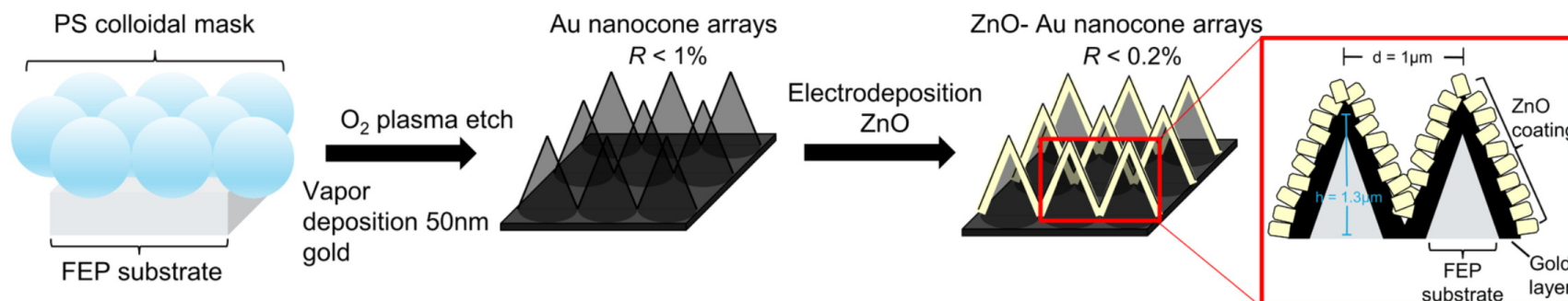
*microarray
fabrication*



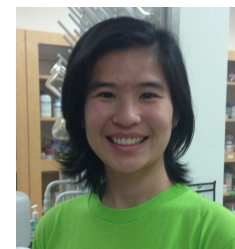
Mana Toma, Gabriel Loget and Robert M. Corn,
"Flexible Teflon Nanocone Array Surfaces with Tunable Superhydrophobicity
for Self-Cleaning and Aqueous Droplet Patterning"
ACS Appl. Mater. Interfaces, **6** 11110-11117 (2014).



Composite Au - ZnO Nanostructured Nanocone Arrays



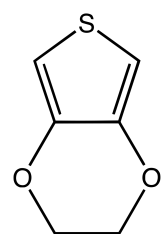
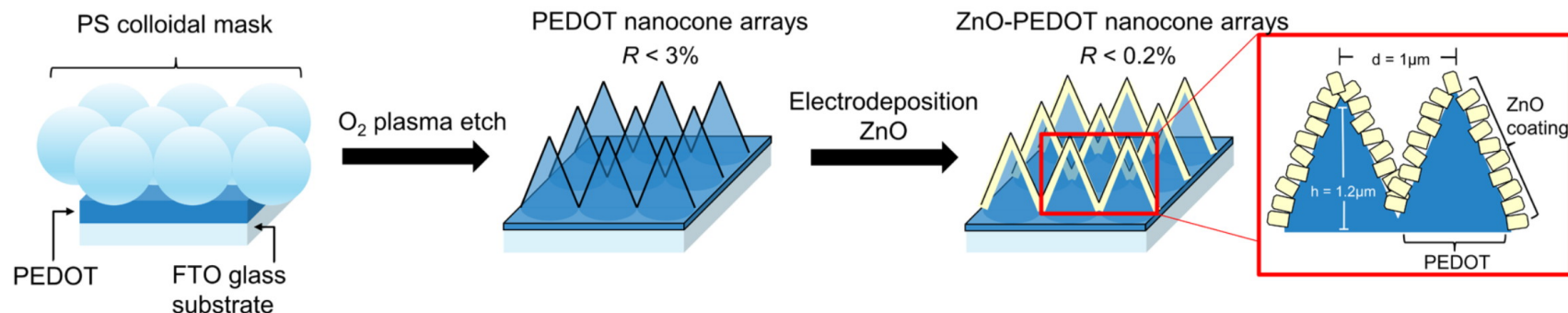
Dr. Seulgi So



Millie Fung

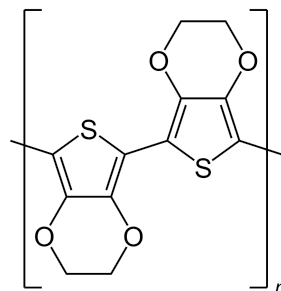


Composite PEDOT - ZnO Nanostructured Nanocone Arrays



EDOT

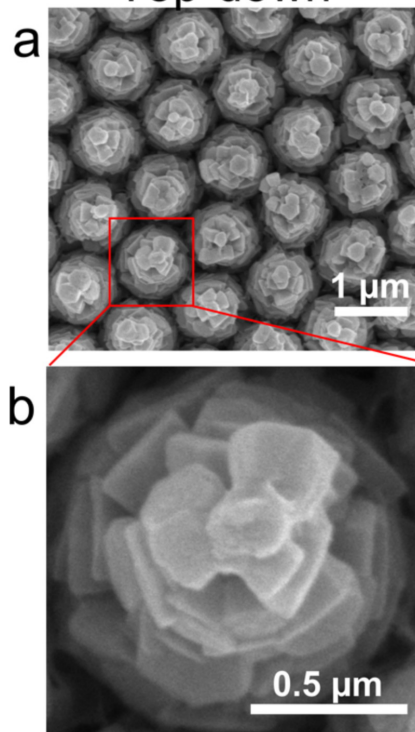
electrodeposition



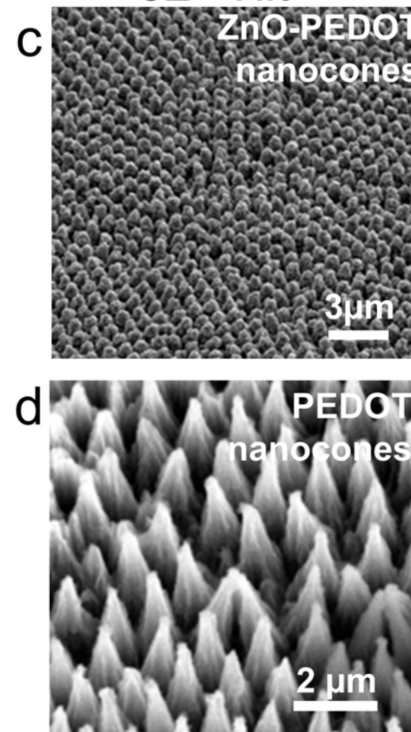
PEDOT

PEDOT - poly(3,4-ethylenedioxythiophene)

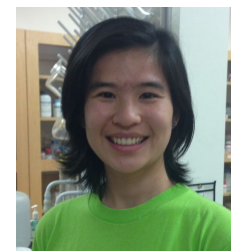
Top-down



52° Tilt



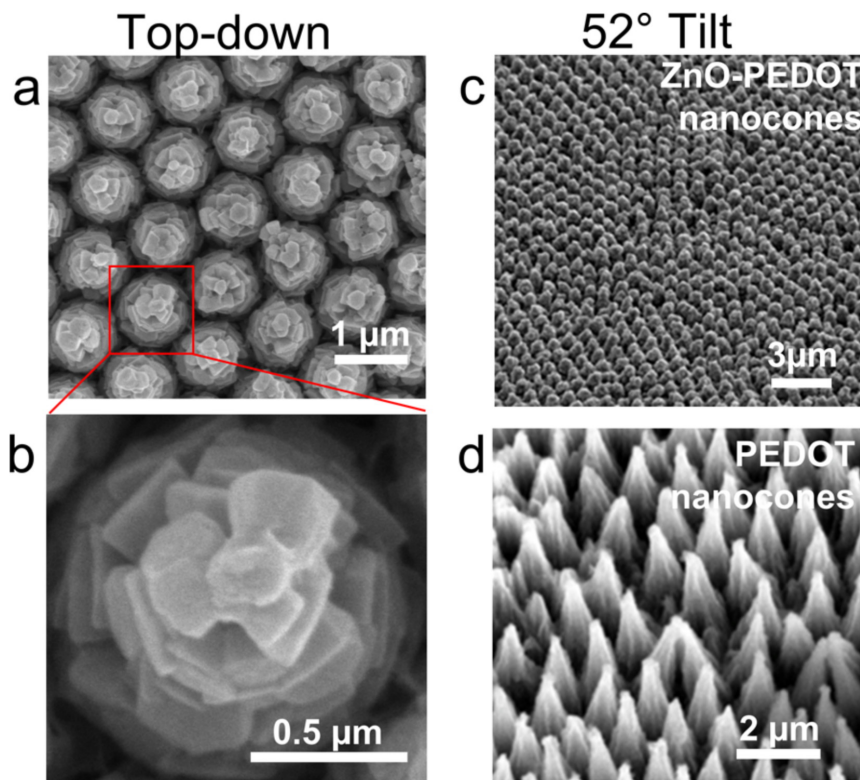
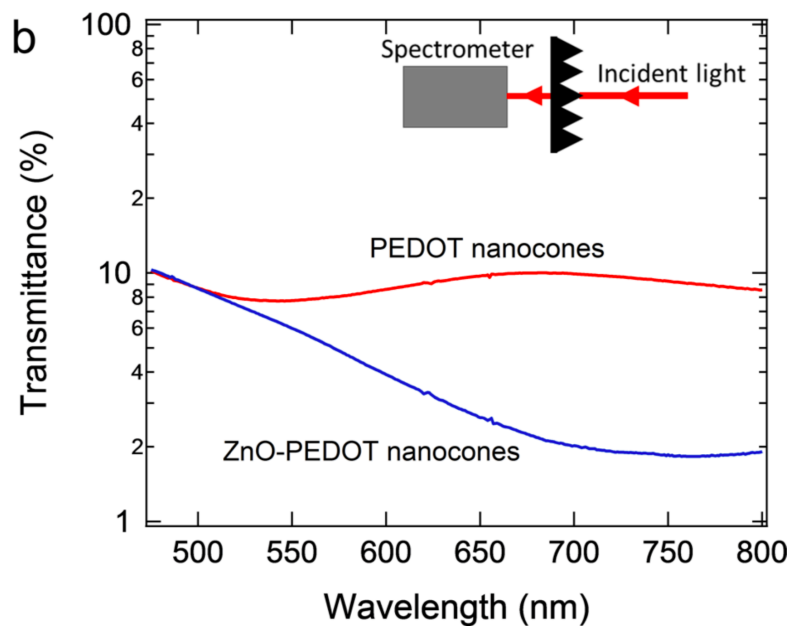
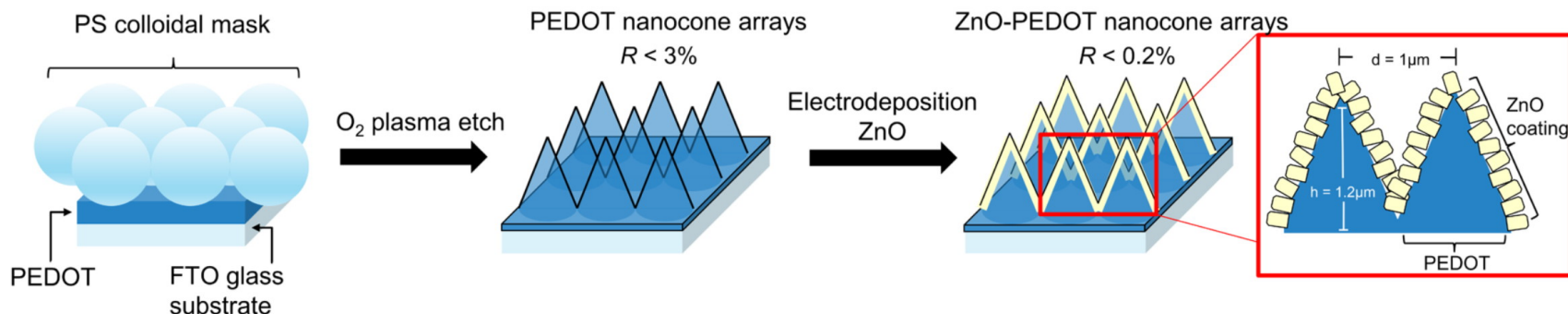
Dr. Seulgi So



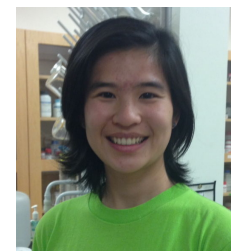
Millie Fung



Composite PEDOT - ZnO Nanostructured Nanocone Arrays



Dr. Seulgi So

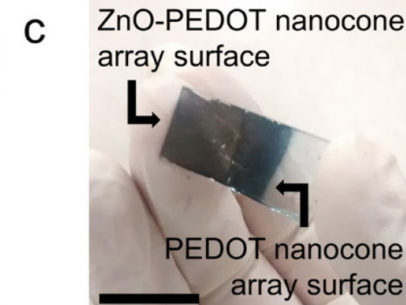
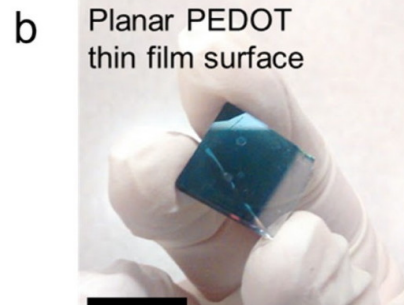
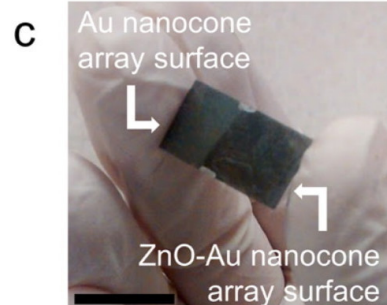
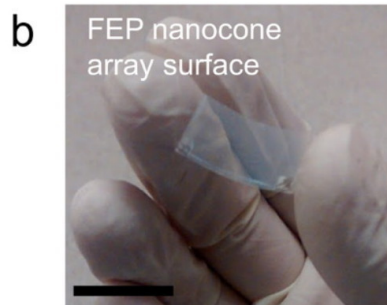
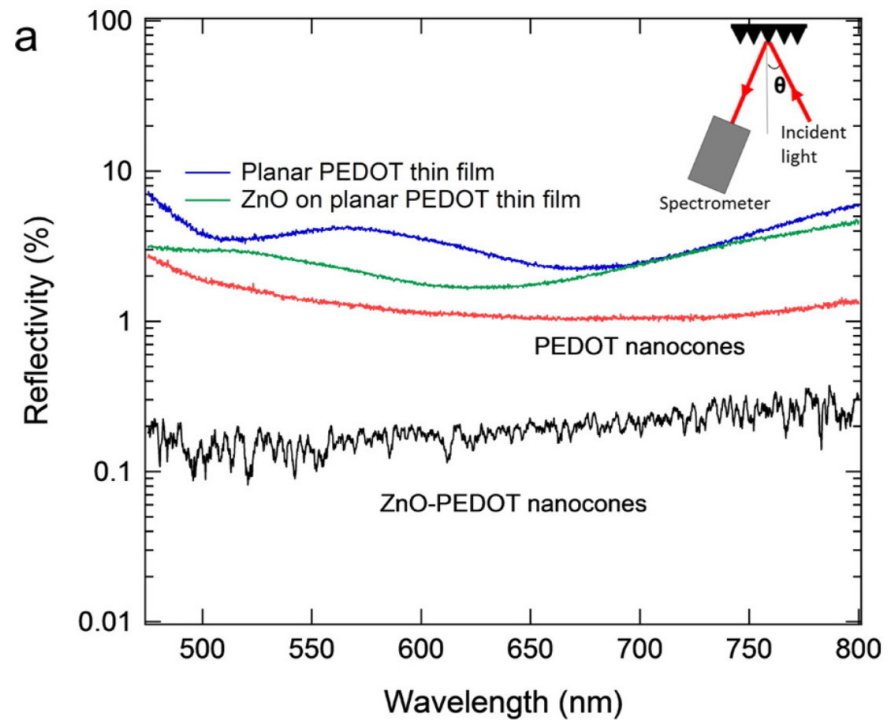
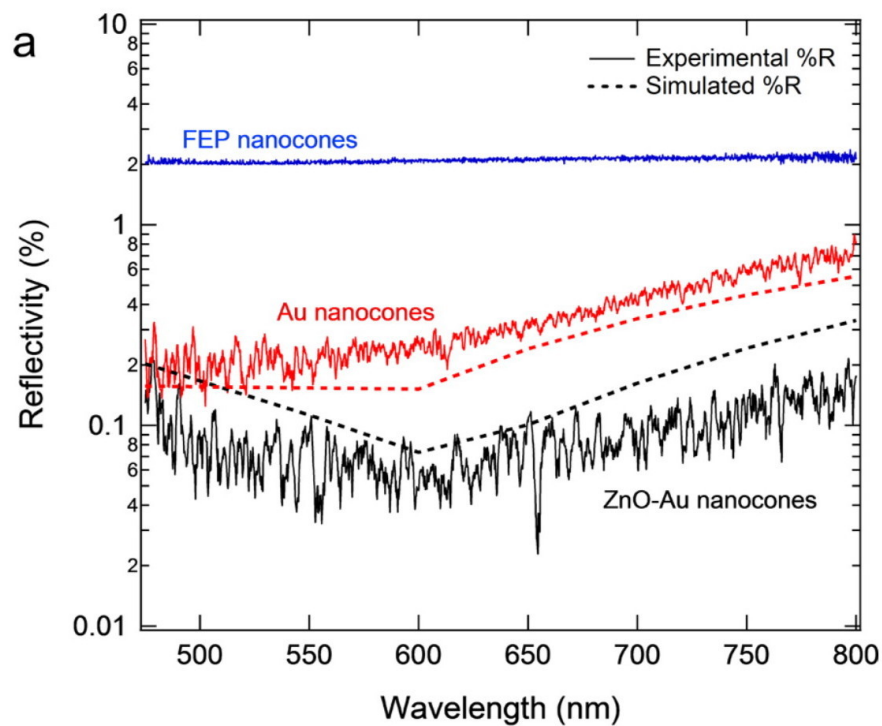


Millie Fung



Broadband Nanocone Array Anti-Reflection Surfaces

Electrodeposited ZnO Enhances Broadband Anti-Reflection

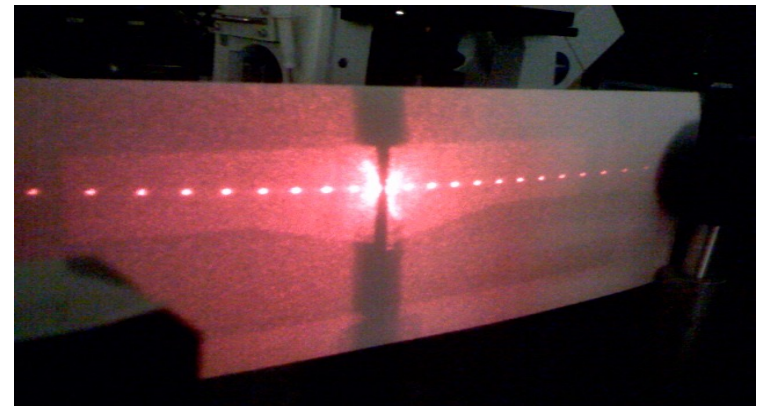
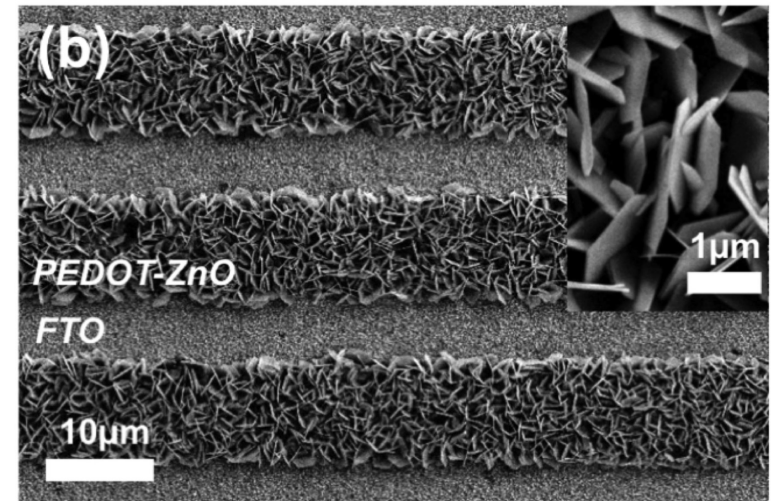


Nanostructured Mesoscale Optical Materials

Gratings



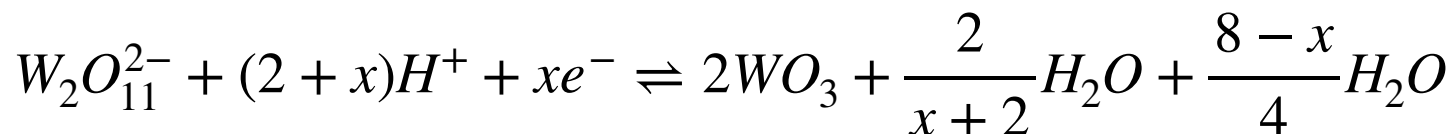
Nanostructured Gratings



Electrodeposited Electrochromic Materials

- PEDOT - poly(3,4-ethylenedioxythiophene)
- Tungsten Oxide - WO_3

Electrodeposition Reaction



Combined electrochemical reduction and disproportionation of the four peroxide anions in the peroxytungstate

x is either 0, 4, or 8

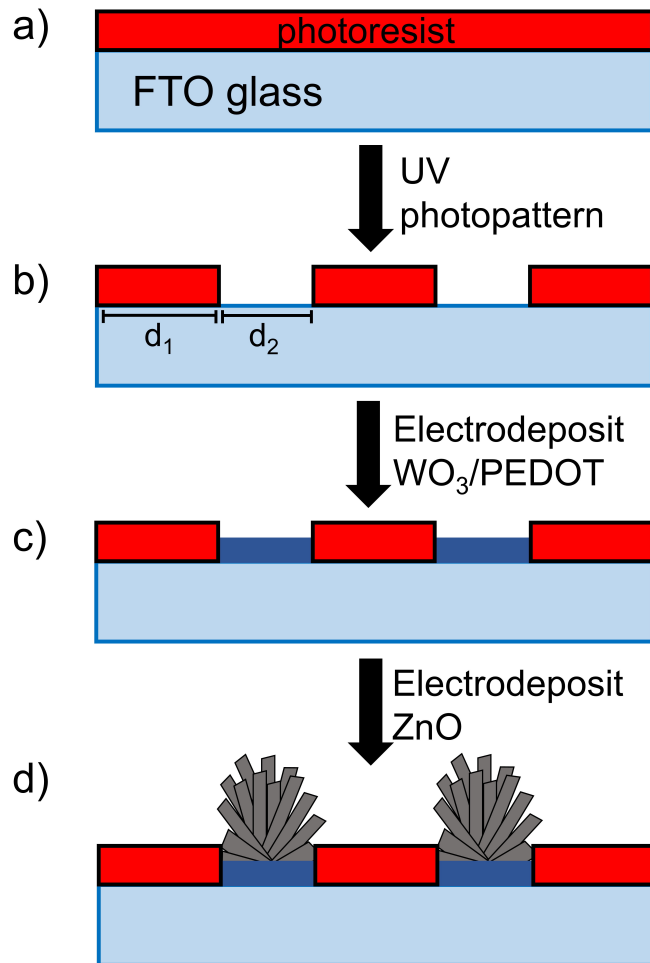


Kellen Kartub

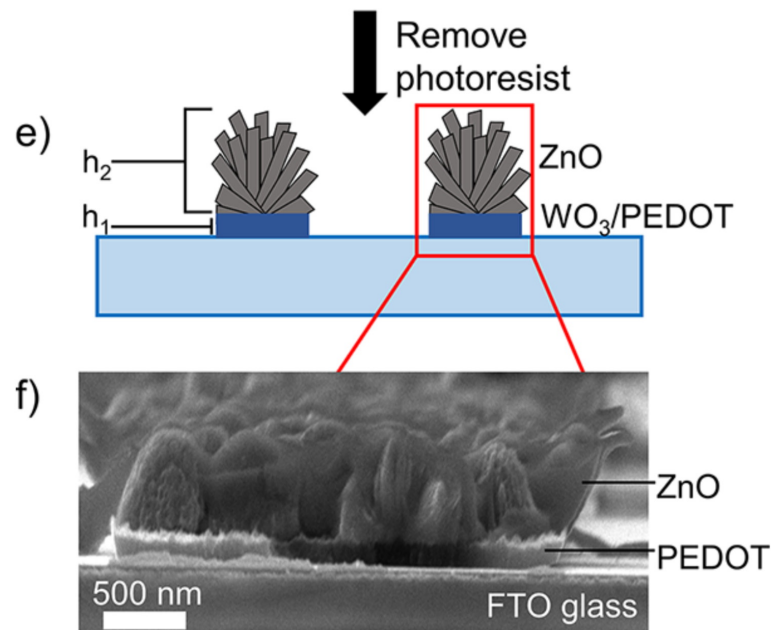
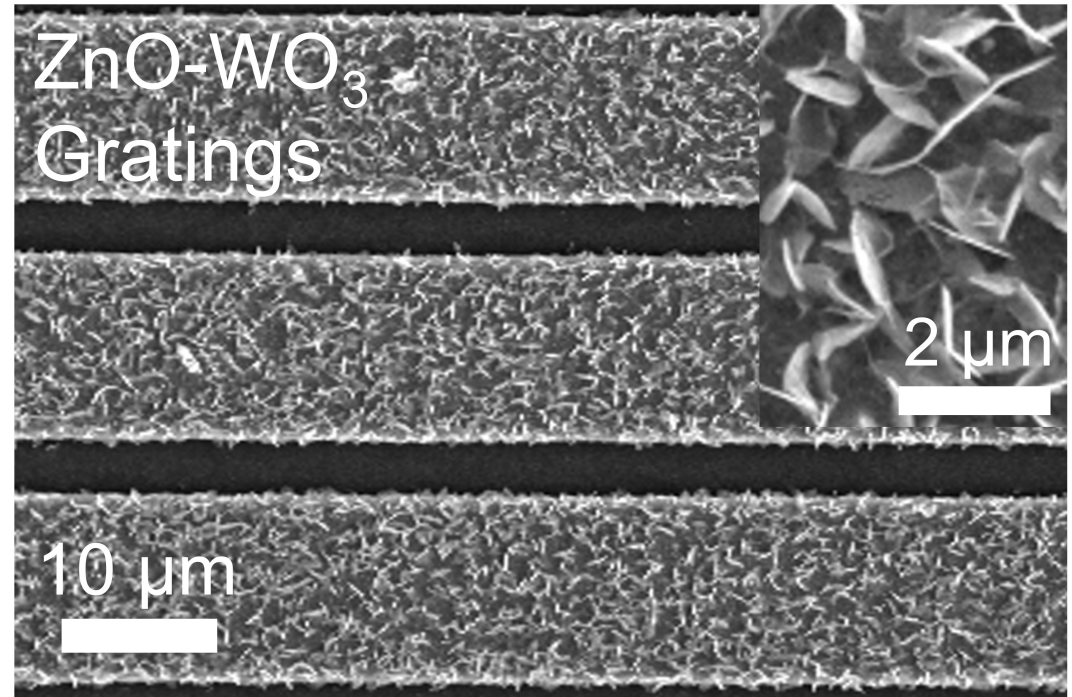
Electrochromic Reaction



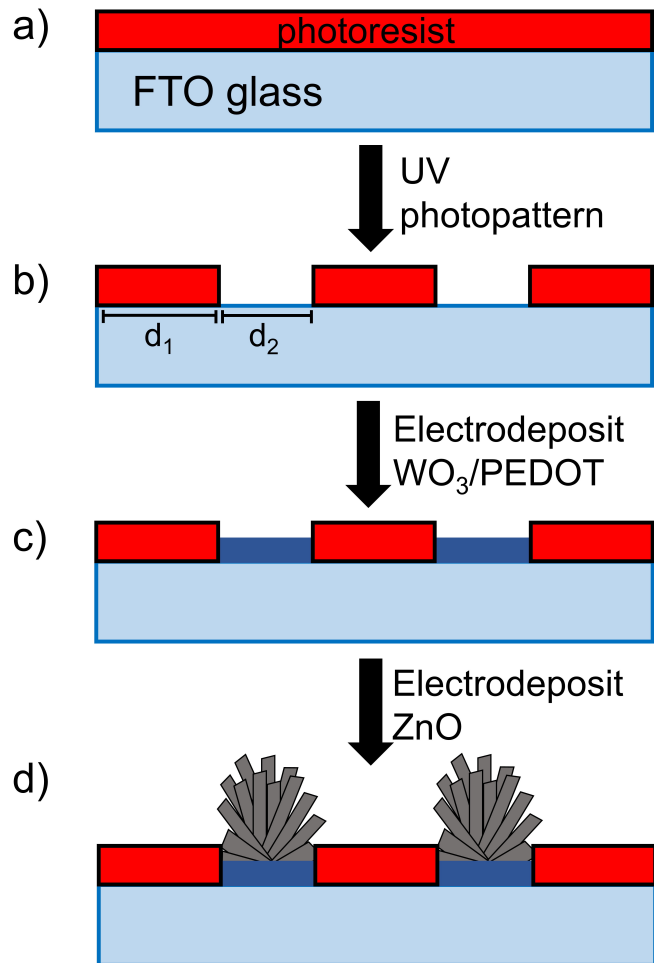
Photopatterned Electrodeposited Gratings



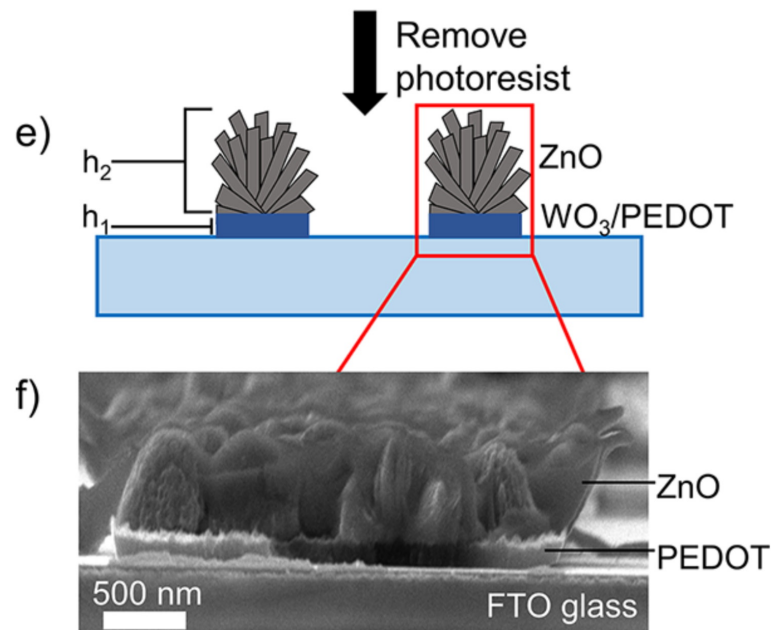
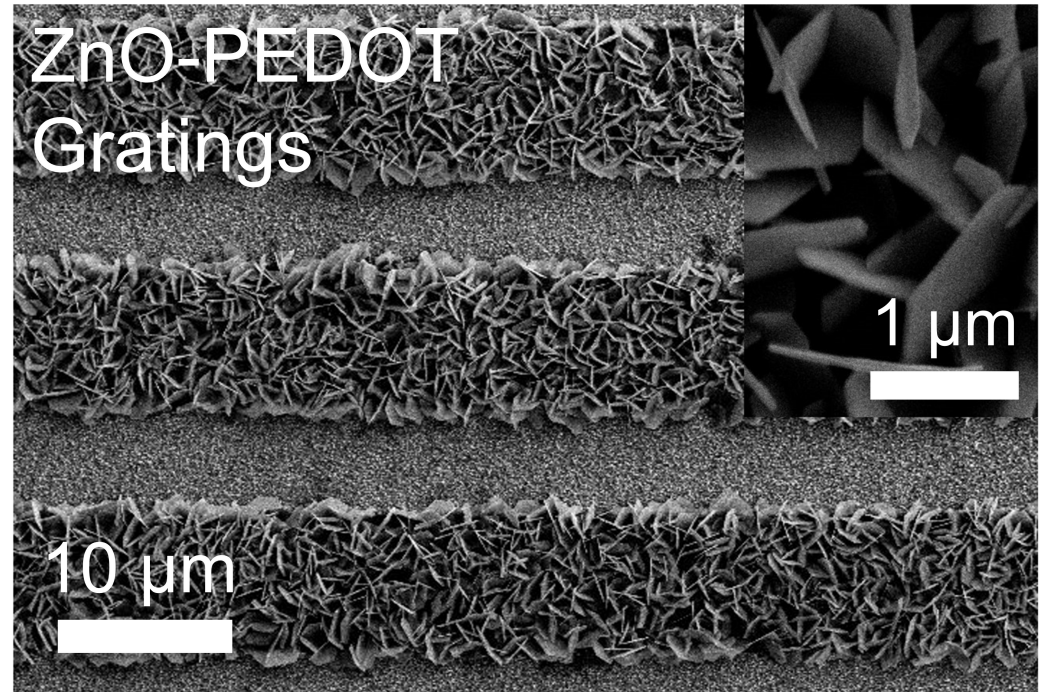
grating spacings typically 5-10 μm



Photopatterned Electrodeposited Gratings



grating spacings typically 5-10 μm



Frequency Dependent Complex Index of Refraction $n(\omega)$

Equation for a light wave traveling in the +z direction in a dielectric:

$$E(z, t) = E_o \cos(kz - \omega t)$$

wavevector

$$k = \frac{2\pi n}{\lambda} = \frac{n\omega}{c}$$

angular frequency

$$\omega = 2\pi\nu = \frac{2\pi c}{\lambda}$$

$$n(\omega) = \eta(\omega) + i\kappa(\omega)$$

$n(\omega)$ complex refractive index

$\eta(\omega)$ real refractive index

$\kappa(\omega)$ extinction coefficient

The complex refractive index n defines
a light wave's velocity and absorption in a material.

@633 nm

$$n_{\text{ZnO}} = 1.988 + 0i$$

$$n_{\text{Au}} = 0.183 + 3.433i$$



Frequency Dependent Complex Index of Refraction $n(\omega)$

Equation for a light wave traveling in the +z direction in a dielectric:

$$E(z, t) = E_0 \cos(kz - \omega t) \quad n(\omega) = \eta(\omega) + i\kappa(\omega)$$

wavevector

$$k = \frac{2\pi n}{\lambda} = \frac{n\omega}{c}$$

$n(\omega)$ complex refractive index

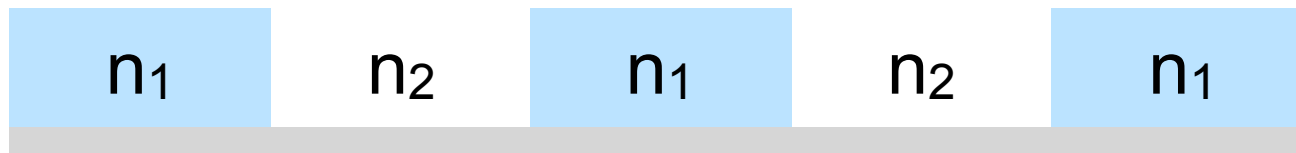
$\eta(\omega)$ real refractive index

angular frequency

$$\omega = 2\pi\nu = \frac{2\pi c}{\lambda}$$

$\kappa(\omega)$ extinction coefficient

Diffraction Grating



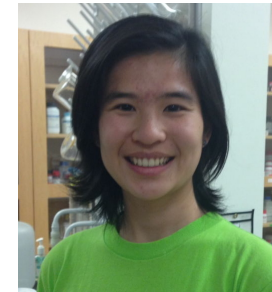
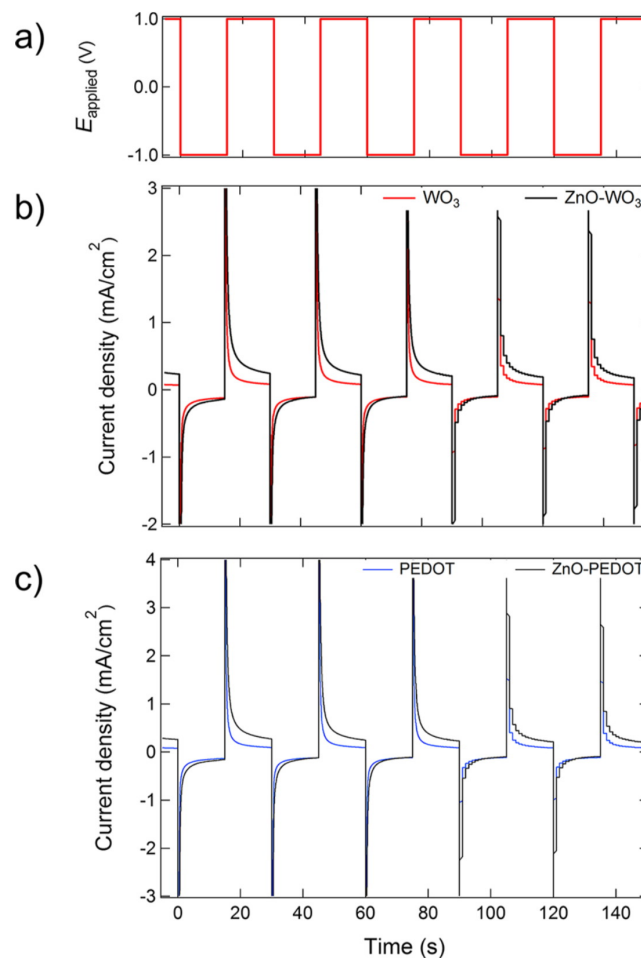
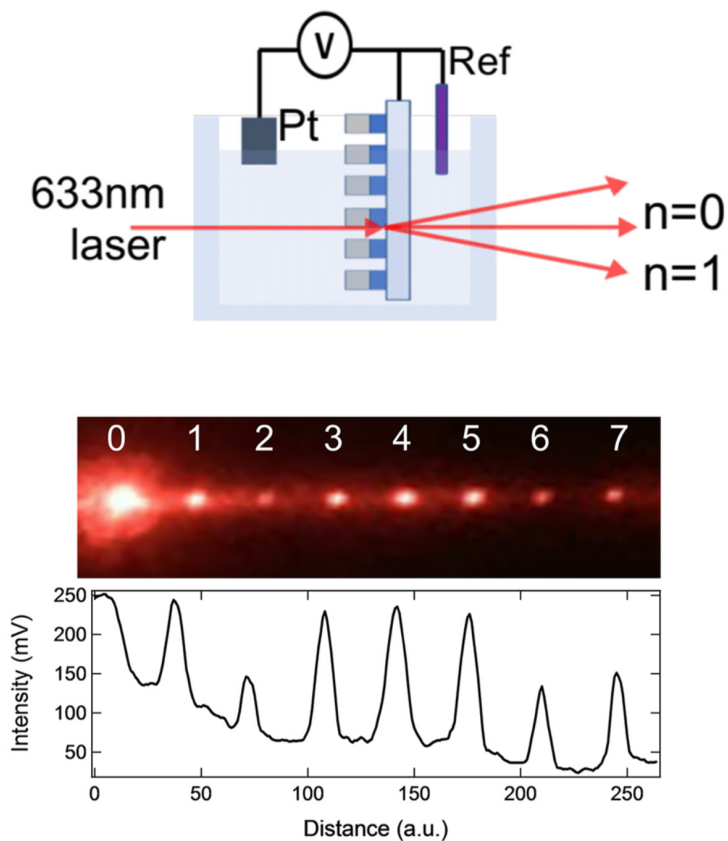
$\Delta \eta = \text{phase grating}$

$\Delta \kappa = \text{absorption grating}$



Electrochromic and Electrodiffractive Composite Gratings

ZnO acts as an antenna and enhances the electrodiffractive response of the electrochromic WO_3 or PEDOT



Millie



Kellen

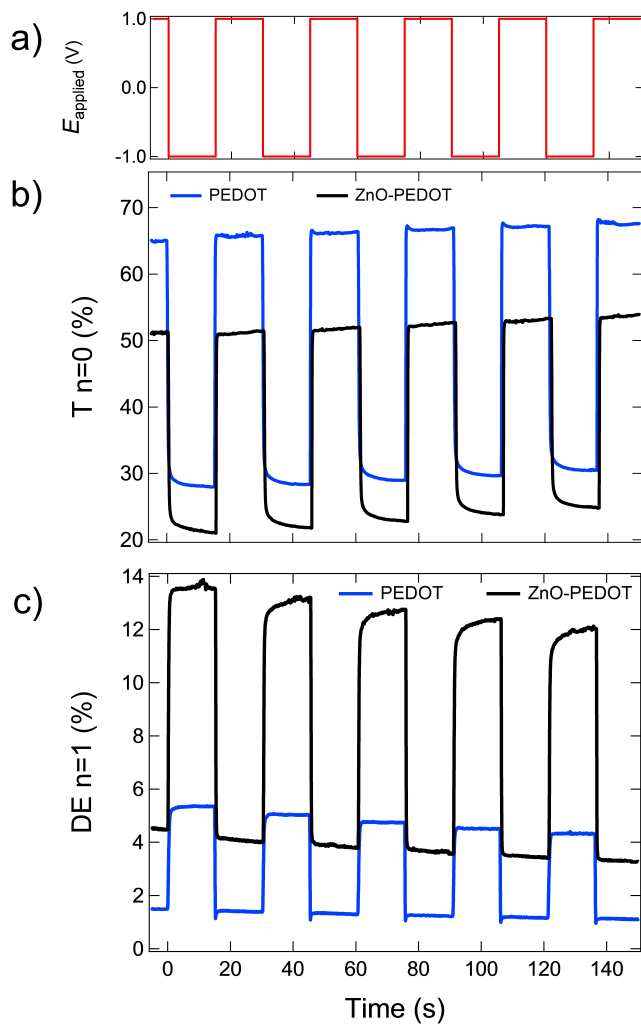


Seulgi

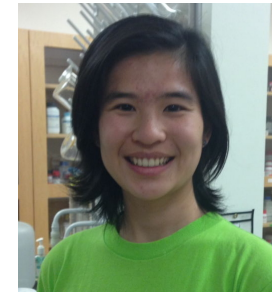
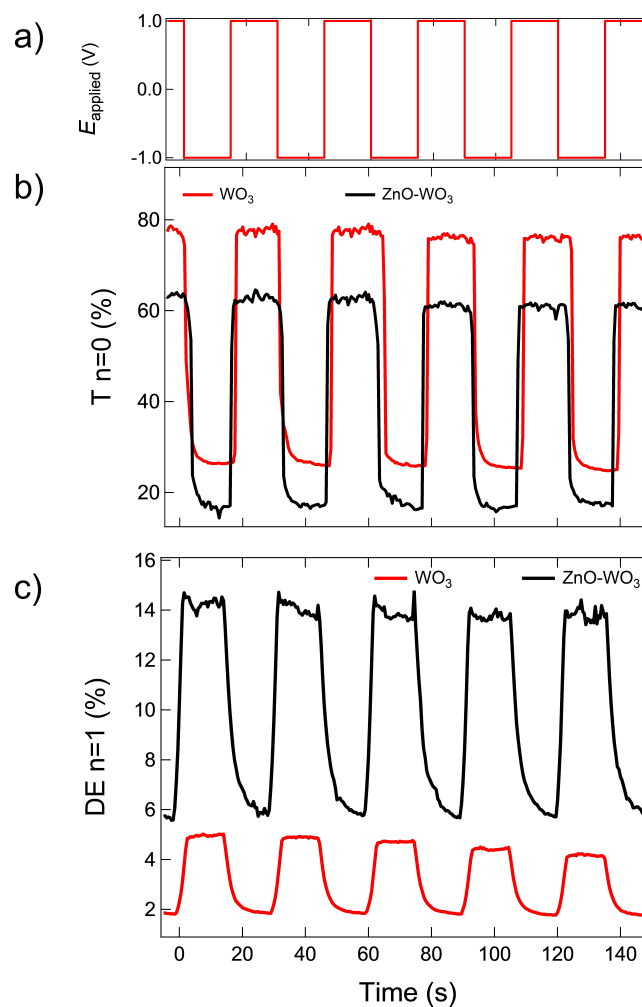
Electrochromic and Electrodiffractive Composite Gratings

ZnO acts as an antenna and enhances the electrodiffractive response of the electrochromic WO_3 or PEDOT

PEDOT



WO_3



Millie



Kellen

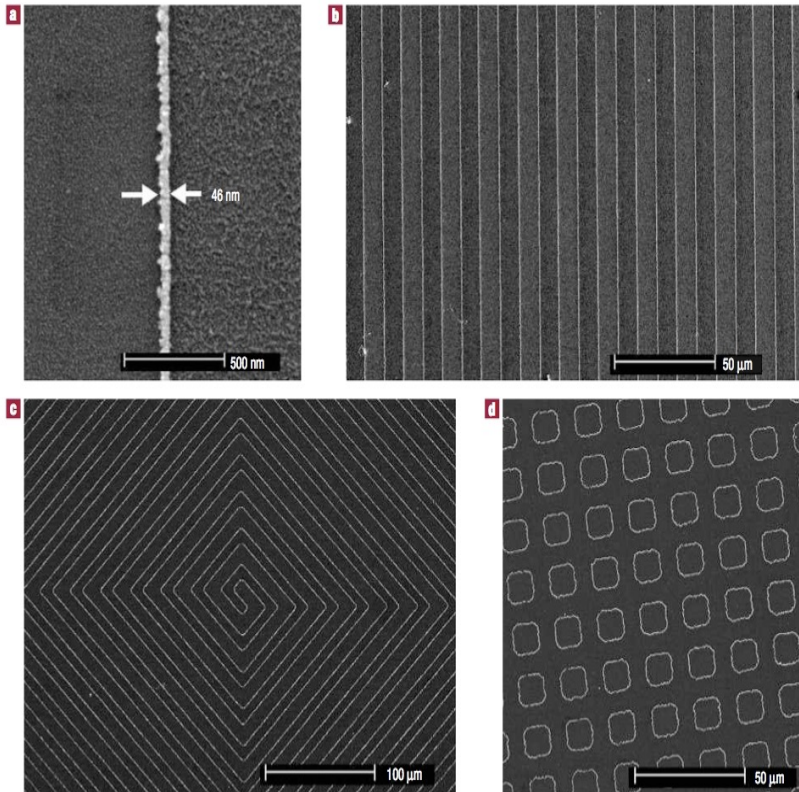


Seulgi



Optical Diffraction from Nanowire Arrays

Lithographically Patterned Nanowire Electrodeposition (LPNE)



A versatile process for large scale nanowire fabrication.



Prof. Reg Penner
UCI



Aaron Halpern

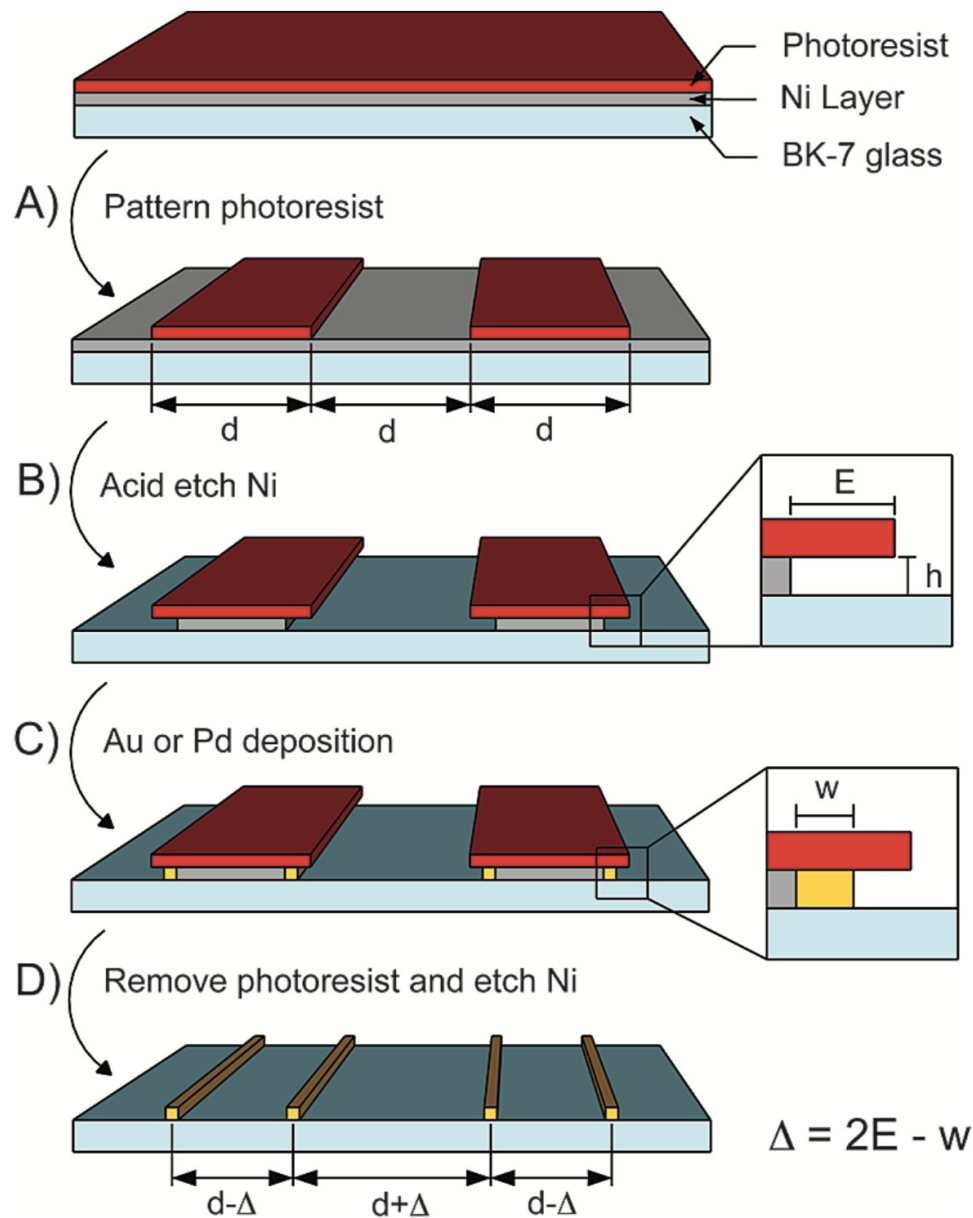


Dr. Naoya Nishi
Kyoto University

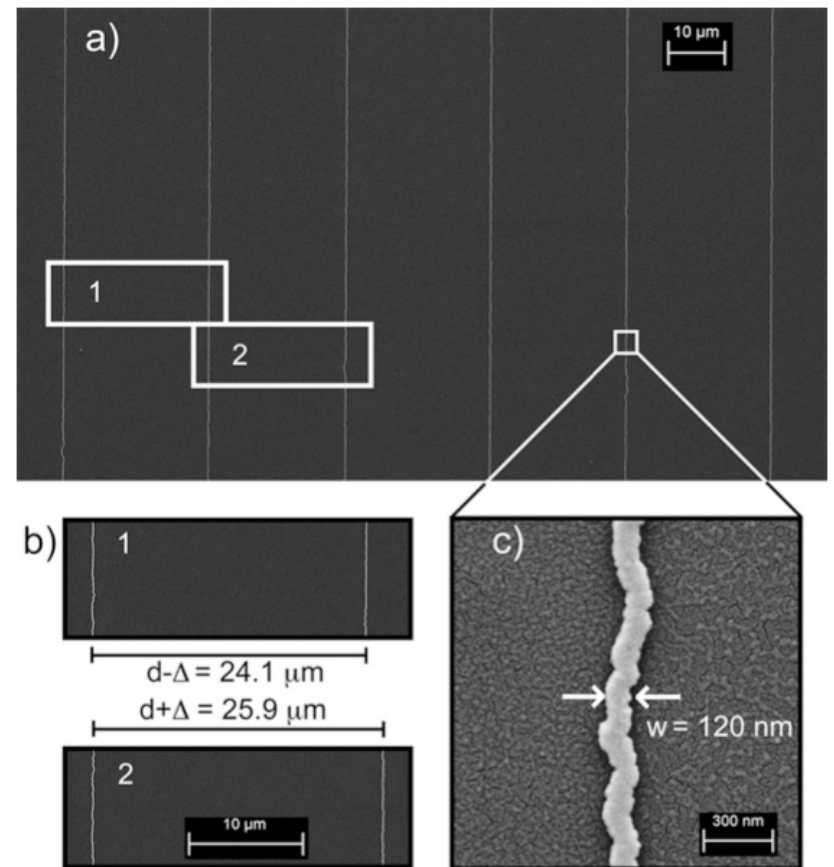


A. R. Halpern, N. Nishi, J. Wen, F. Yang, C. Xiang, R. M. Penner, and R. M. Corn *Chem.*, **81**, 5585-5592 (2009).

Lithographically Patterned Nanowire Electrodeposition (LPNE)



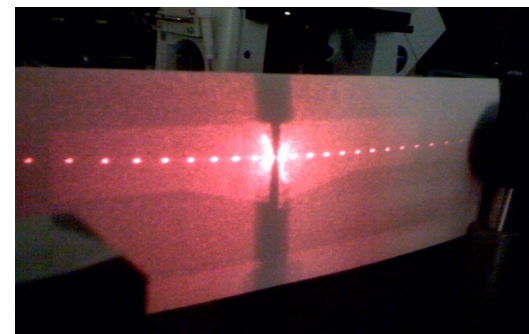
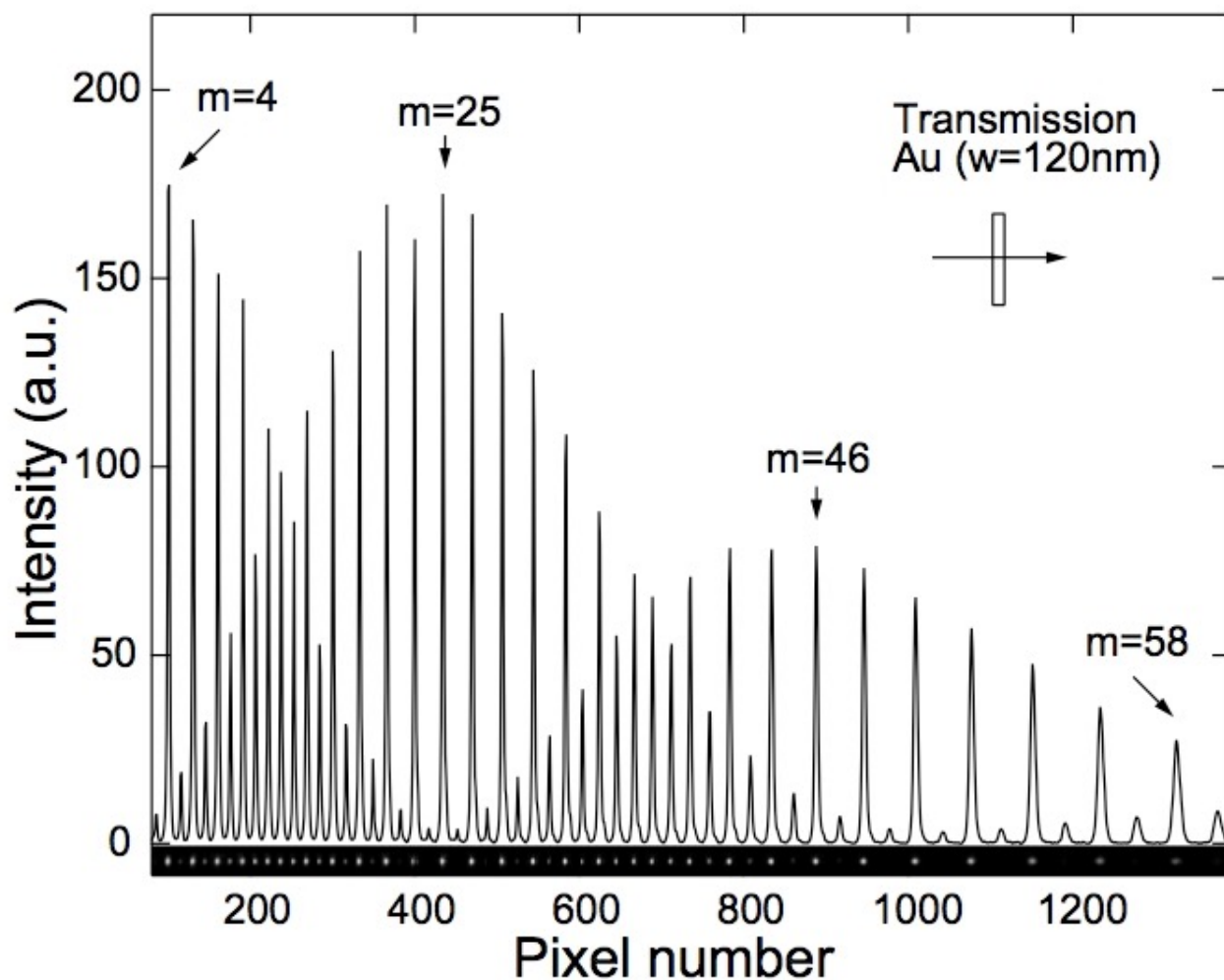
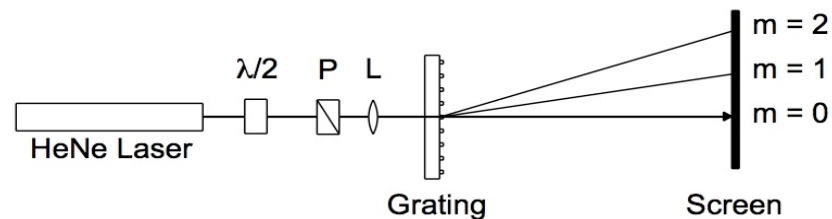
Gold nanowires are electrodeposited onto nanoscale Ni electrodes



A. R. Halpern, N. Nishi, J. Wen, F. Yang, C. Xiang, R. M. Penner, and R. M. Corn Chem., **81**, 5585-5592 (2009).

Nanowire Diffraction Gratings

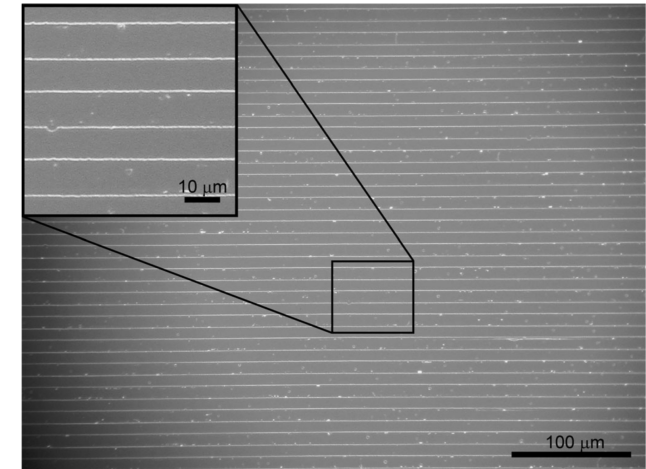
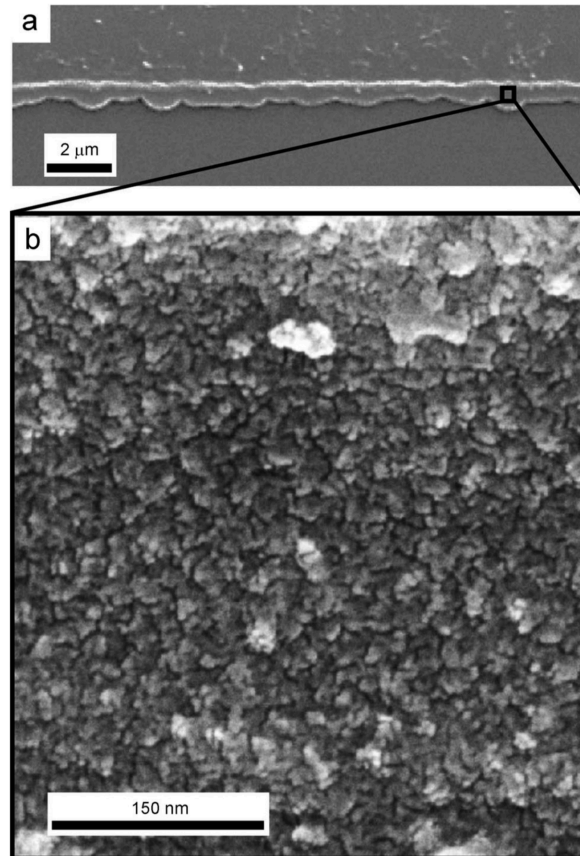
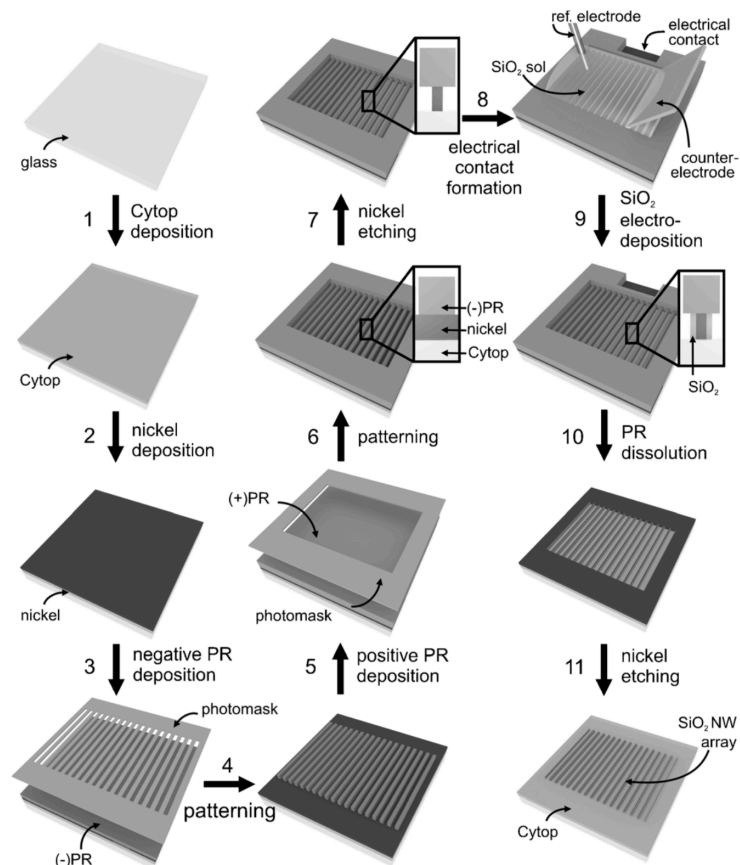
0.5% surface coverage



A. R. Halpern, N. Nishi, J. Wen, F. Yang, C. Xiang, R. M. Penner, and R. M. Corn Chem., **81**, 5585-5592 (2009).

Silica nanowires for diffraction biosensing

Electrodeposition of porous silica nanowires



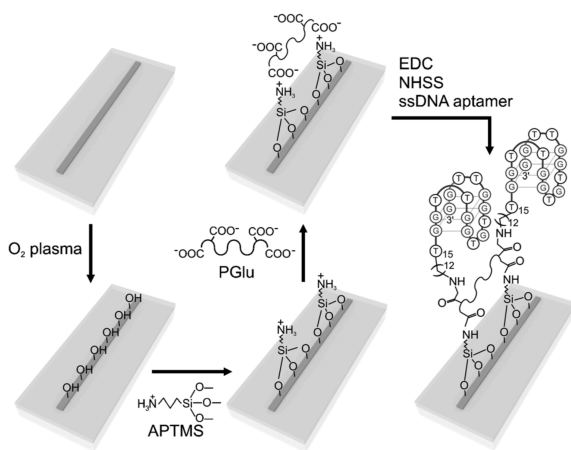
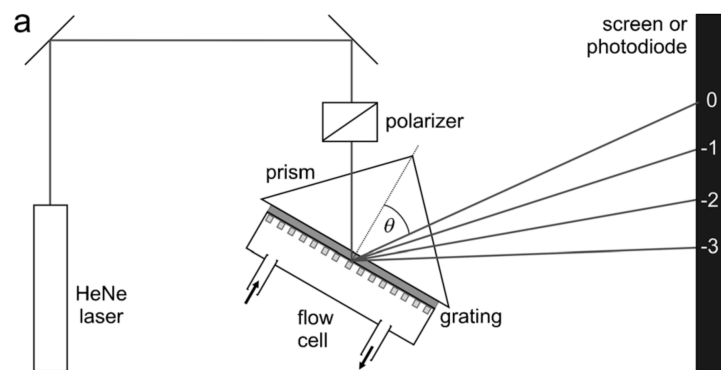
Dr. Gabriel Loget

Gabriel Loget and Robert M. Corn,
"Silica Nanowire Arrays for Diffraction-Based Bioaffinity Sensing"
Chemistry - A European Journal, **20** 10802-10810 (2014).



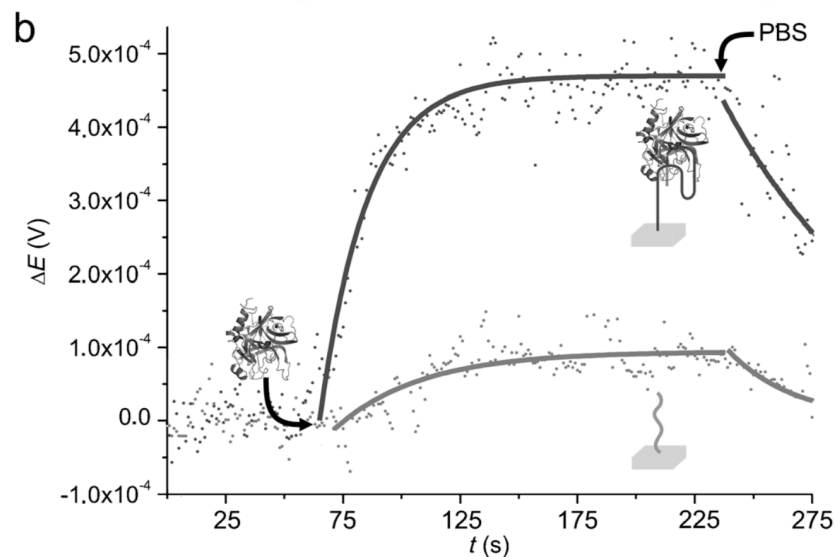
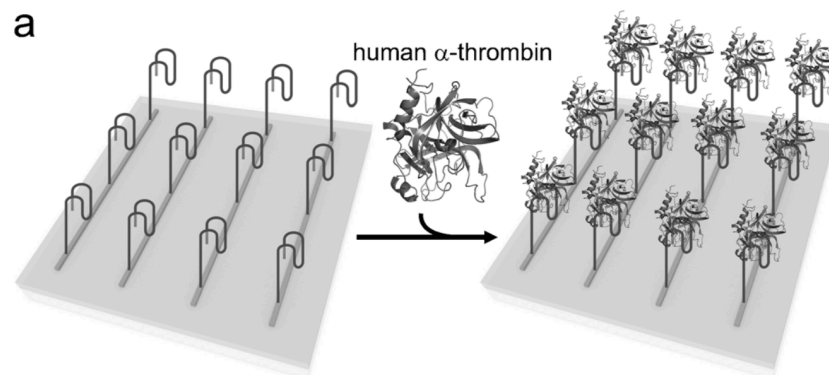
Silica nanowires for diffraction biosensing

in situ diffraction biosensing



DNA aptamer surface attachment chemistry

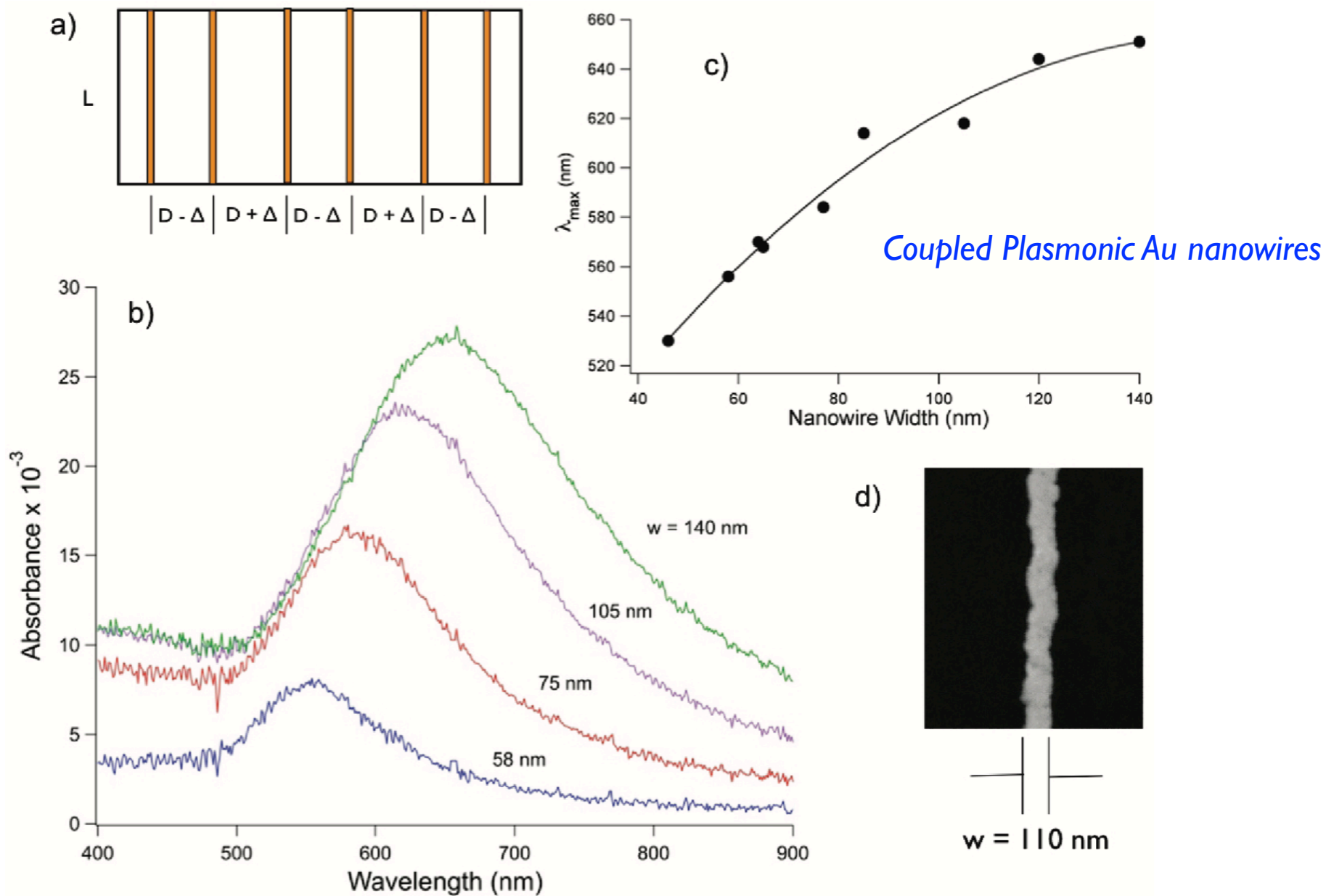
Aptamer-based human thrombin detection



$$K_{ads} = 8.2 \times 10^7 \text{ M}^{-1}$$



Plasmonic Gold Nanowire Gratings



Plasmonic Materials $\epsilon(\omega)$

$$n(\omega) = \eta(\omega) + i\kappa(\omega)$$

Dielectric Constant $\epsilon(\omega) = [n(\omega)]^2$

$$\epsilon(\omega) = n^2 = (\eta^2 - \kappa^2) + (2\eta\kappa)i$$

*Plasmonic materials have a
negative real dielectric constant*

@633 nm

$$n_{Au} = 0.183 + 3.433i$$
$$\epsilon_{Au} = -11.75 + 1.26i$$
$$Re(\epsilon) < 0$$

Au is a plasmonic material!

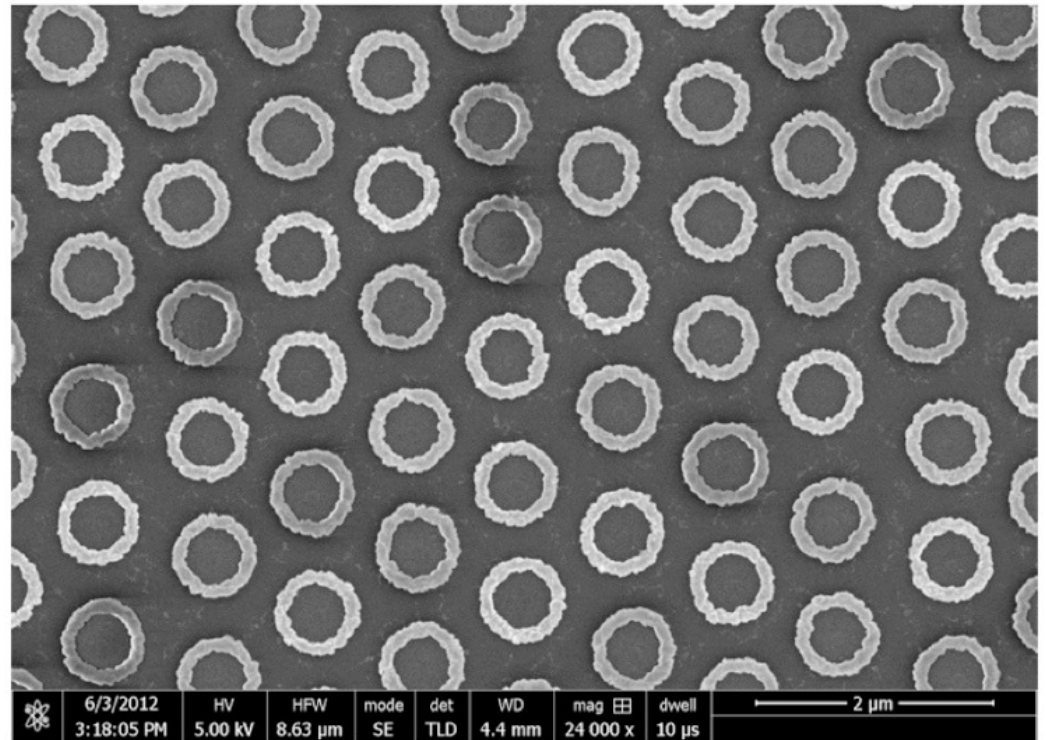


Nanostructured Mesoscale Optical Materials

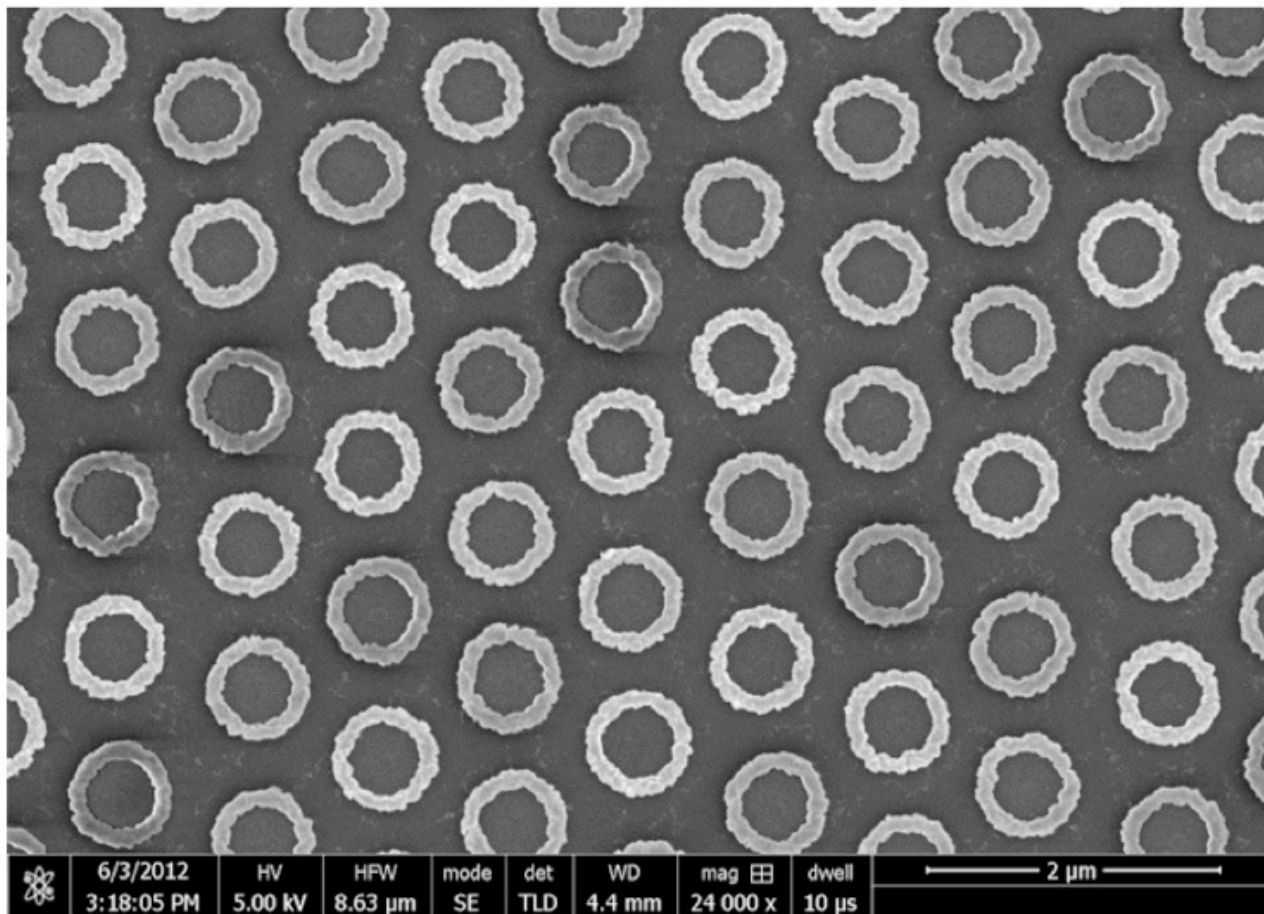
Rings



Nanorings



Electrodeposited Nanoring Arrays (Au, Ag, Ni, CdTe)



Colloidal Lithography & Lithographically Patterned Nanoscale Electrodeposition (LPNE)

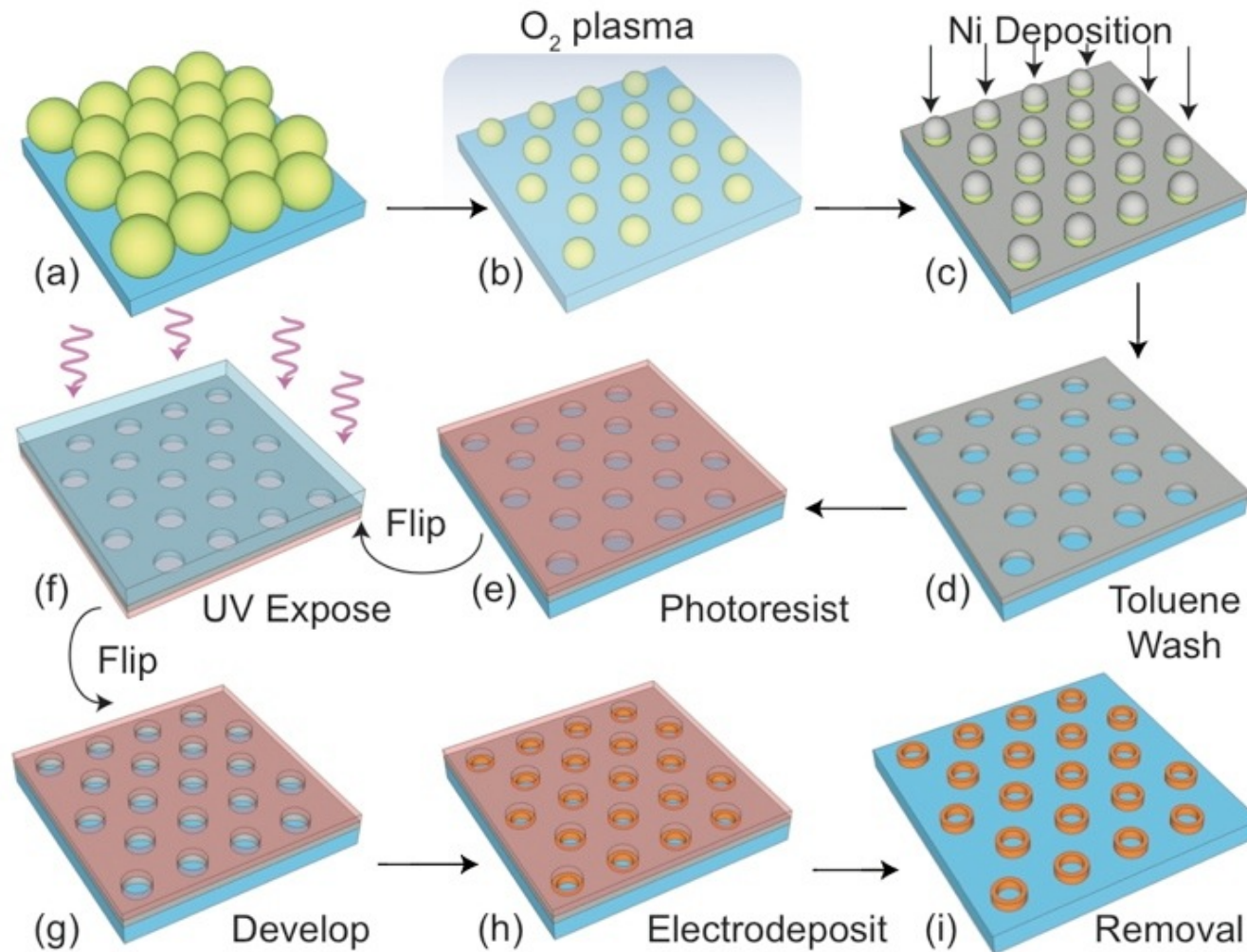
Dr. Aaron Halpern



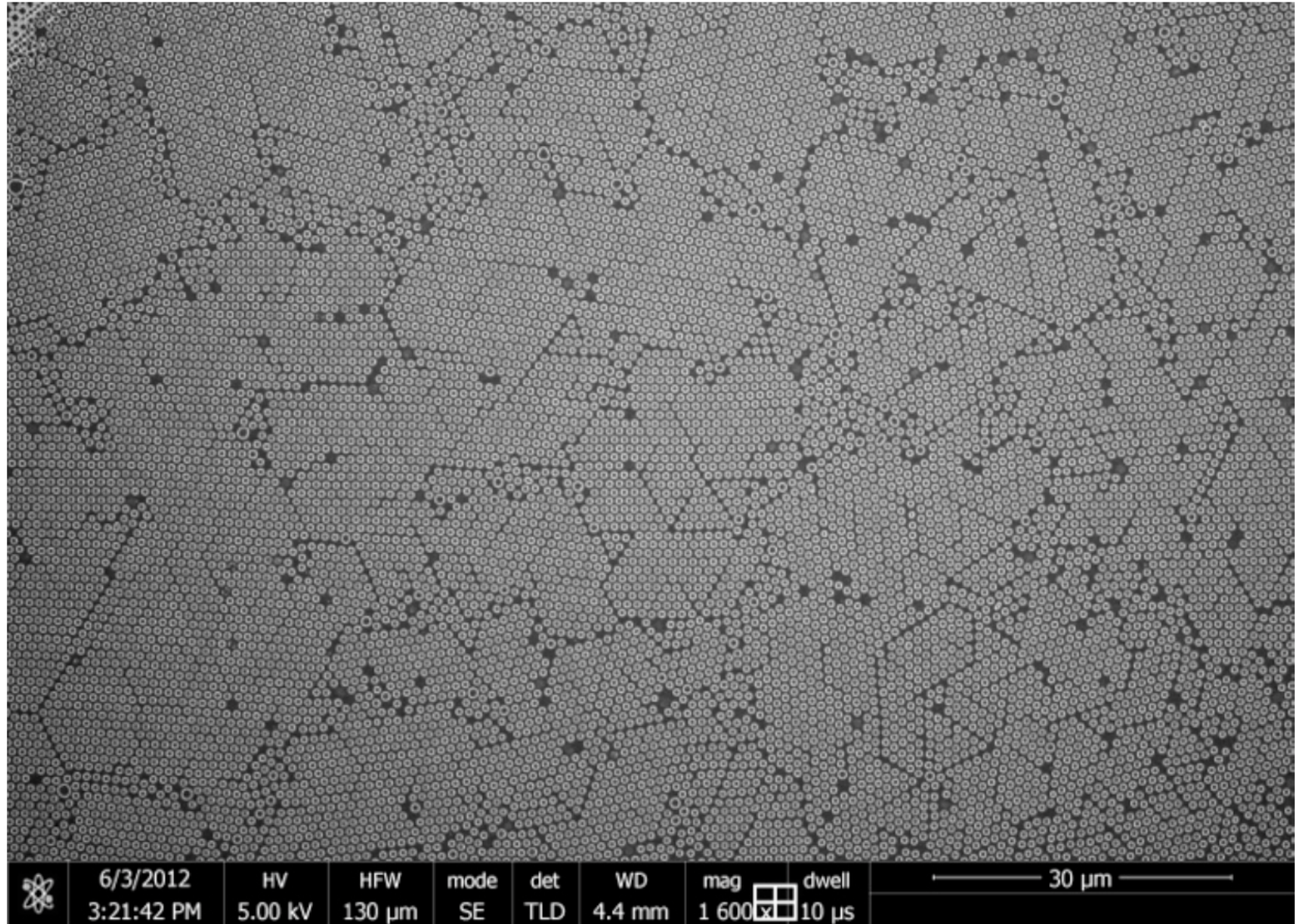
A. R. Halpern and R. M. Corn, *ACS Nano*, **7** 1755-1762 (2013).

Electrodeposited Nanoring Arrays

A Combination of Colloidal Lithography and Lithographically Patterned Nanoscale Electrodeposition (LPNE)



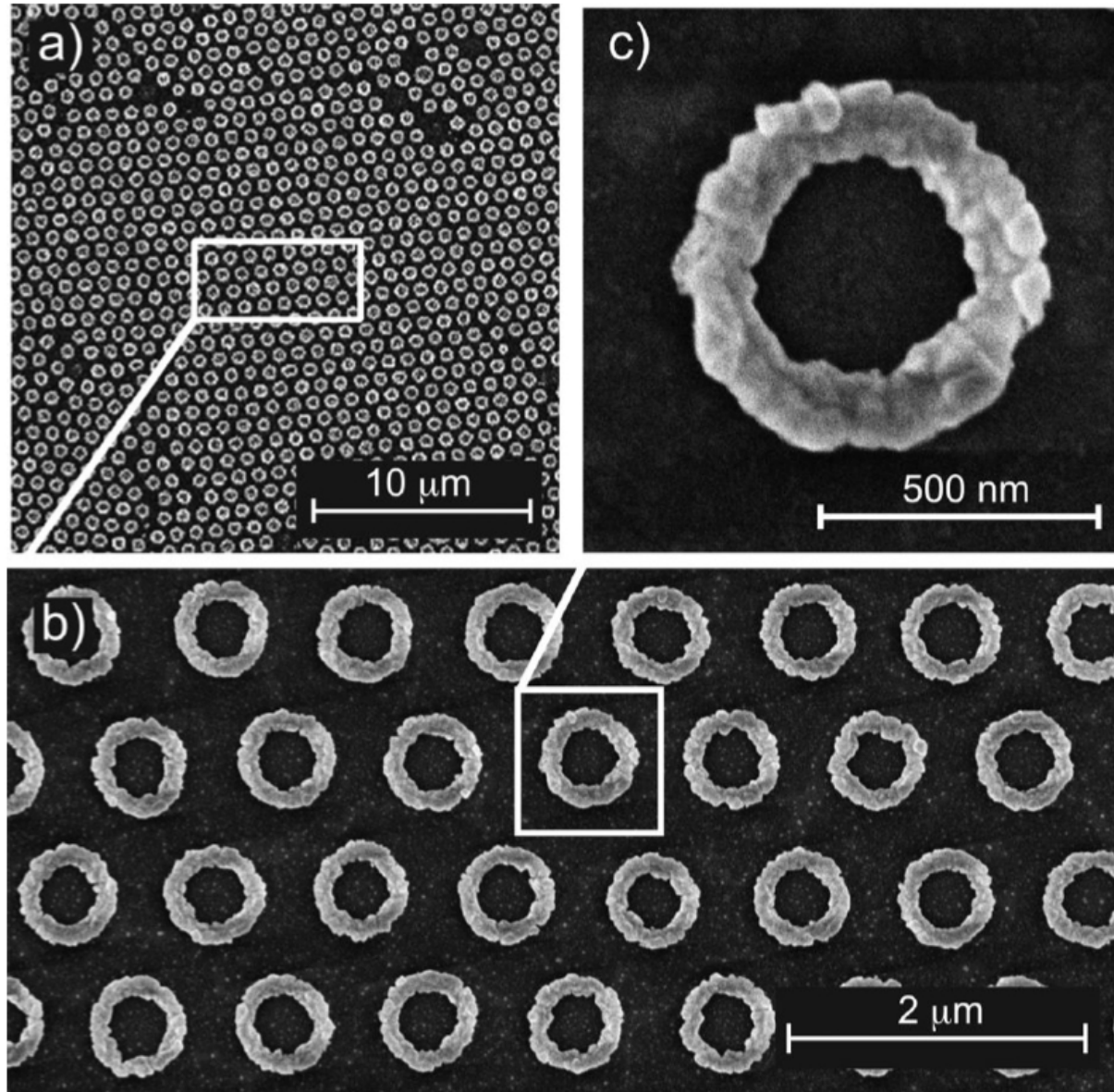
Electrodeposited Nanoring Arrays



Gold Nanoring Arrays

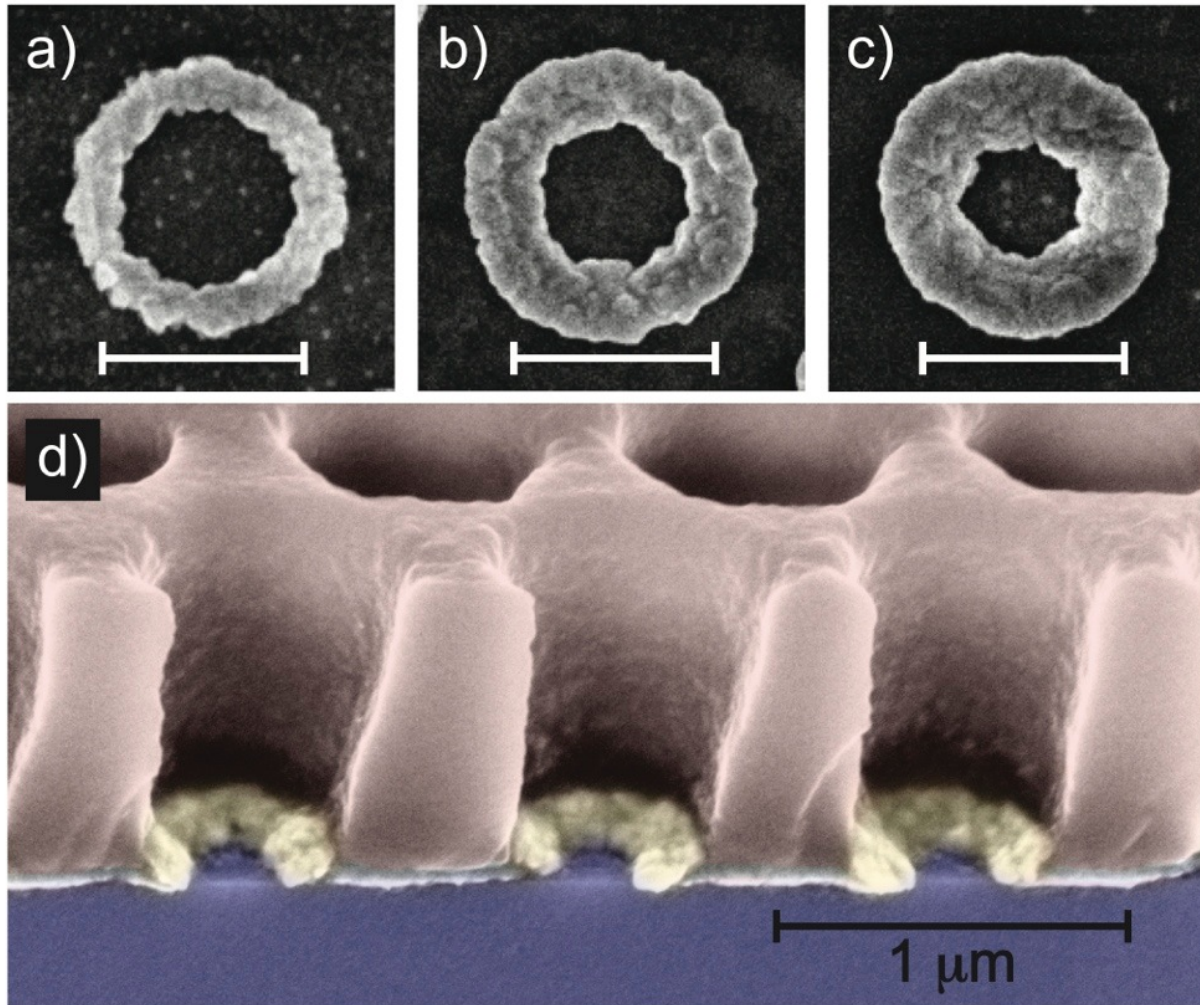


Electrodeposited Nanoring Arrays



Gold Nanoring Arrays

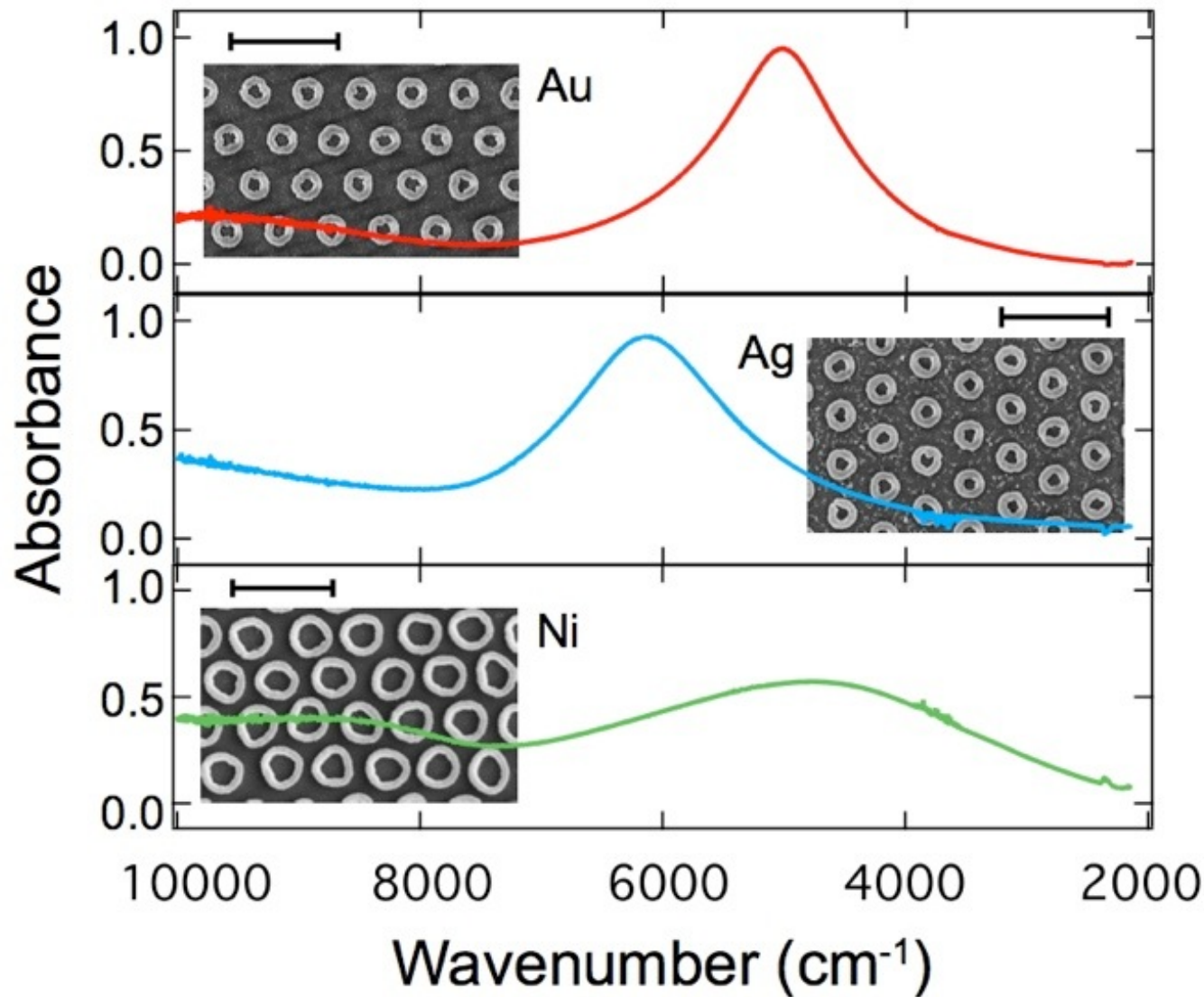
Electrodeposited Nanoring Arrays



*Electrodeposition
time controls ring
width*

Electrodeposited Nanoring Arrays

NIR: Near Infrared
(0.75 to 3 microns)

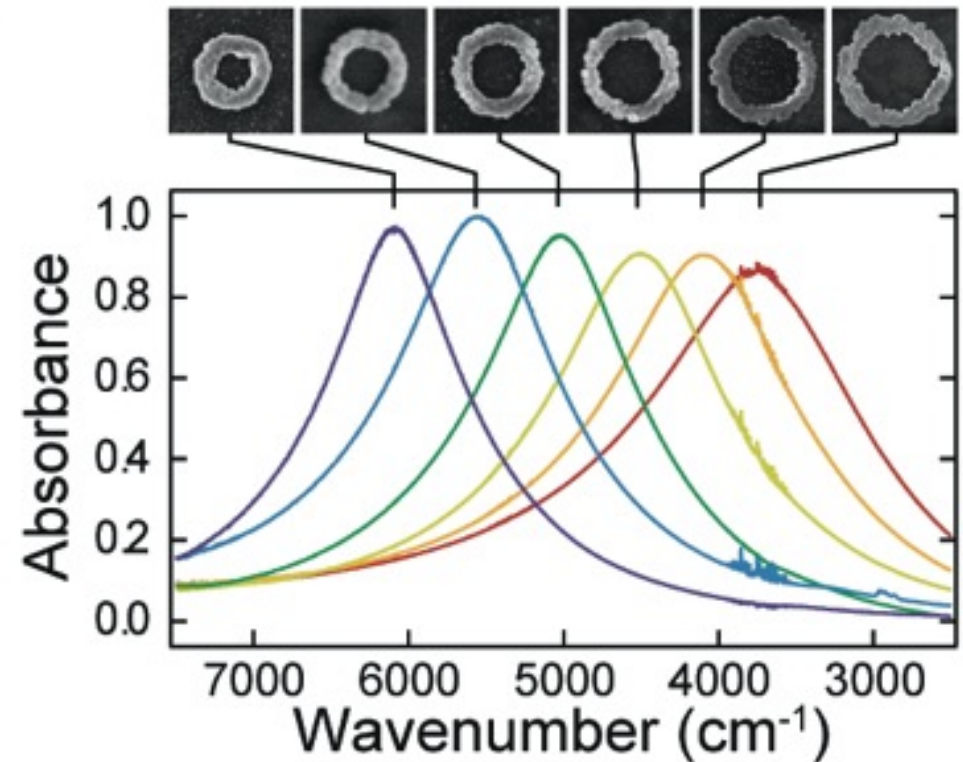
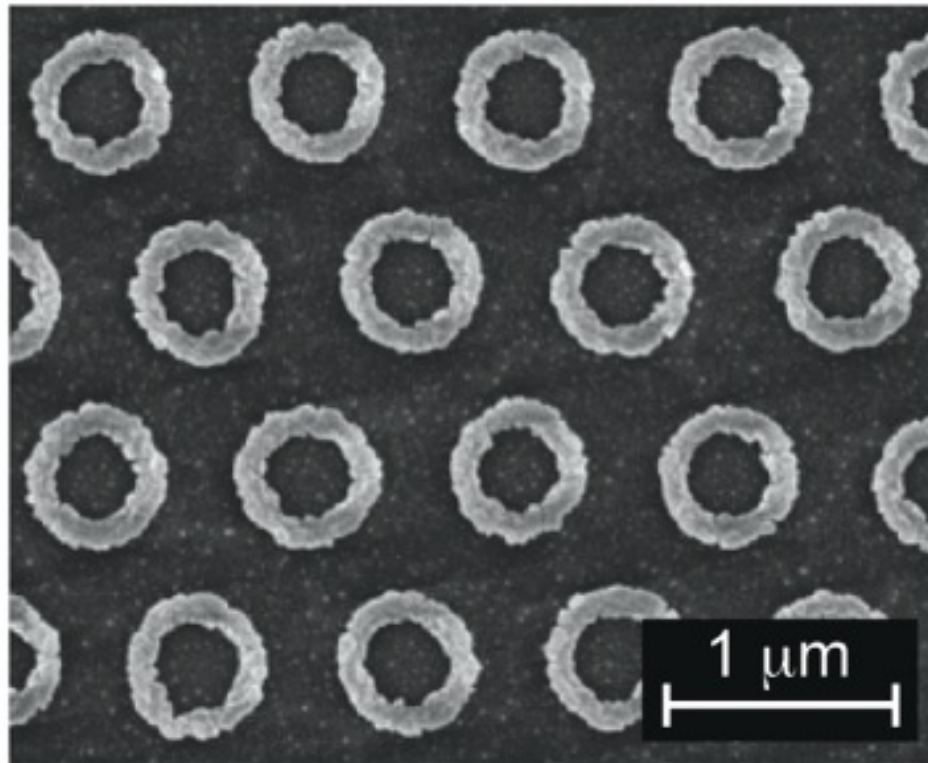


NIR Plasmonic
Resonances
for Gold (Au), Silver
(Ag) and Nickel
(Ni) Nanorings

5000 wavenumbers
corresponds to:
2 microns
2000 nanometers

A. R. Halpern and R. M. Corn, *ACS Nano*, **7** 1755-1762 (2013).

Electrodeposited Nanoring Arrays

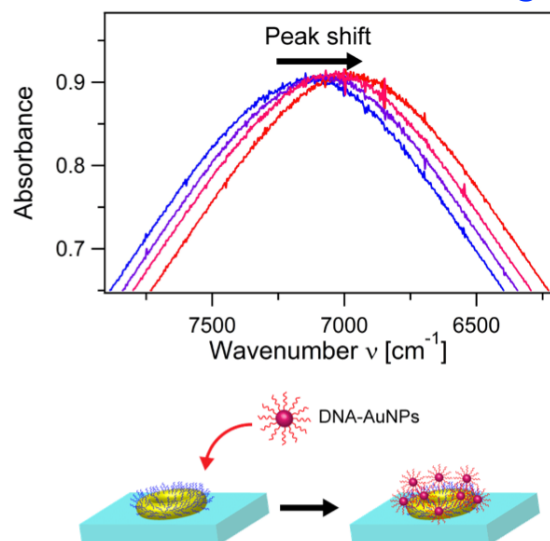


Gold Nanoring Arrays
Tunable NIR Plasmonic Resonance (1 to 3 microns)
A combination of SPR and LSPR

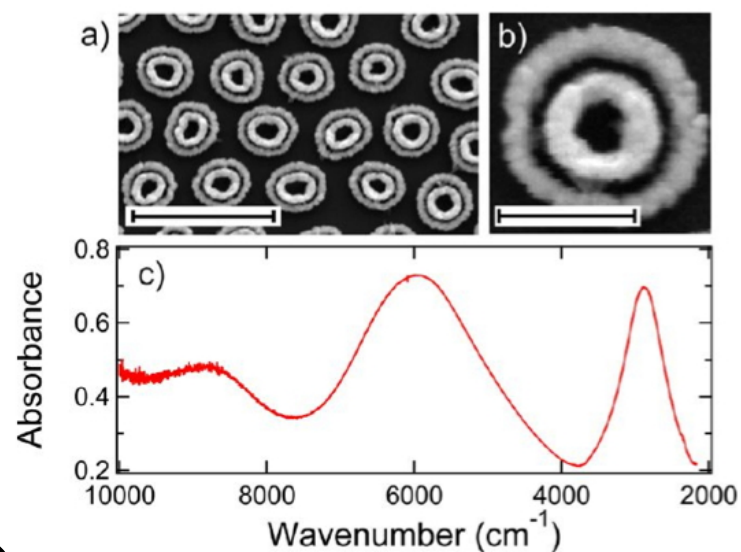
A. R. Halpern and R. M. Corn, *ACS Nano*, **7** 1755-1762 (2013).

Application and Extensions of Nanoring Arrays

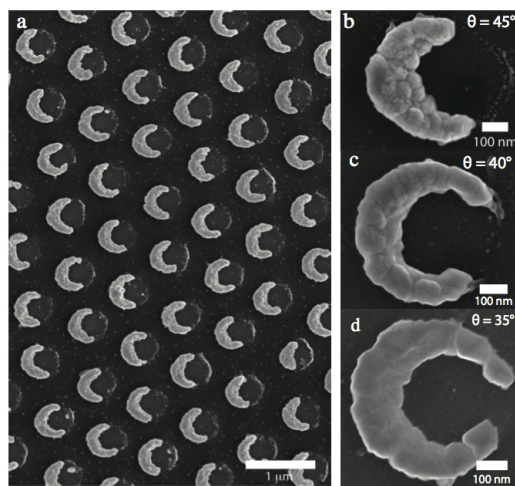
NIR LSPR Biosensing



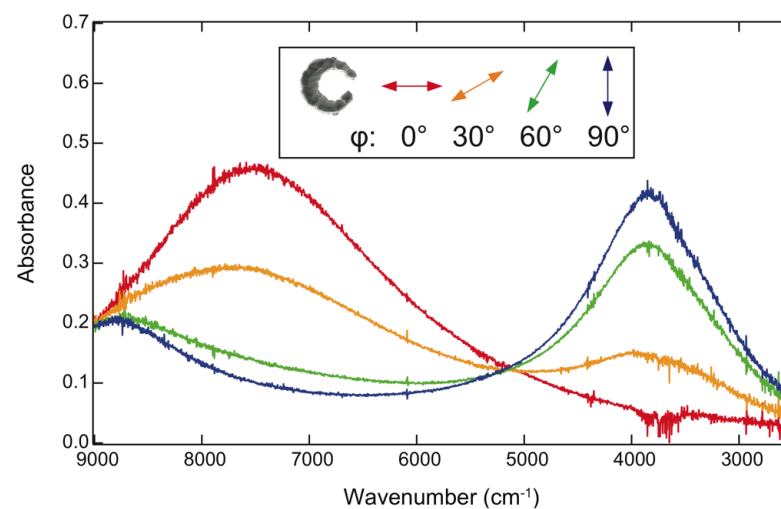
Double Nanoring Arrays



Split Nanoring Arrays



Dichroic Filters



It Takes a World of Help: Great Group Members and Collaborators!

Postdoctoral Scientists and Visitors



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Gabriel Loget 🇫🇷



Seulgi So 🇰🇷 🇩🇪



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 Yufei Cheng 🇨🇳 🇸🇰
 WenJuan Zhou 🇨🇳 🇫🇷



Grad Students

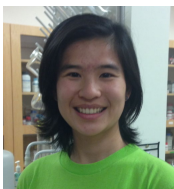
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 Brandon Matthews
 Kellen Kartub
 Adam Maley
 Millie Fung
 Gerald Manuel
 Mike Cho
 Jennifer Fasoli
 Aaron Halpern
 Megan Szyndler
 Nico Hu
 Yulin Chen
 Yuan Li

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 Prof. Yoshiko Miura (Kyushu)
 Prof. Lasse Murtomaki (Aalto)
 Prof. Andrej Luptak (UCI)
 Prof. Reg Penner (UCI)
 Prof. Ken Shea (UCI)
 Prof. Donghyun Kim (Yonsei)

Funding: NIH
 NSF

WenJuan Zhou



A quick note on Surface Plasmon Polaritons and SPR vs. LSPR

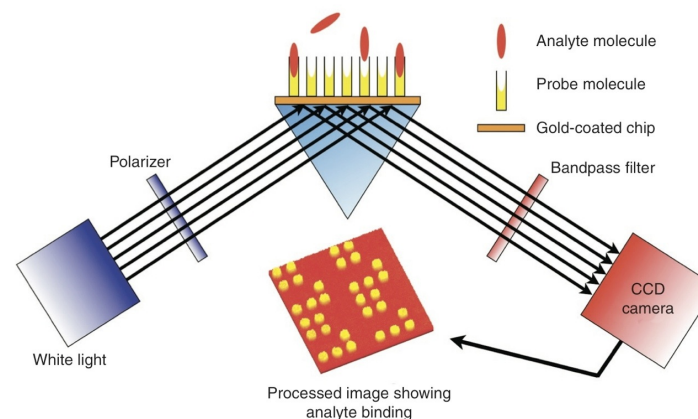
Surface plasmon polaritons (SPPs) are propagating electromagnetic waves that can be created on a planar gold thin films (45 nm).

- SPPs are solutions to Maxwell's equations and can be created at all wavelengths above the SP cutoff wavelength (540 nm for gold).

Localized SPR (LSPR) is the excitation of a standing SPP wave on a gold nanoparticle.

- LSPR Resonances occur at specific wavelengths as determined by the shape, size and dielectric constant of the material from Mie theory.

The mesoscale nanoring array surfaces have coupled plasmonic resonances that are a combination of LSPR and SPPs.

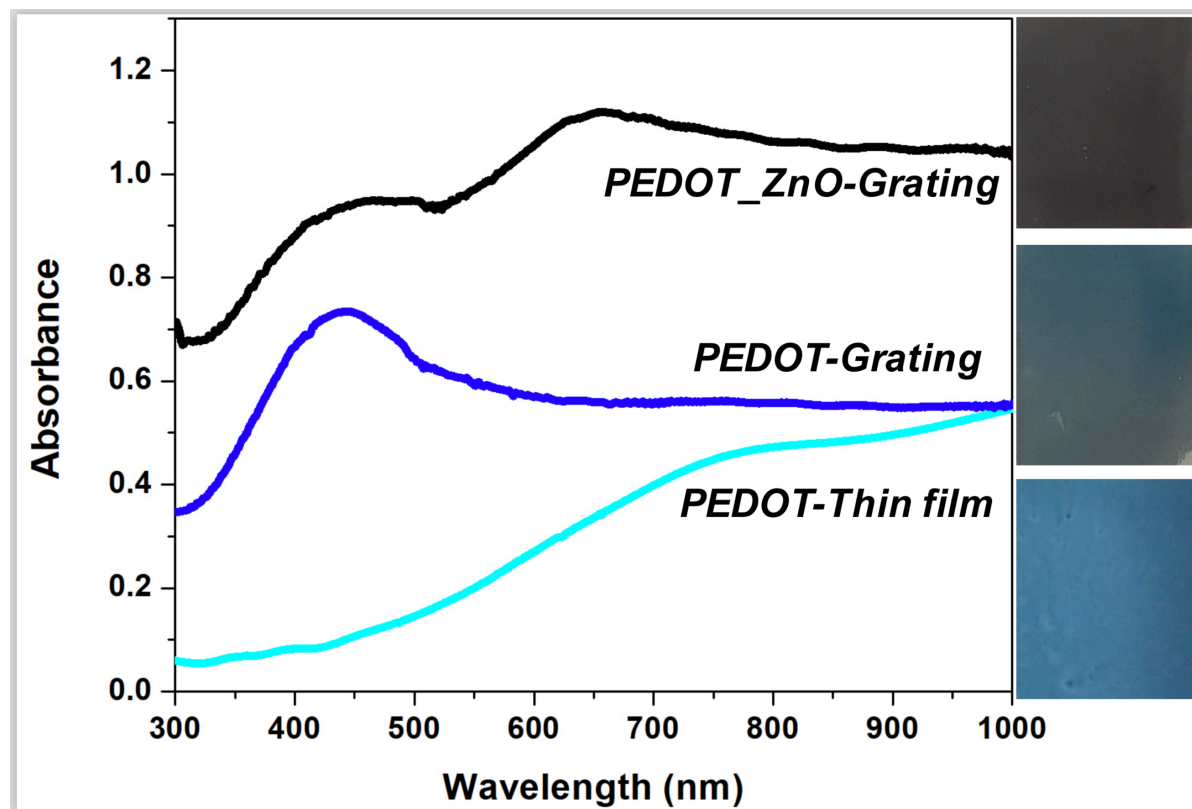


SPR Imaging uses SPPs

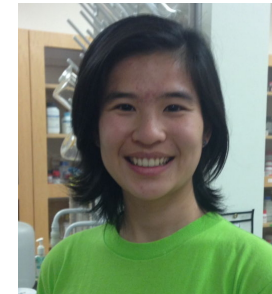


Electrochromic and Electrodiffraction Composite Gratings

ZnO also enhances the optical absorption spectra of WO_3 or PEDOT



Normal Incidence Transmission Spectrum



Millie



Kellen



Seulgi

