In-Situ TEM of Electropolymerization: Direct Monitoring of Liquid-Solid Transitions

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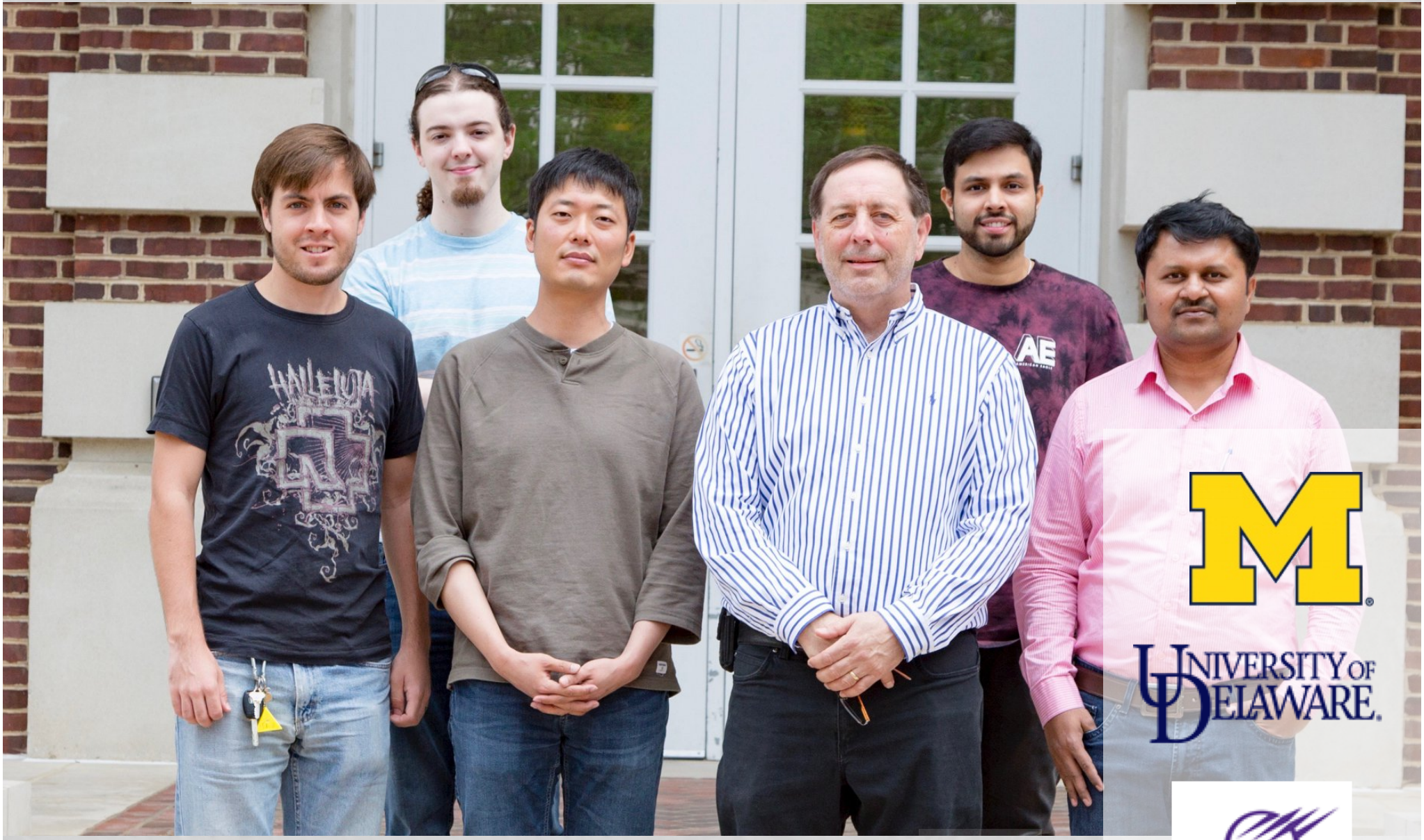
UD-UC-UM IUCRC Planning Meeting May 14th, 2020

Organic Electronics and Electroactive Biomaterials



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MRS Communications

Polymers/Soft Matter Prospective Article

Molecular design, synthesis, and characterization of conjugated polymers for interfacing electronic biomedical devices with living tissue

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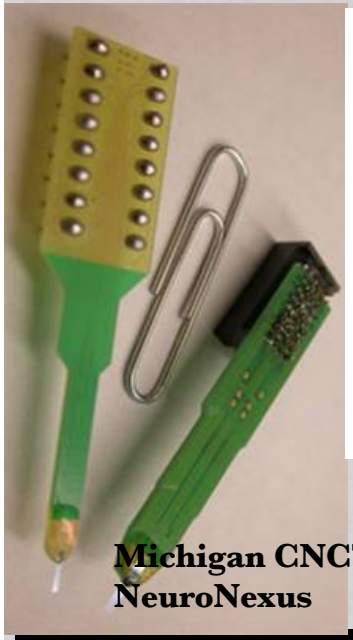
Abstract

Conjugated polymers are being considered for use at the interface between hard inorganic metallic and semiconducting electrodes and soft biological tissues. These organic materials have properties that are intermediate to these two extremes, and their chemistry, structure, and performance can be precisely manipulated over a large range. Examples of current interest included copolymers of poly(3,4-ethylene dioxythiophene) and poly(3,4-propylene dioxythiophene). This paper will review past efforts, recent activities, and future possibilities in this rapidly expanding area of materials research and technology.

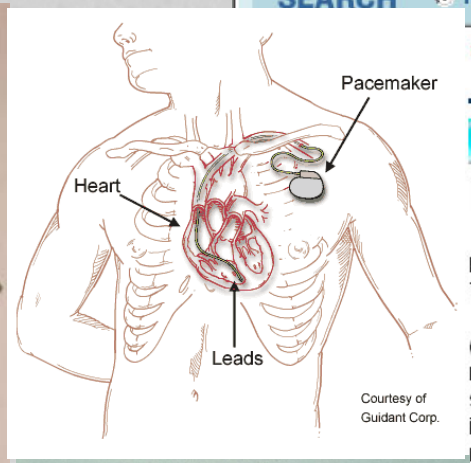
MRS Communications, 5(2), 131-153, (2015).
http://dx.doi.org/10.1557/mrc.2015.17

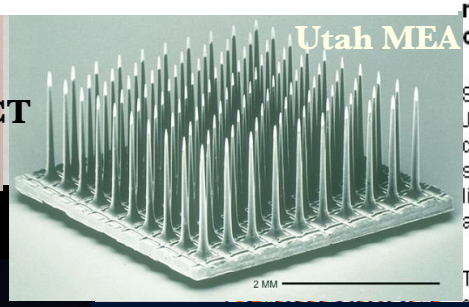
Mag = 2.67 K X 1 µm WD = 4.9 mm EHT = 5.00 kV Signal A = InLens ESB Grid = 500 V Date :20 Oct 2011 Time :16:36:18
Auriga 60-39-95 FIB Imaging = SEM Noise Reduction = Line Int. Done FIB Probe = 30KV:50pA System Vacuum = 1.38e-006 mbar

Bionic devices: solid electronic wire – wet ionic tissue interfaces



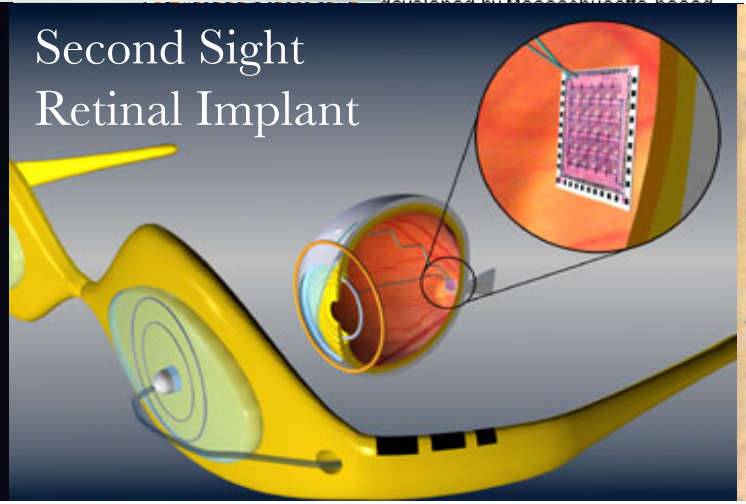
Michigan CNCT
NeuroNexus





Utah MEA

CyberKinetics



Second Sight
Retinal Implant

CNN.com

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TECHNOLOGY

EXPLORERS SPECIAL REPORT

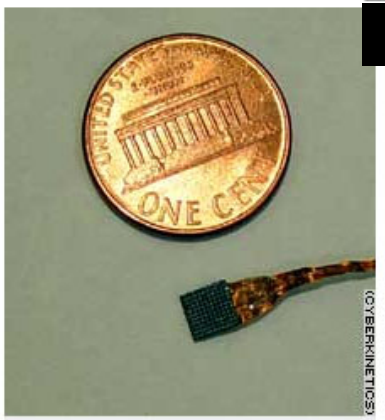
Brain chip offers hope for paralyzed

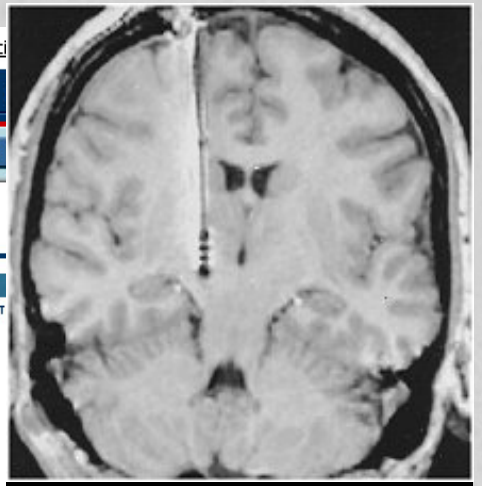
By Simon Hooper for CNN
Thursday, October 21, 2004 Posted: 5:48 AM EDT (0948 GMT)

(CNN) -- A team of neuroscientists have successfully implanted a chip into the brain of a quadriplegic man, allowing him to control a computer.

Since the insertion of the tiny device in June, the 25-year-old has been able to check email and play computer games simply using thoughts. He can also turn lights on and off and control a television, all while talking and moving his head.

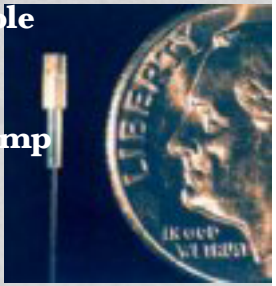
The chip, called BrainGate, is being

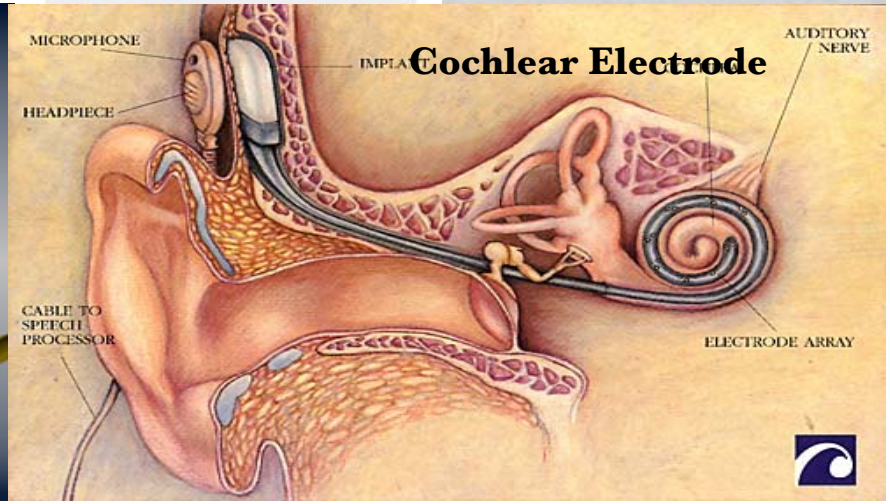




DBS electrode

Implantable glucose sensor + insulin pump

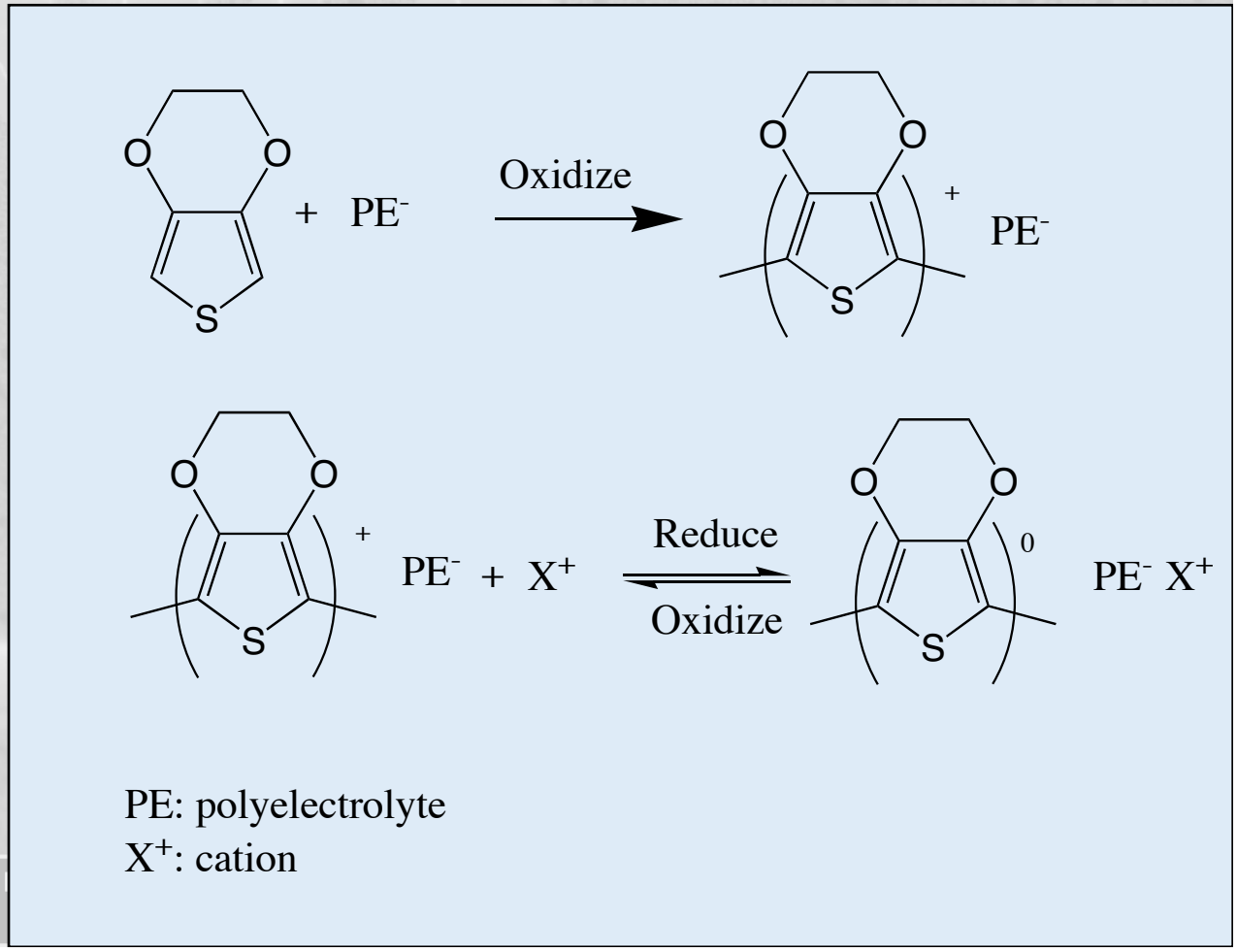




Cochlear Electrode

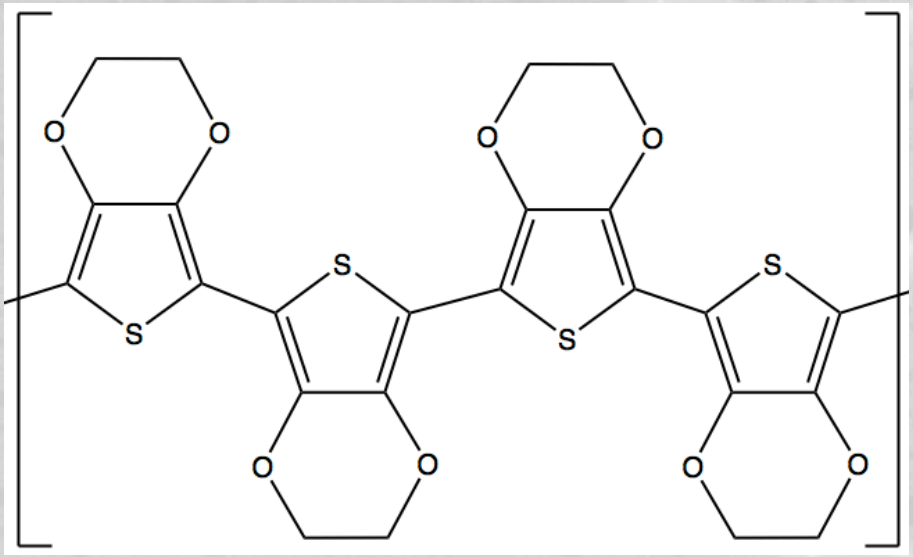
Electrochemical Polymerization of Conjugated Polymers: PEDOT

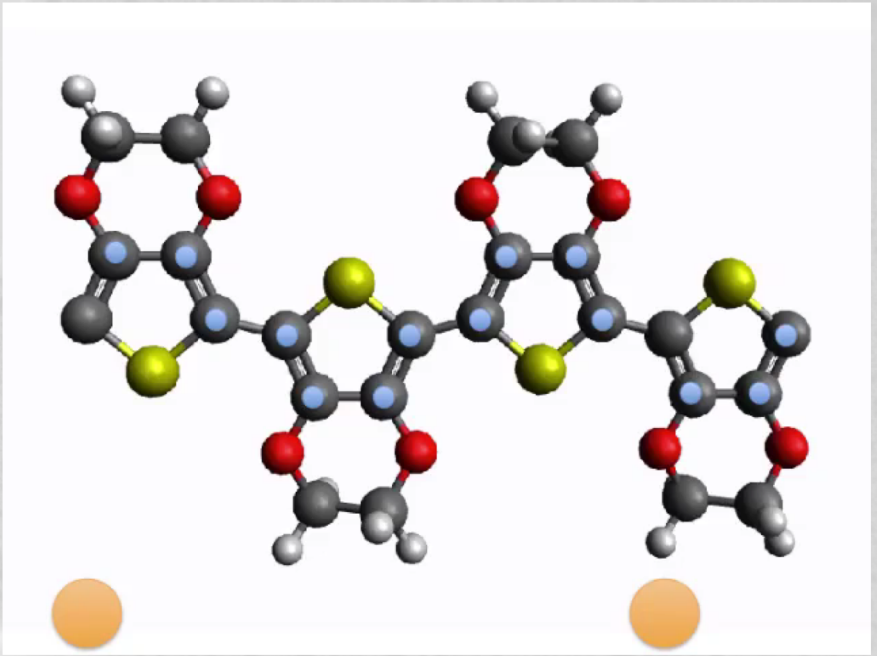
- Controlled deposition directly onto electrode from aqueous solution (~1 V)
- Ability to use biologically active molecules as counterions
- Creates rough, soft surface that facilitates charge transport, promotes favorable biological interactions
- EDOT monomer, chemically oxidized PEDOT/PSS suspension available commercially
- Much more chemically stable than PPy: only 2 reactive hydrogens on conjugated ring



Mag = 2.67 K X 1 µm WD = 4.9 mm
Auriga 60-39-95 FIB Imaging = SEM

PEDOT Molecular Design Features





Conjugated backbone: electrical and optical activity
Only 2 reactive hydrogens on EDOT monomer: no branching defects
No hydrogens directly on PEDOT polymer backbone: chemical stability
Oxygens pendant to the backbone: enhanced electron density

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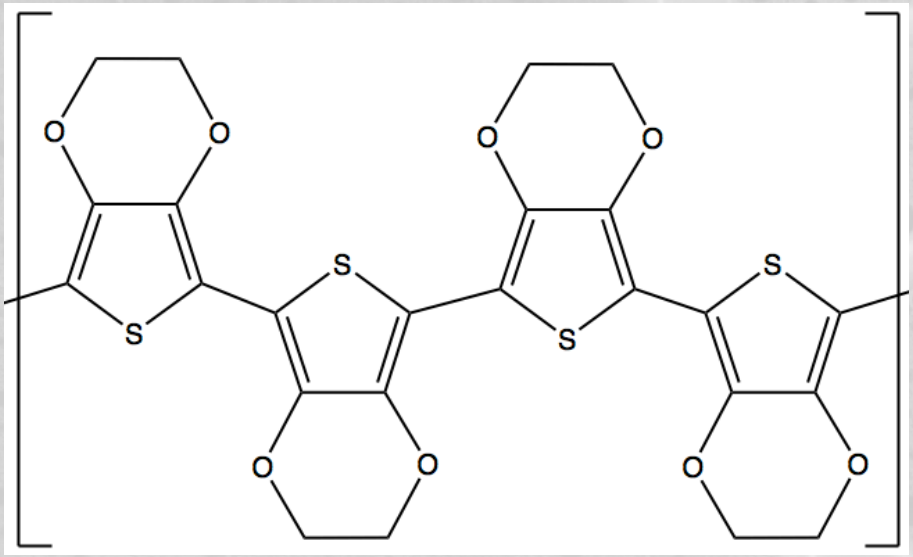
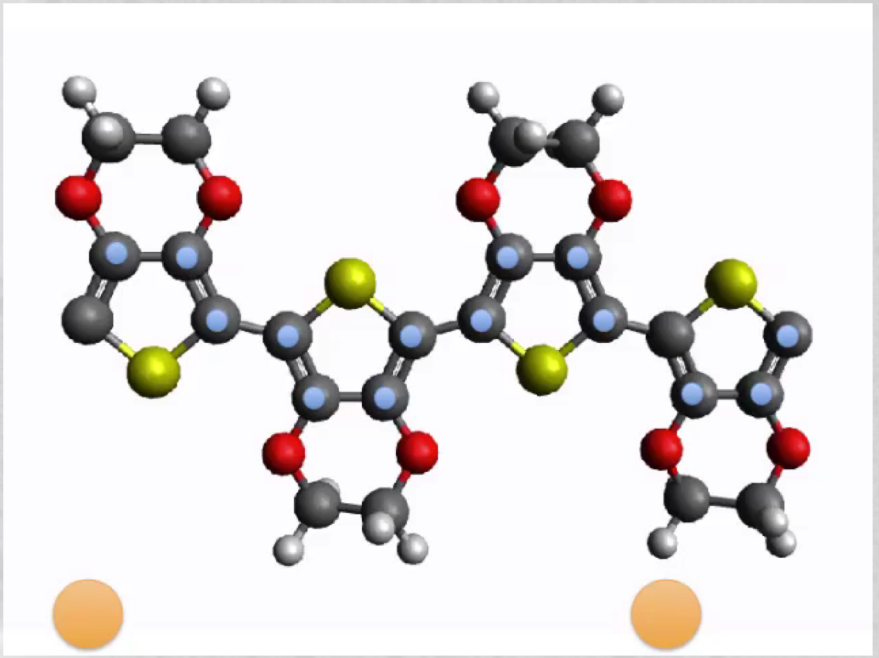
Molecular Wires





Conjugated polymers facilitate electron/hole transport along the backbone, as well as anion and cation transport via charge exchange with dopants

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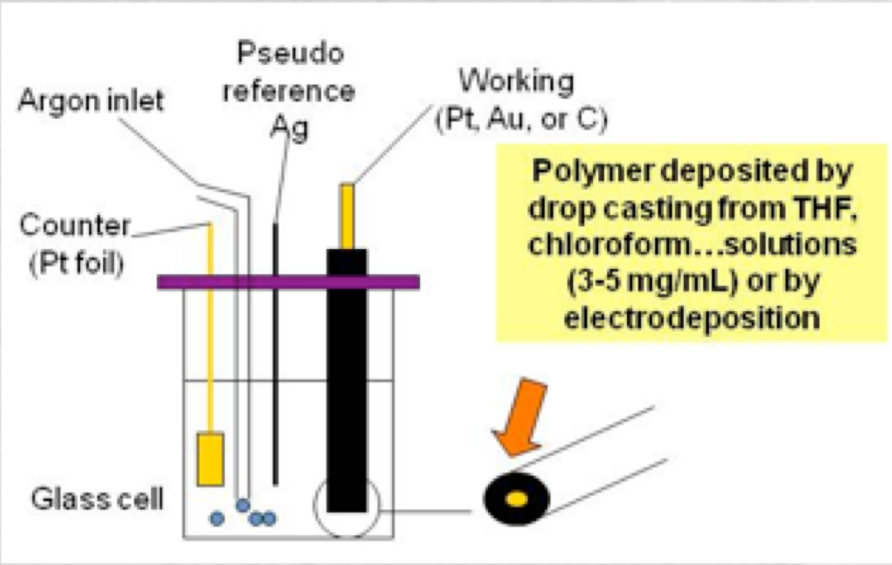
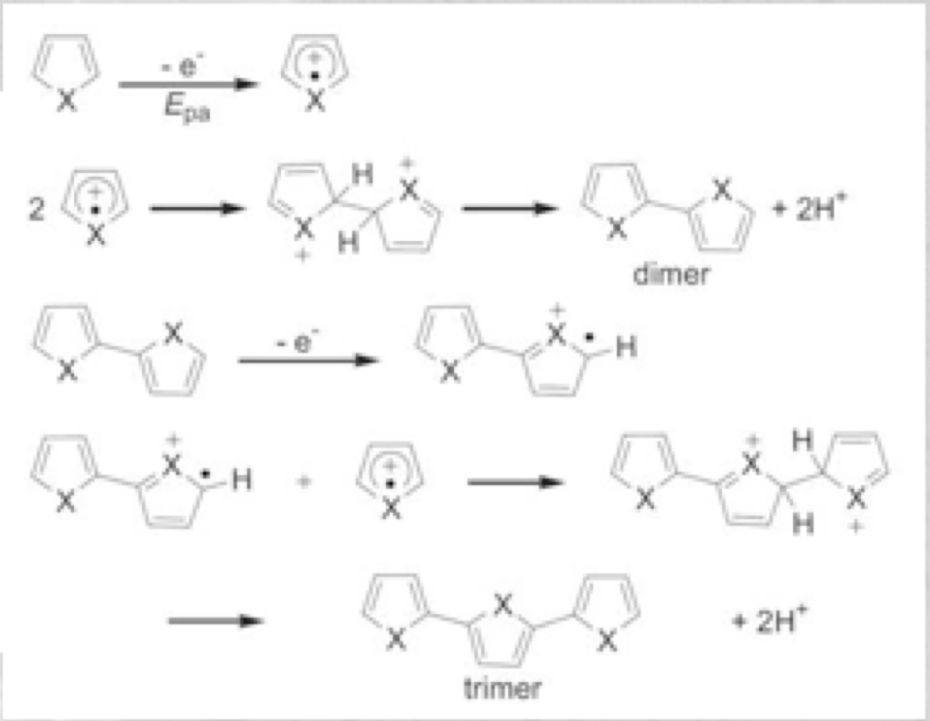
Electrochemical Polymerization





https://ww2.chemistry.gatech.edu/reynolds/research/electrochemistry

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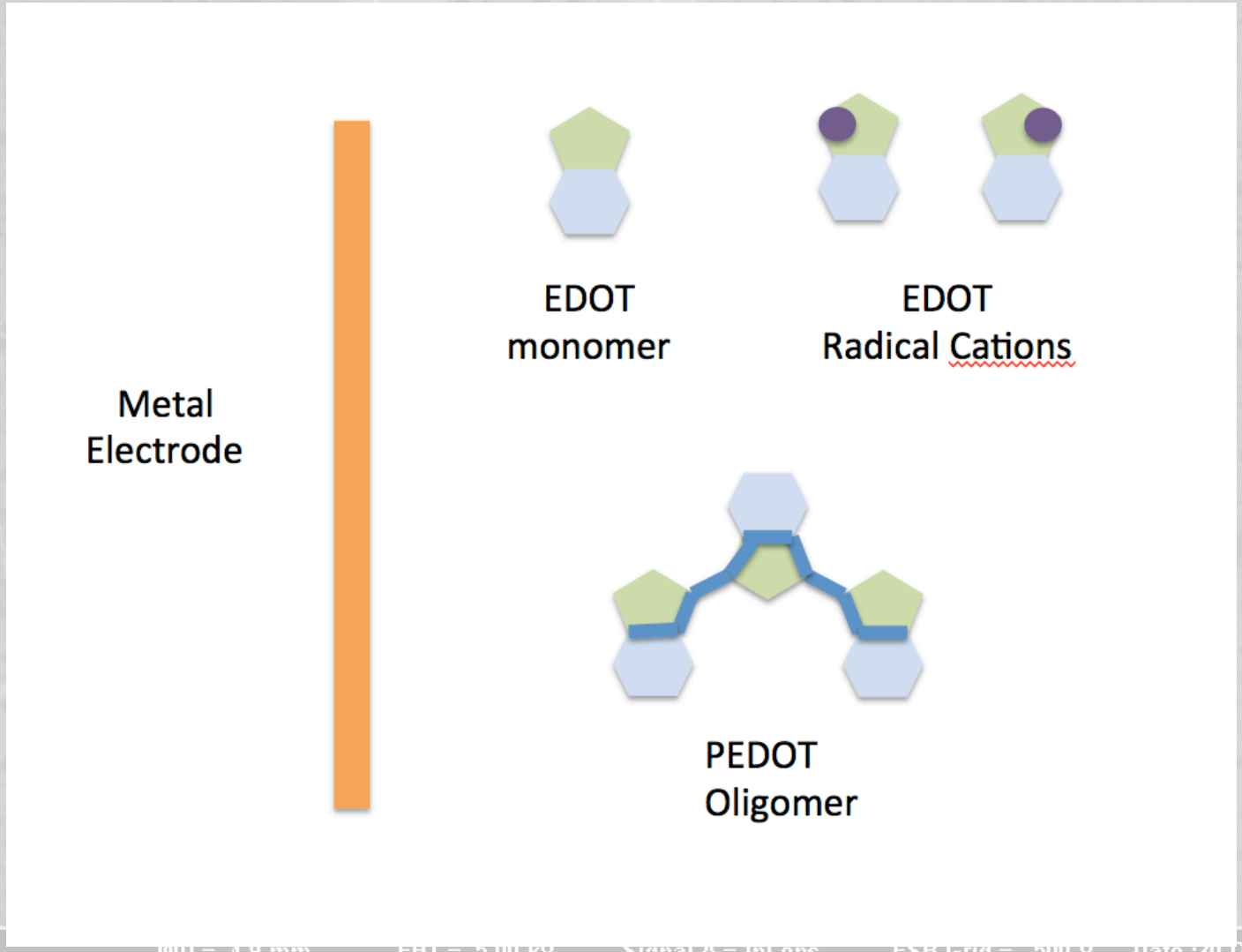
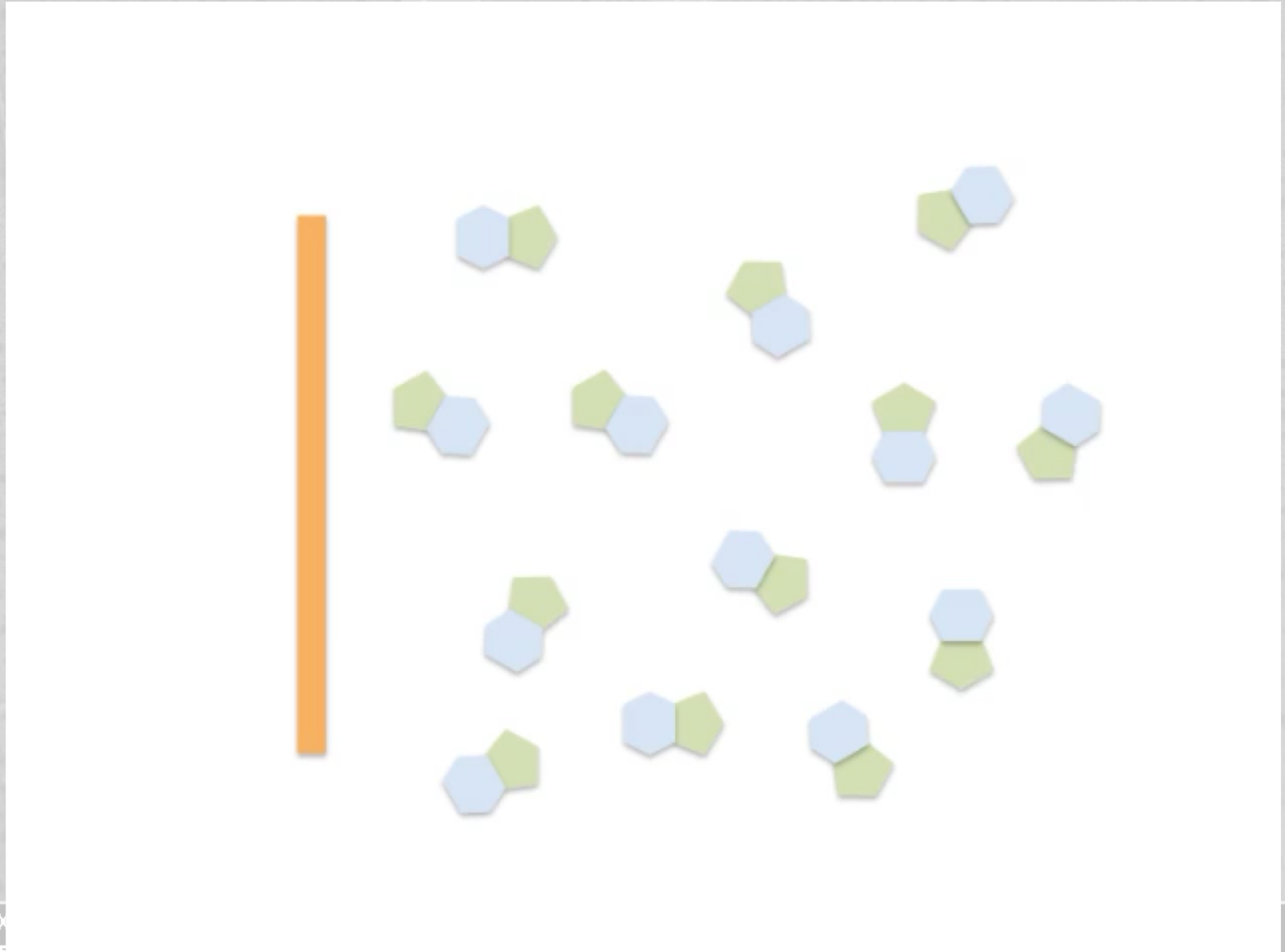
Auriga 60-39-95 FIB Imaging = SEM Noise Reduction = Line Int. Done FIB Probe = 30KV:50pA System Vacuum = 1.38e-006 mbar

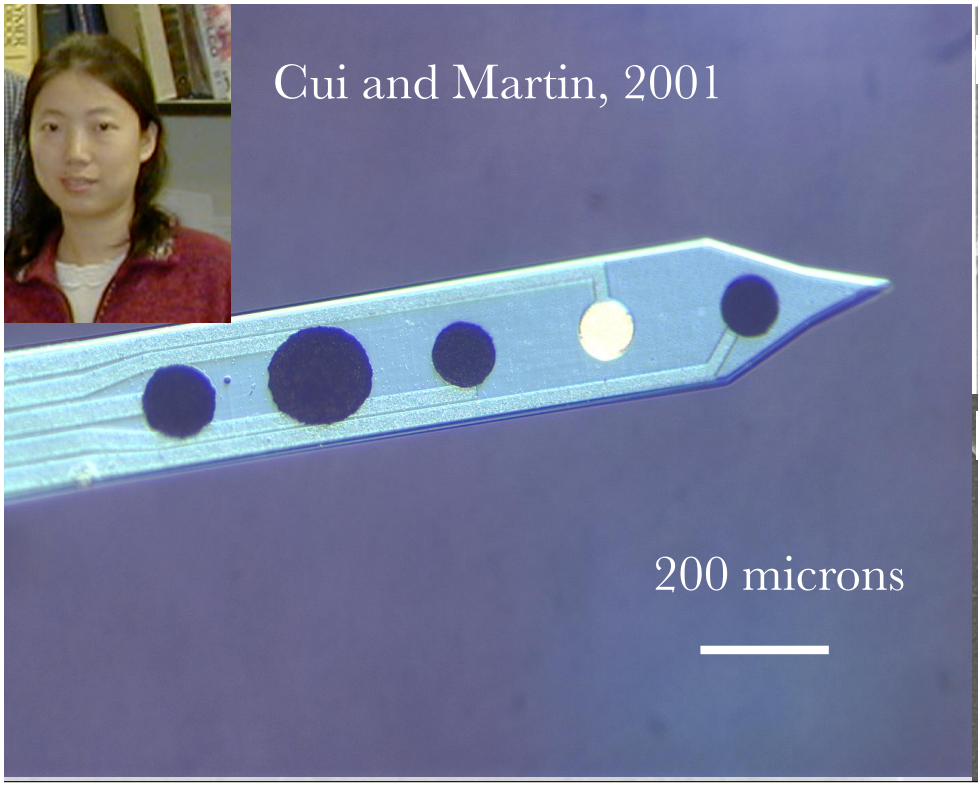
Electrochemical Polymerization of Conjugated Polymers: PEDOT

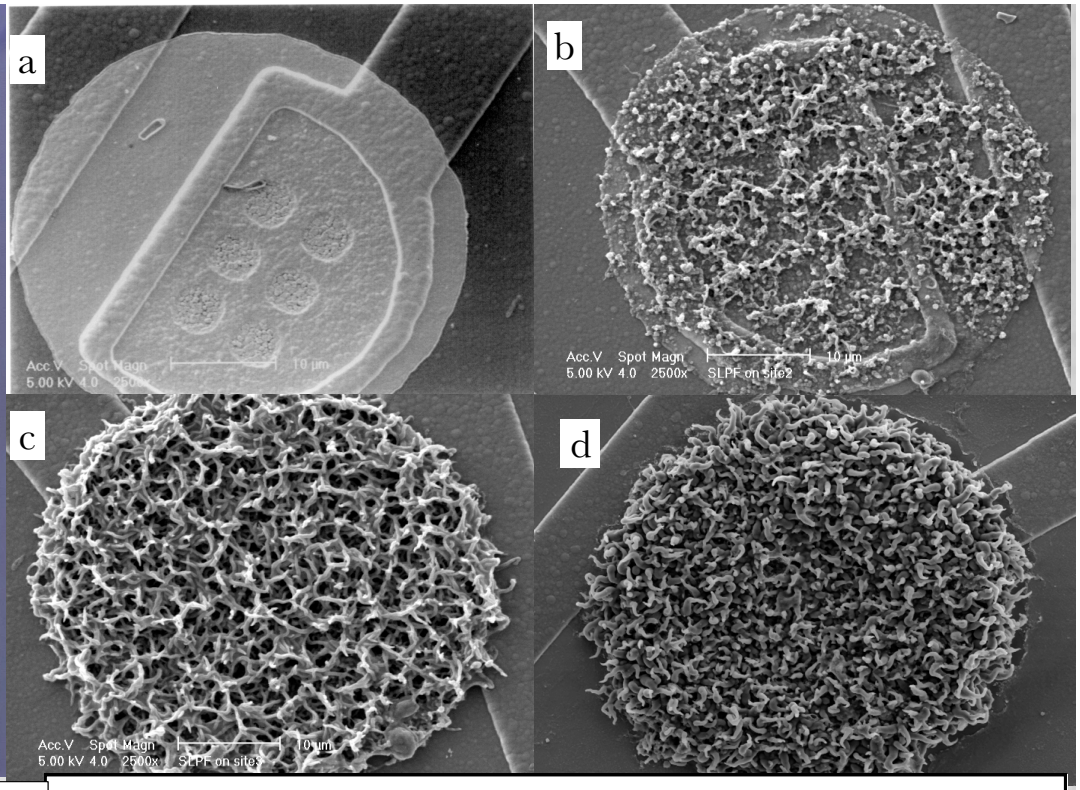


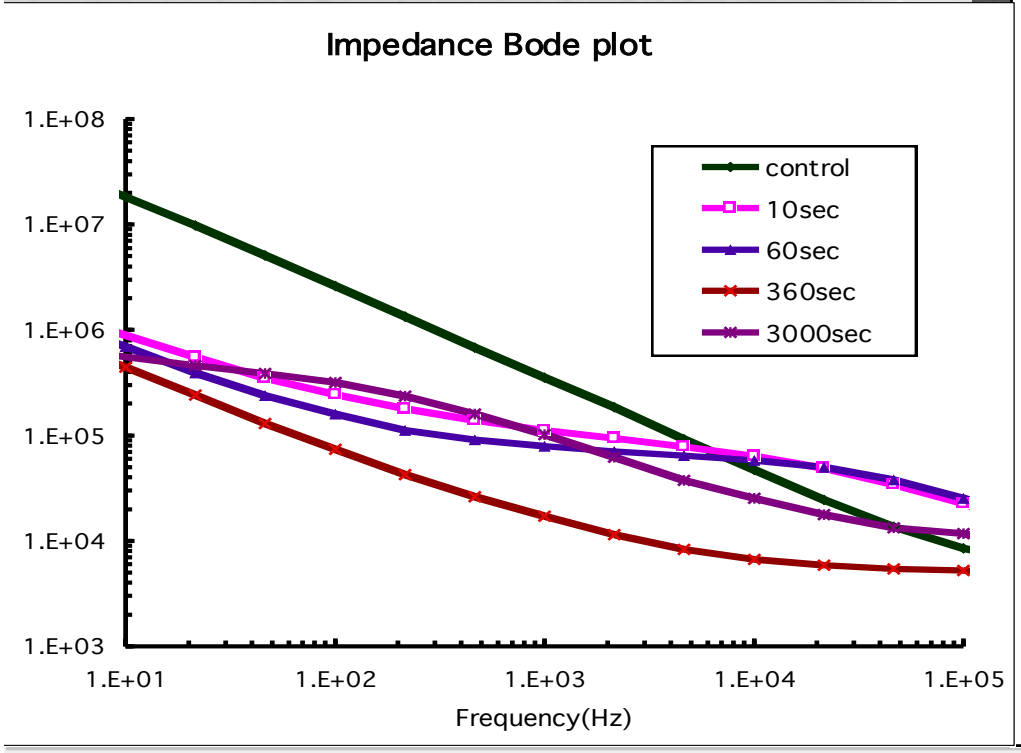
Mag = 2.67 K X 1 µm
Auriga 60-39-95
WD = 4.9 mm
FIB Imaging = SEM
EHT = 5.00 kV
Noise Reduction = Line Int. Done
Signal A = InLens
FIB Probe = 30KV:50pA
ESB Grid = 500 V
Date :20 Oct 2011 Time :16:36:18
System Vacuum = 1.38e-006 mbar

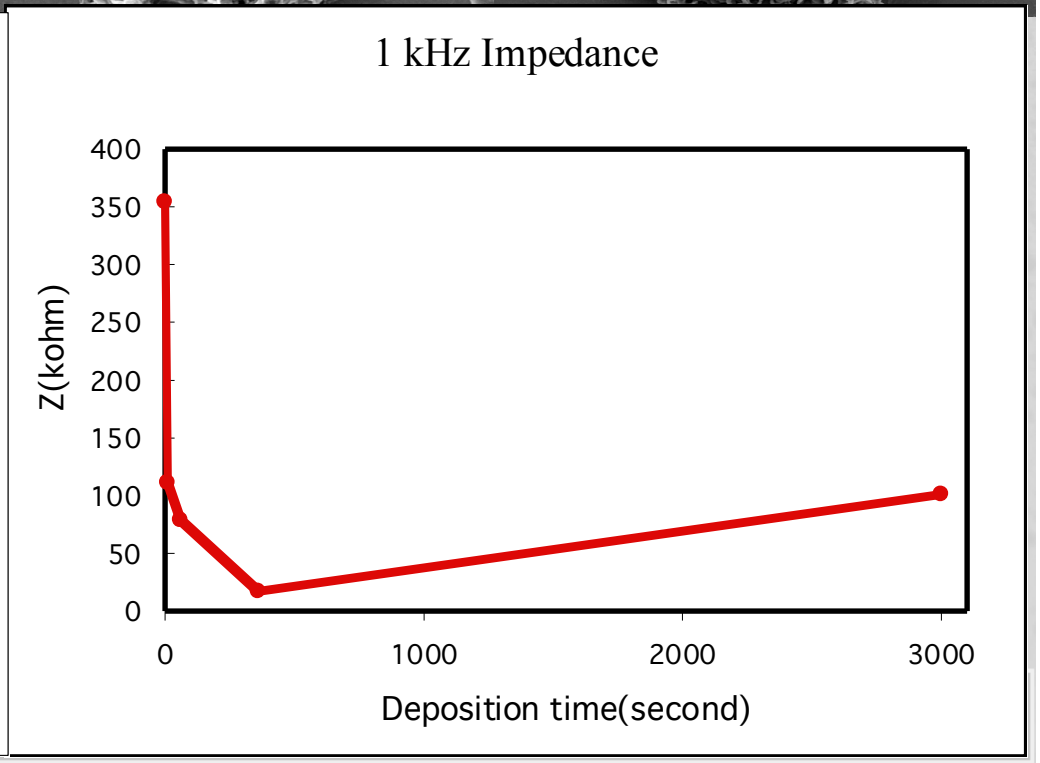
Electrochemical Polymerization of Conjugated Polymers: PEDOT

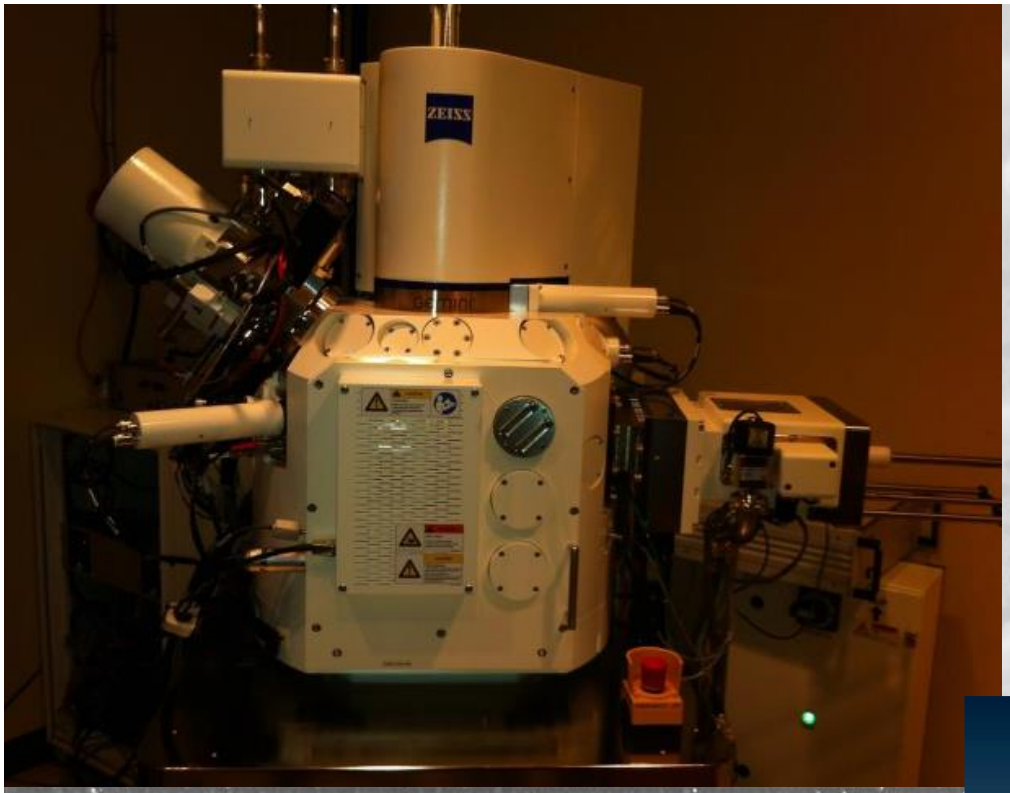



Cui and Martin, 2001
200 microns


a
b
c
d

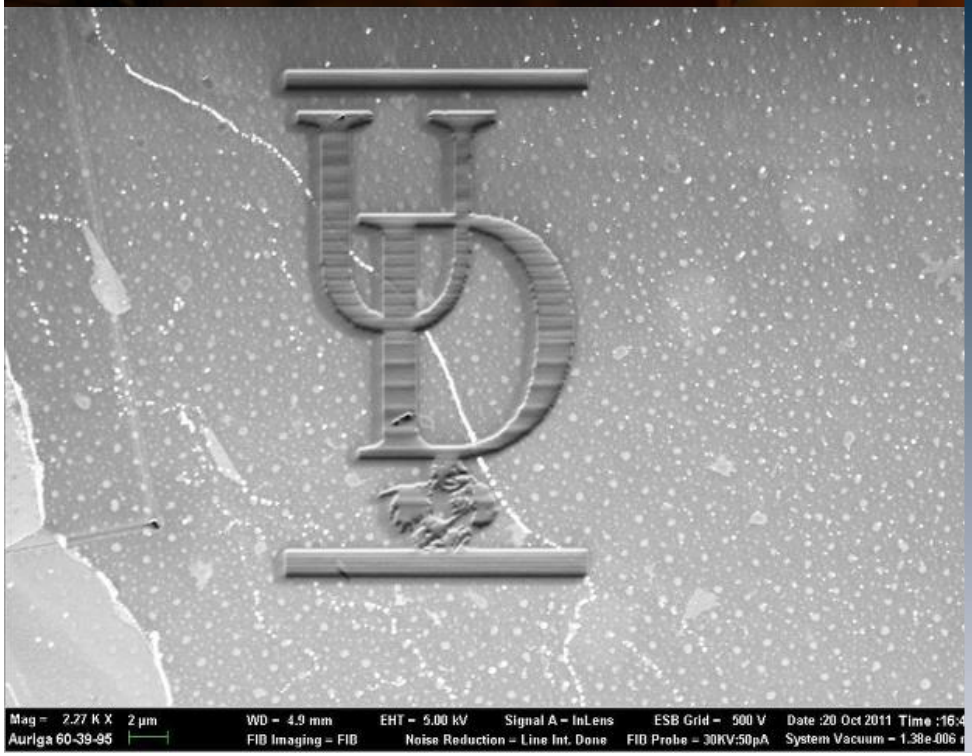

Impedance Bode plot
1.E+08
1.E+07
1.E+06
1.E+05
1.E+04
1.E+03
1.E+01
1.E+02
1.E+03
1.E+04
1.E+05
Frequency(Hz)
control
10sec
60sec
360sec
3000sec

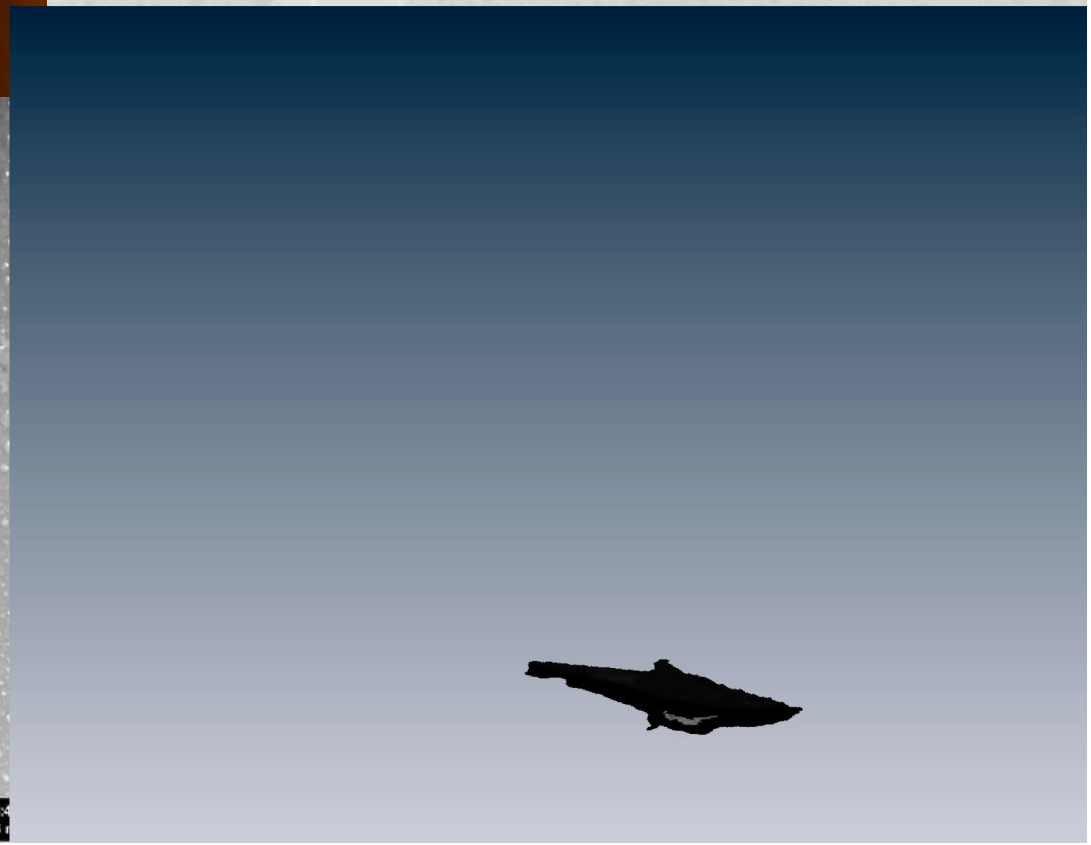

1 kHz Impedance
400
350
300
250
200
150
100
50
0
Z(kohm)
0
1000
2000
3000
Deposition time(second)



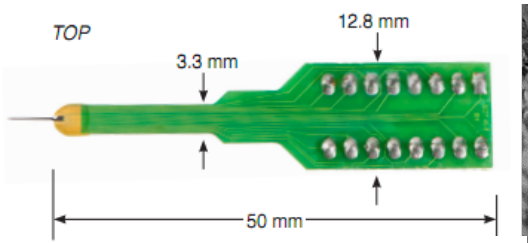
Zeiss Auriga 60 FIB/SEM

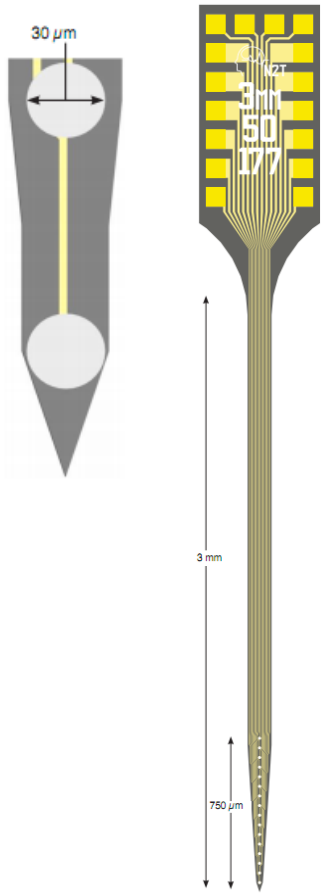
1 nm resolution
STEM, EDS, EsB detectors
Cryo-stage
Omni-probe for TEM prep
3D reconstructions
Correlative Optical Microscopy:
Computerized sample stage

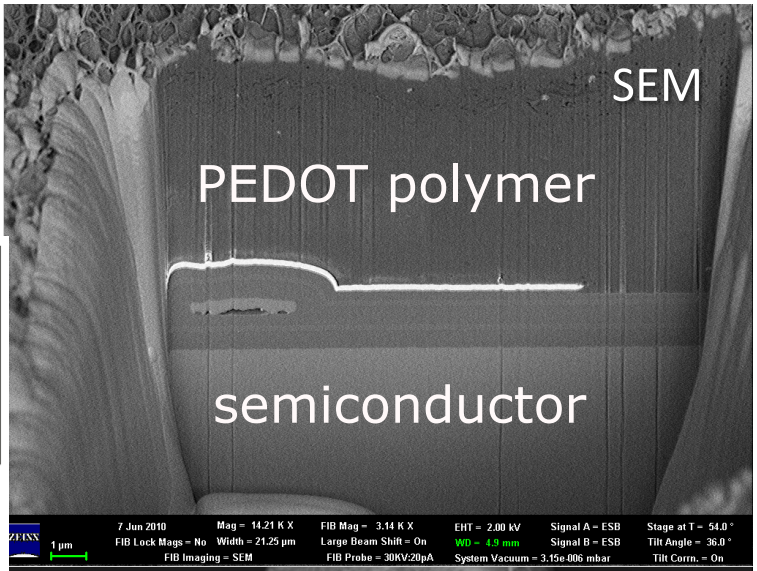


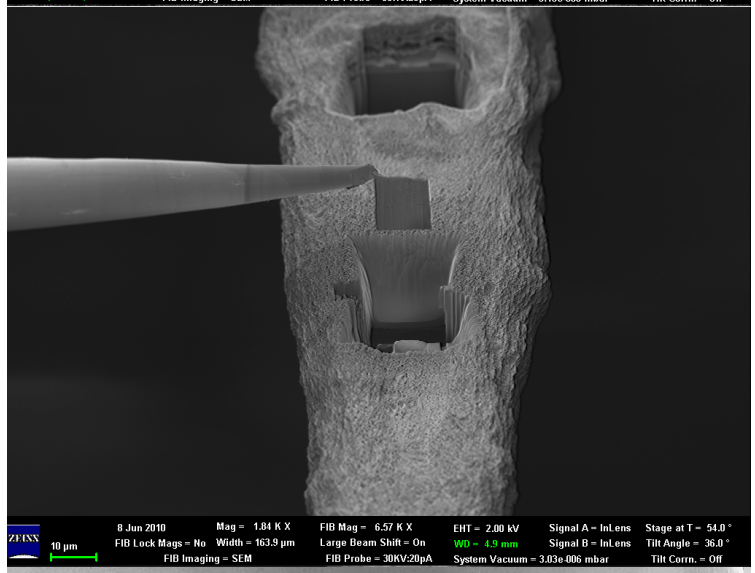


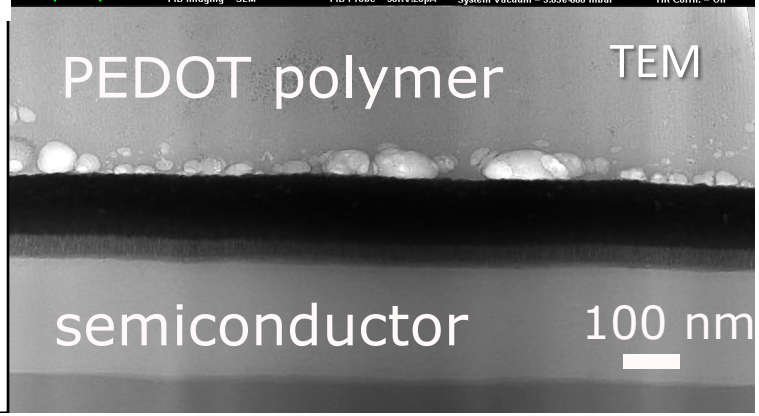
Auriga 60
FIB/SEM

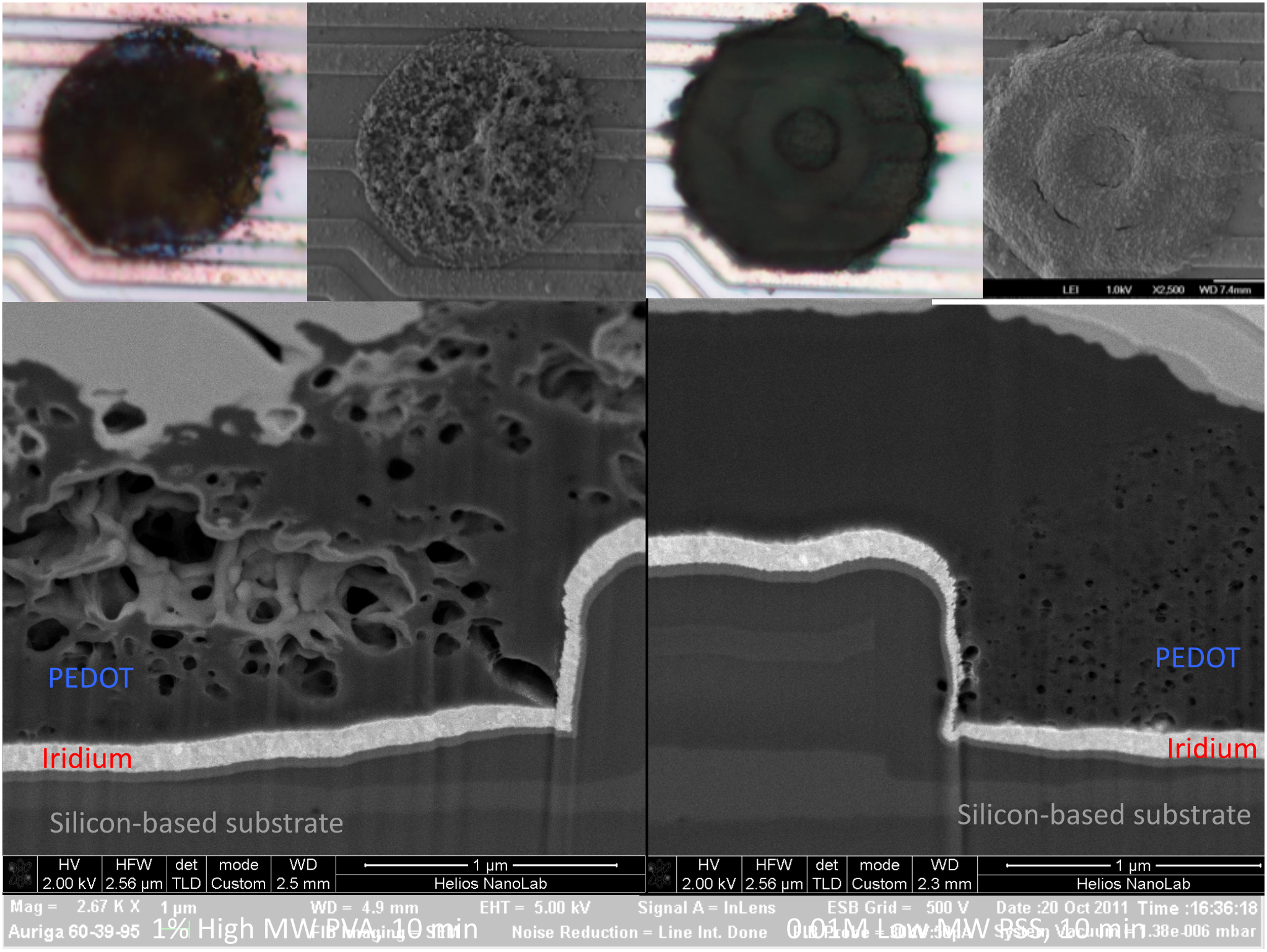











LEI 1.0kV X2,500 WD 7.4mm
PEDOT
Iridium
Silicon-based substrate
HV 2.00 kV
HFW 2.56 µm
det TLD
mode Custom
WD 2.5 mm
1 µm
Helios NanoLab
PEDOT
Iridium
Silicon-based substrate
HV 2.00 kV
HFW 2.56 µm
det TLD
mode Custom
WD 2.3 mm
1 µm
Helios NanoLab
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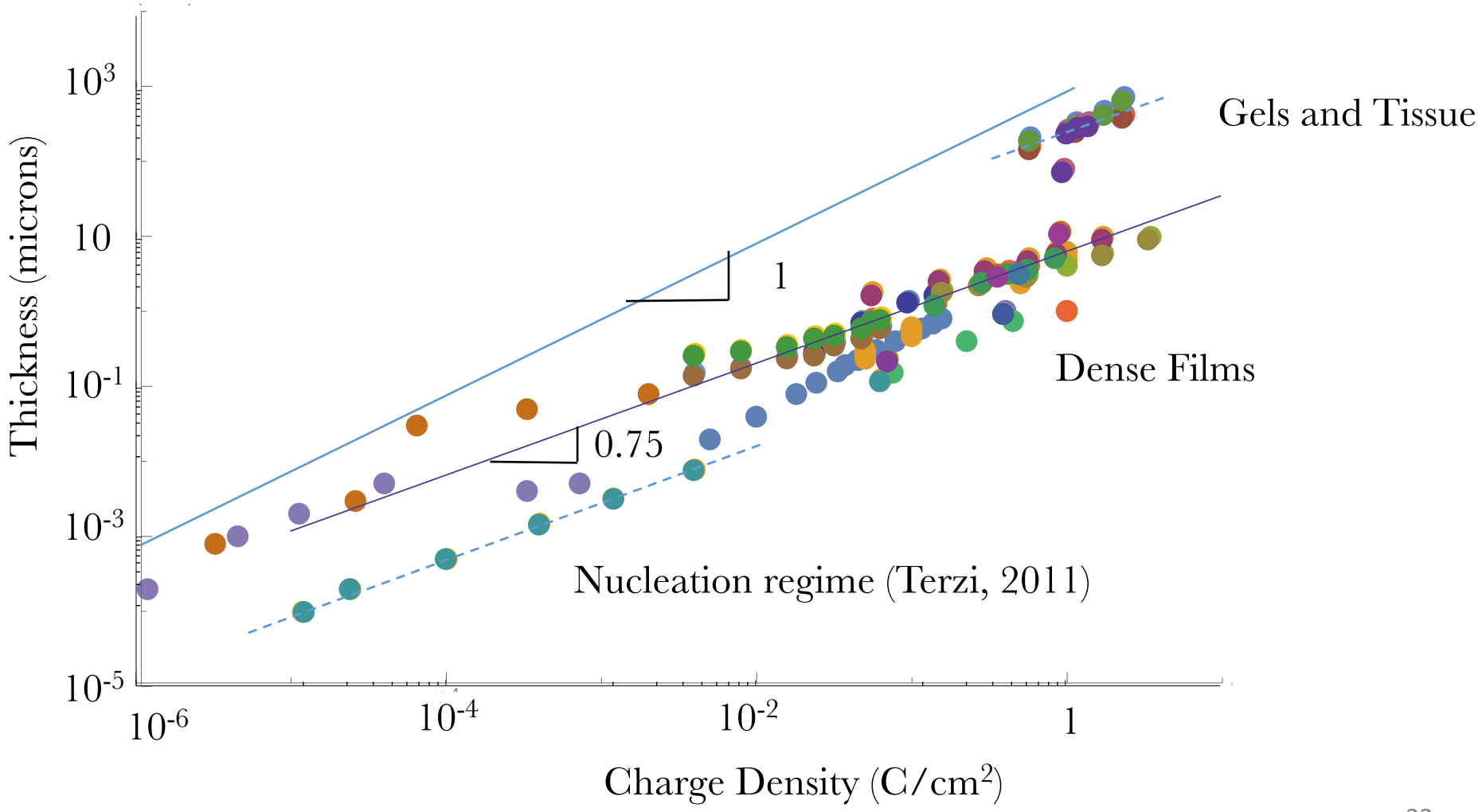
Auriga 60-39-95 FIB Imaging + SEM Noise Reduction = Line Int. Done
1% High MW PVA, 10 min
0.01M Low MW PSS, 10 min

PEDOT electrochemical deposition

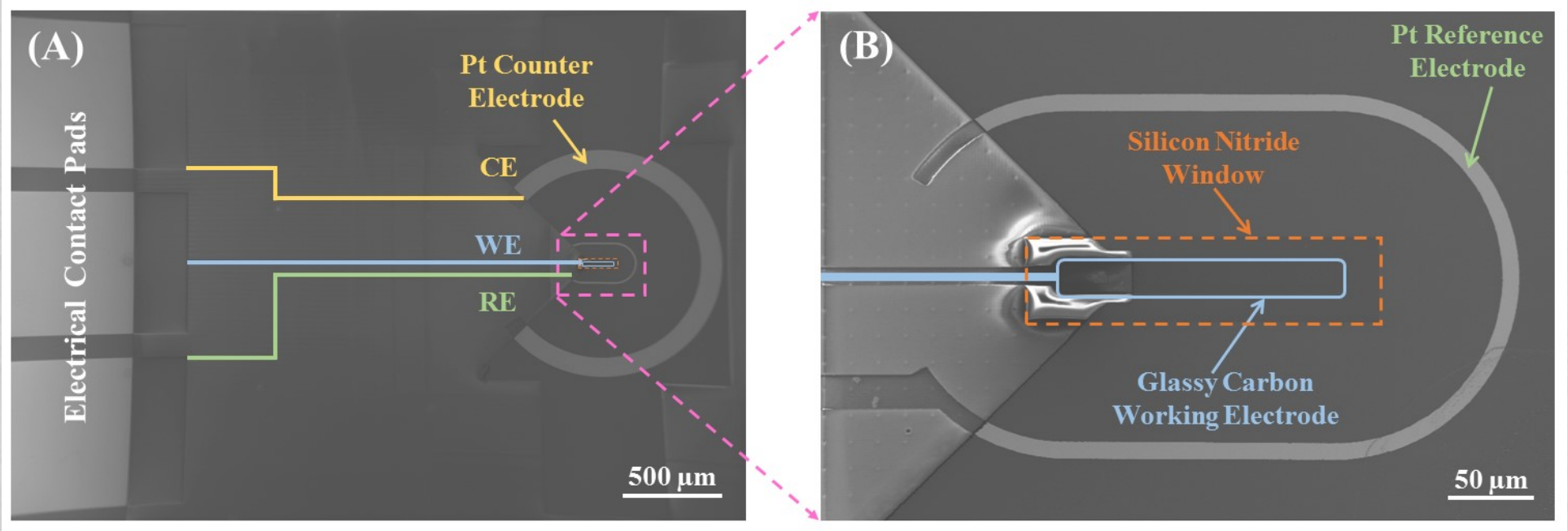


In-situ TEM imaging of the electrochemical deposition of PEDOT – experimental setup

Macro Letters, (2015), http://dx.doi.org/10.1021/acsmacrolett.5b00479

http://www.protochips.com/products/poseidon-500.html

Microfabricated Electrochemical chip



SEM images of the top electrochemical chip. (**A**) Electrical contact pads with the liquid flow cell and platinum reference and counter electrodes; (**B**) Higher magnification image showing the silicon nitride viewing window and glass carbon working electrode.

Macro Letters, (2015), http://dx.doi.org/10.1021/acsmacrolett.5b00479

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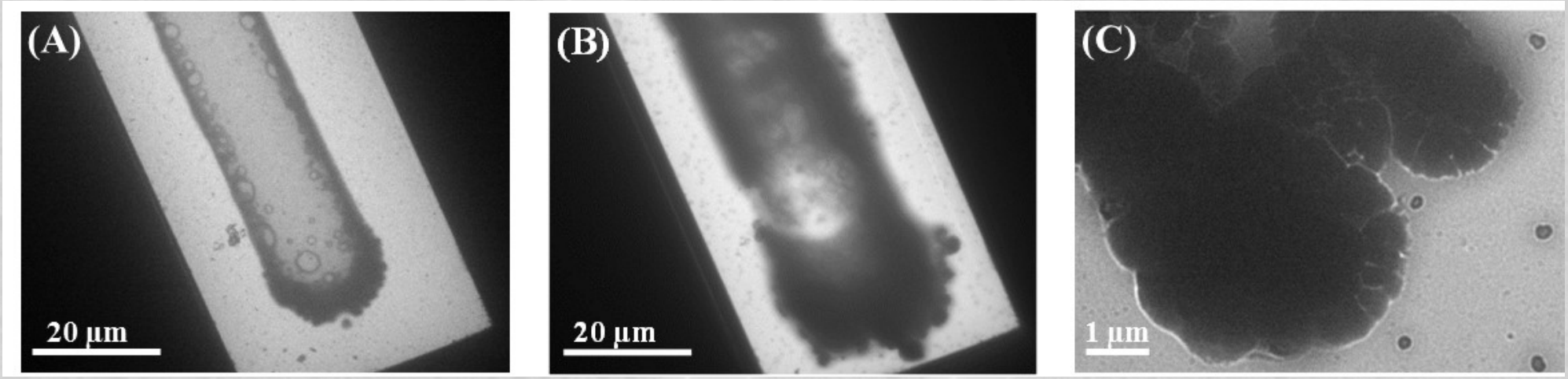
TEM Images of PEDOT Electrodeposition



Bright field TEM images of *in situ* electrochemical deposition of PEDOT. (**A**) Early stage in the process (right after initial CV deposition on bench) showing the dark PEDOT depositing from an aqueous solution onto a 20 µm wide glassy carbon working electrode (anode) supported on a thin silicon nitride membrane. (**B**) Later stage in the process (after subsequent constant voltage deposition), showing the increased thickness and formation of rough protrusions at the edge of the PEDOT film. (**C**) Higher magnification view of the rough edge of the PEDOT film after further deposition.

Macro Letters, (2015), http://dx.doi.org/10.1021/acsmacrolett.5b00479

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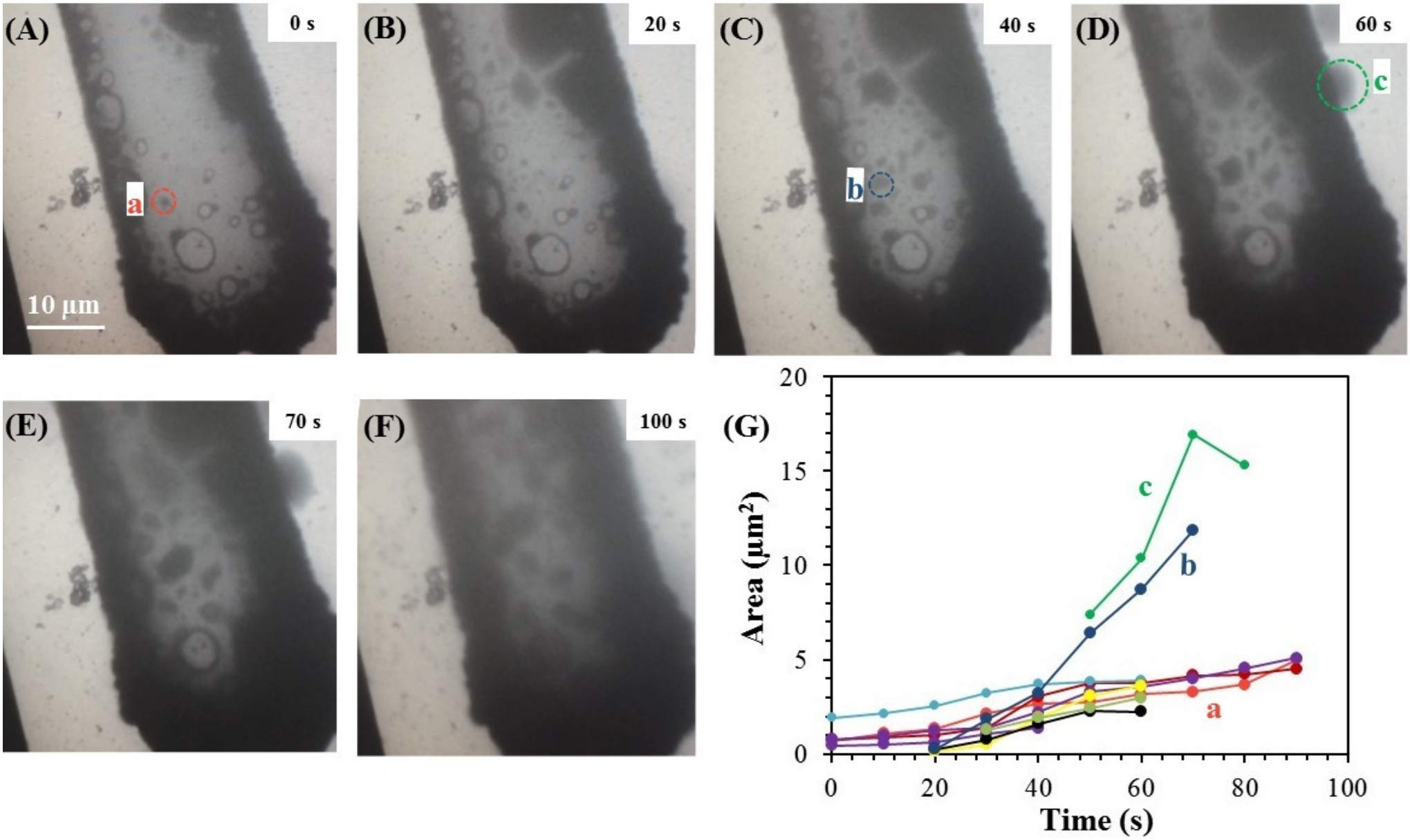

Growth of PEDOT clusters during electrochemical deposition. (A) – (F) Captured frames from live video recording of *in situ* PEDOT deposition under TEM at constant voltage of +1.20 V; (G) Projected areas of individual PEDOT clusters measured from the video.

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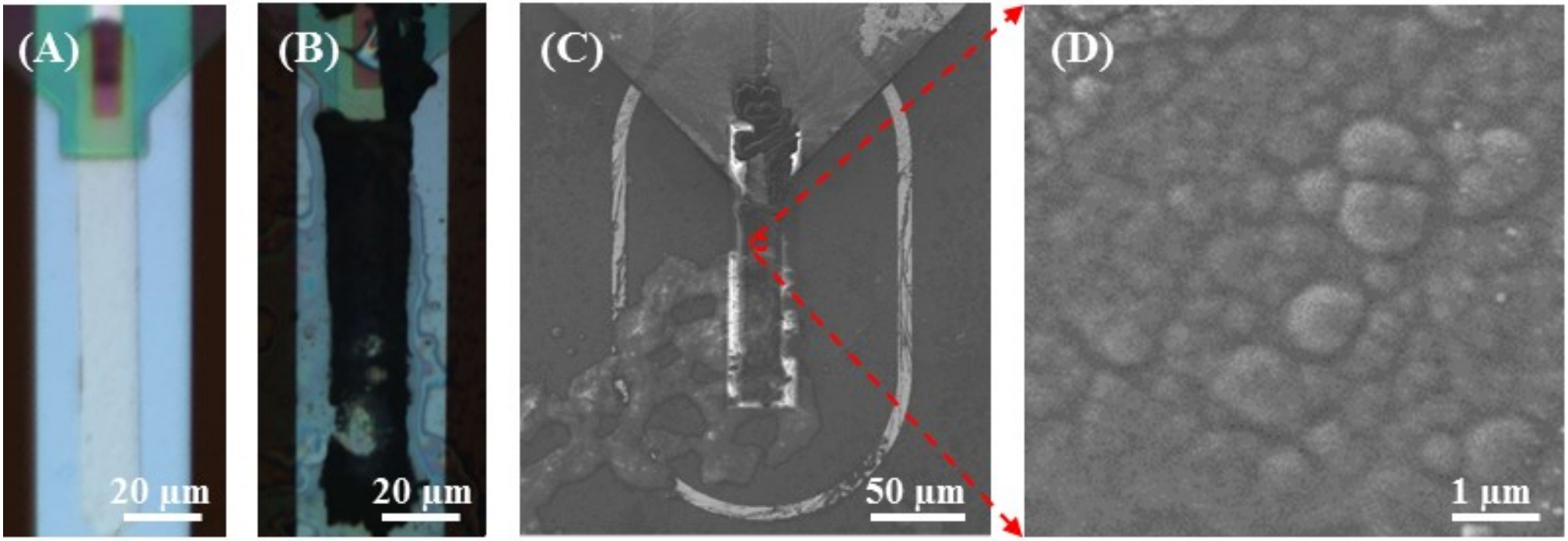
Morphology of deposited PEDOT film



Optical and SEM images after electrochemical deposition. (**A**) Optical micrograph before deposition showing bare working electrode; (**B**) Optical micrograph after deposition showing accumulated dark PEDOT on the working electrode; (**C**) SEM image after deposition; (**D**) Higher magnification SEM image showing the "bumpy" surface morphology of the deposited PEDOT film.

Macro Letters, (2015), http://dx.doi.org/10.1021/acsmacrolett.5b00479

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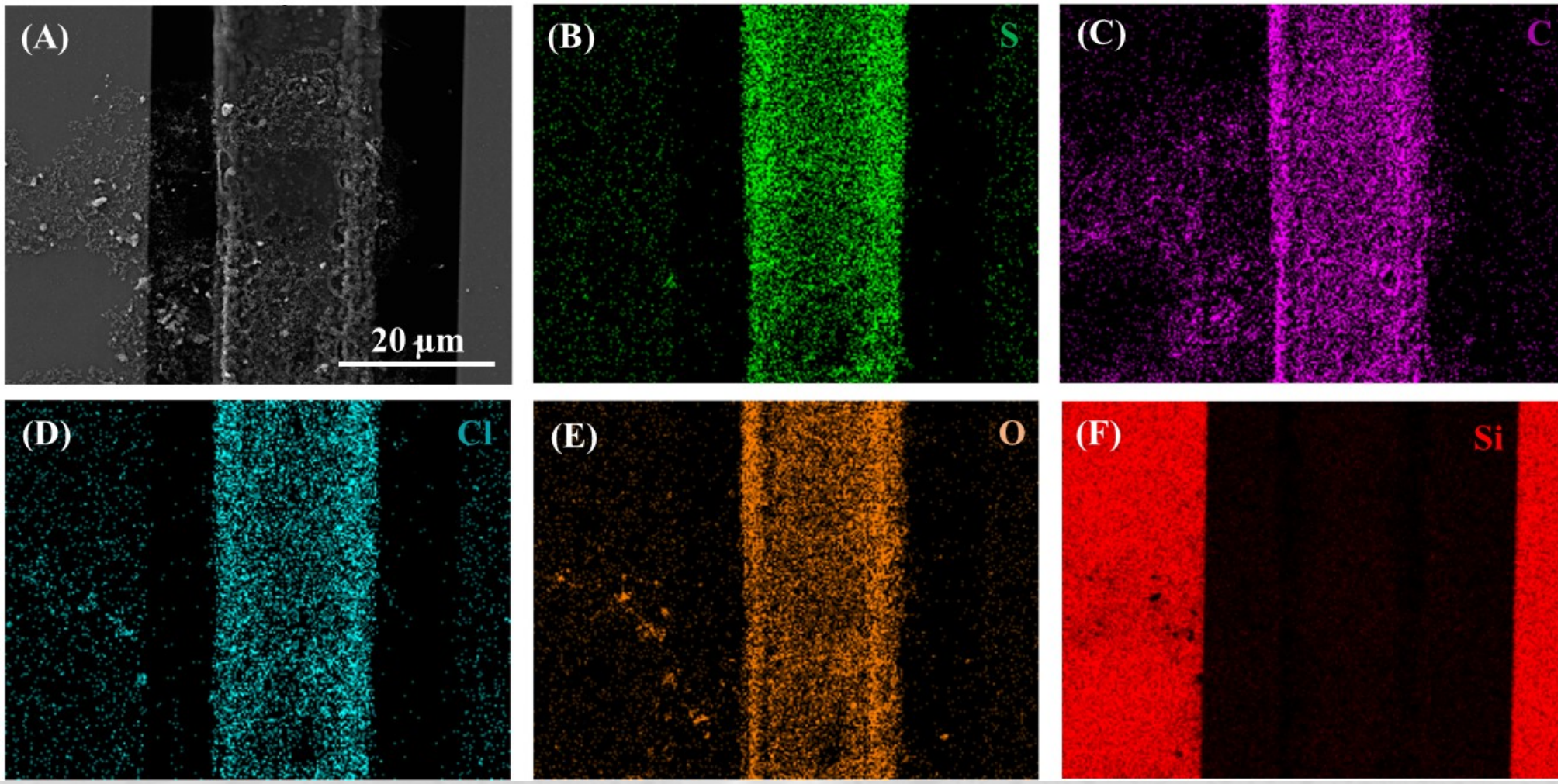
Elemental mapping: EDS



EDS elemental mapping after *in situ* electrochemical deposition of PEDOT. (**A**) Secondary electron image; (**B**) sulfur (PEDOT); (**C**) carbon (PEDOT and glassy carbon working electrode); (**D**) chlorine (perchlorate dopant); (**E**) oxygen (PEDOT and perchlorate dopant) and (**F**) silicon (microfabricated substrate).

Mag = 2.67 K X 1 µm | WD = 4.9 mm | EHT = 5.00 kV | Signal A = InLens | ESB Grid = 500 V | Date :20 Oct 2011 Time :16:36:18
Auriga 60-39-95 | FIB Imaging = SEM | Noise Reduction = Line Int. Done | FIB Probe = 30KV:50pA | System Vacuum = 1.38e-006 mbar

Total dose ~ 0.1-1 mC/cm^2
Critical dose for beam damage ~100 mC/cm^2
Features appear similar to those seen by SEM, optical

Next steps:

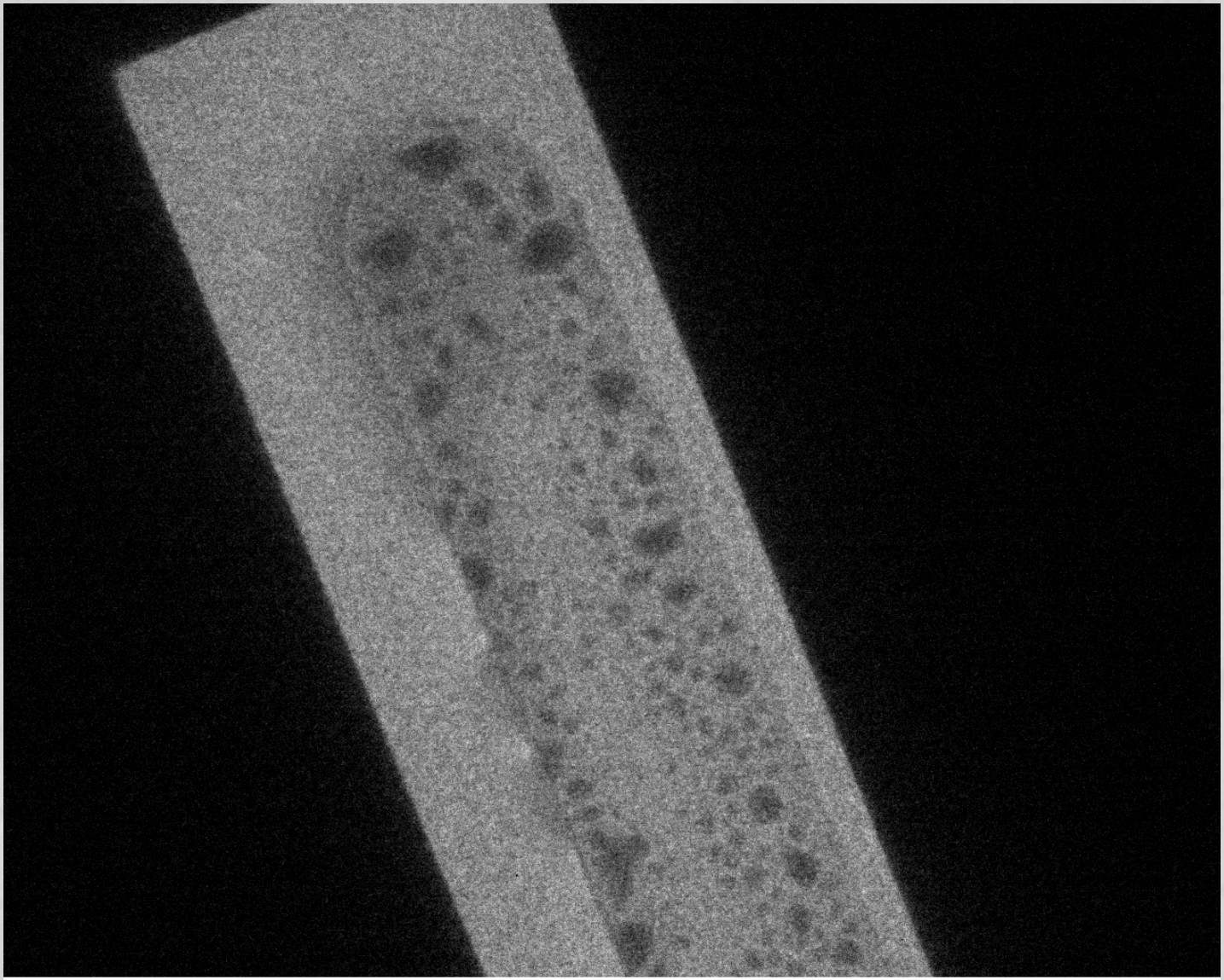
- Correlative Optical Microscopy
- Monomers
  - EDOT+, ProDOT, ProDOT+
- Solvents
- Counterions
- Fluid Flow Conditions
- Gels
- Living Cells

ThermoScientific FEI Talos 200C

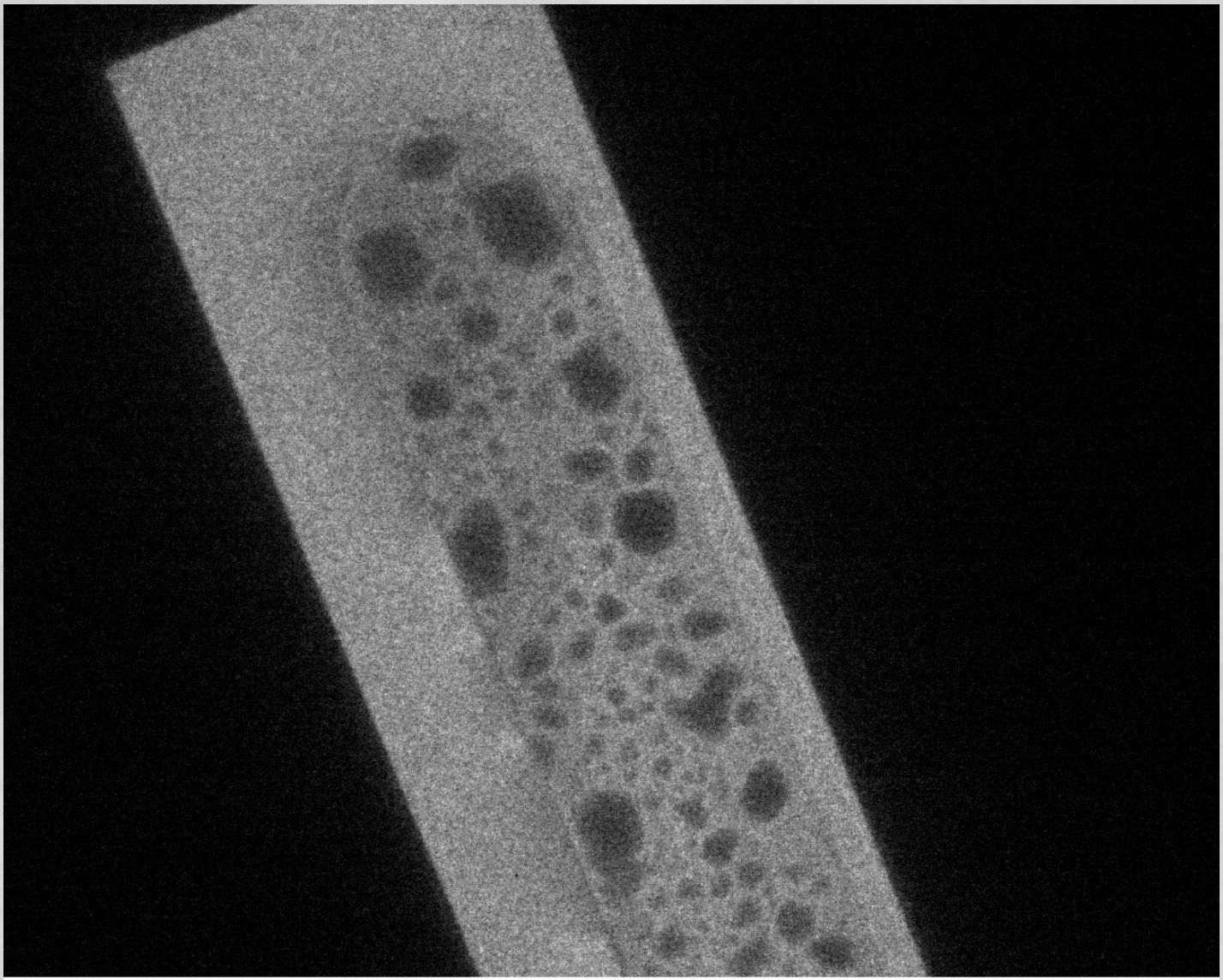
Macro Letters, (2015), http://dx.doi.org/10.1021/acsmacrolett.5b00479

Mag = 2.67 K X 1 µm WD = 4.9 mm EHT = 5.00 kV Signal A = InLens ESB Grid = 500 V Date :20 Oct 2011 Time :16:36:18
Auriga 60-39-95 FIB Imaging = SEM Noise Reduction = Line Int. Done FIB Probe = 30KV:50pA System Vacuum = 1.38e-006 mbar

TEM of PEDOT Electrodeposition



TEM of PEDOT Electrodeposition



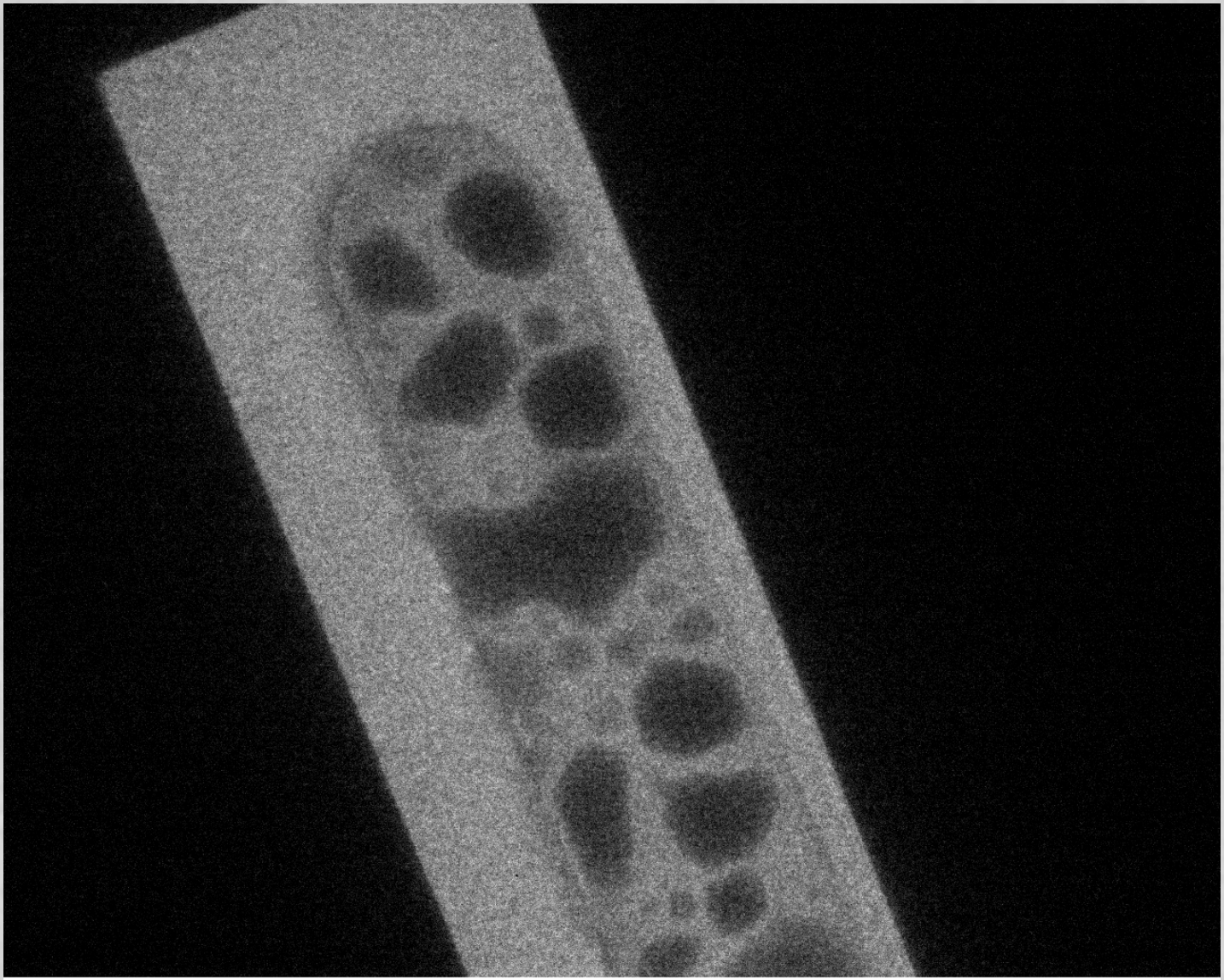
2.tif
Print Mag: 1690x @ 200 mm
14:45 09/02/15
TEM Mode: Imaging

10 microns
HV=300kV
Direct Mag: 200x
X: Y: T:
AMT Camera System

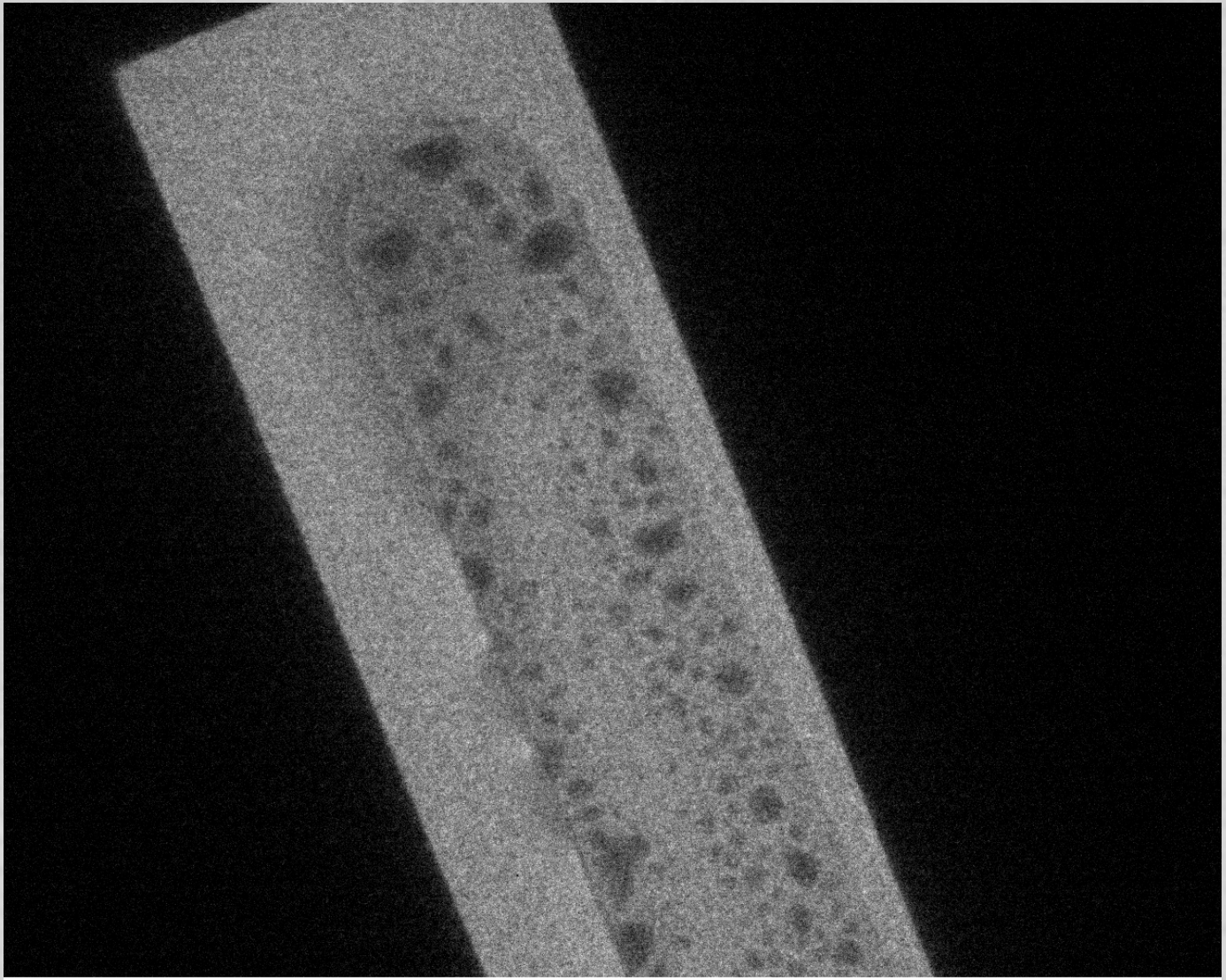
Mag = 2.67 K X 1 µm
Auriga 60-39-95

ct 2011 Time :16:36:18
cuum = 1.38e-006 mbar

TEM of PEDOT Electrodeposition

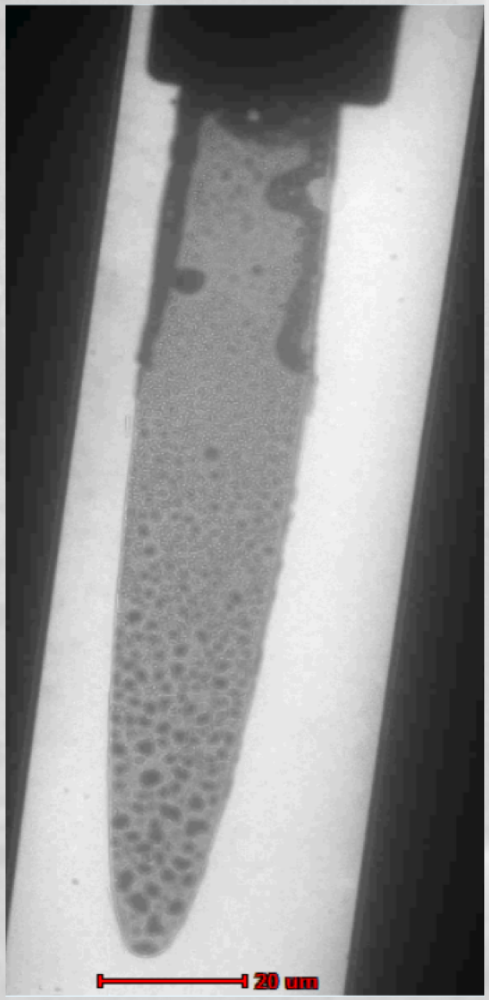


TEM of PEDOT Electrodeposition

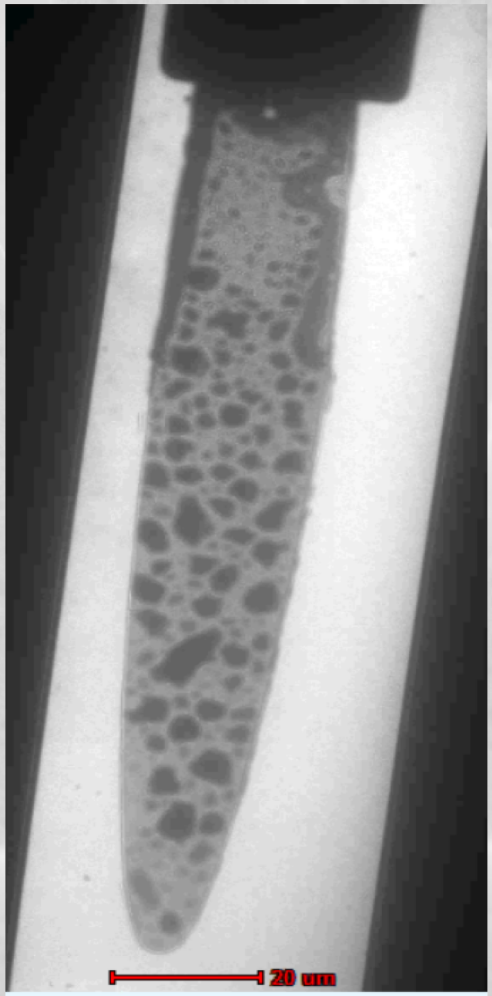


Mag = 2.67 K X 1 µm
Auriga 60-39-95
t 2011 Time :16:36:18
uum = 1.38e-006 mbar

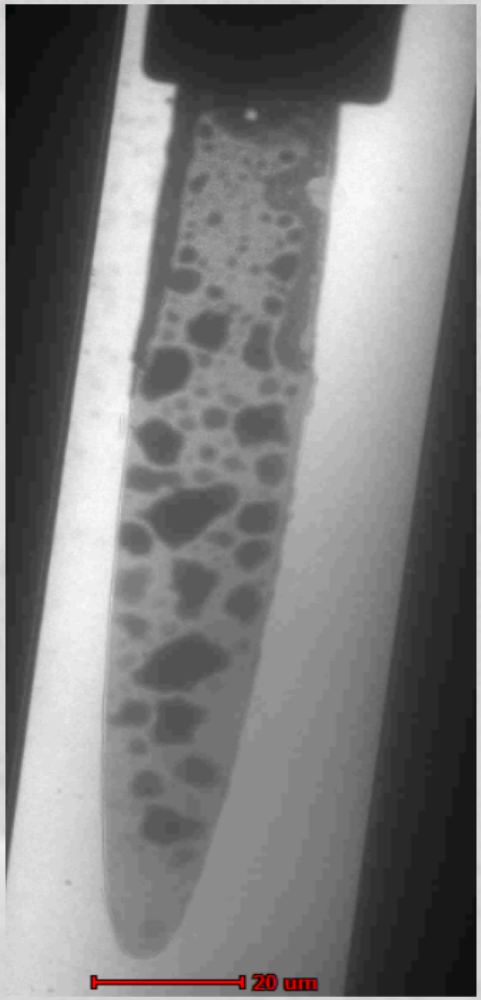
Galvanostatic Conditions
120 kV FEI Talos 200C, 150 nA



Time - 60 s



Time - 85 s

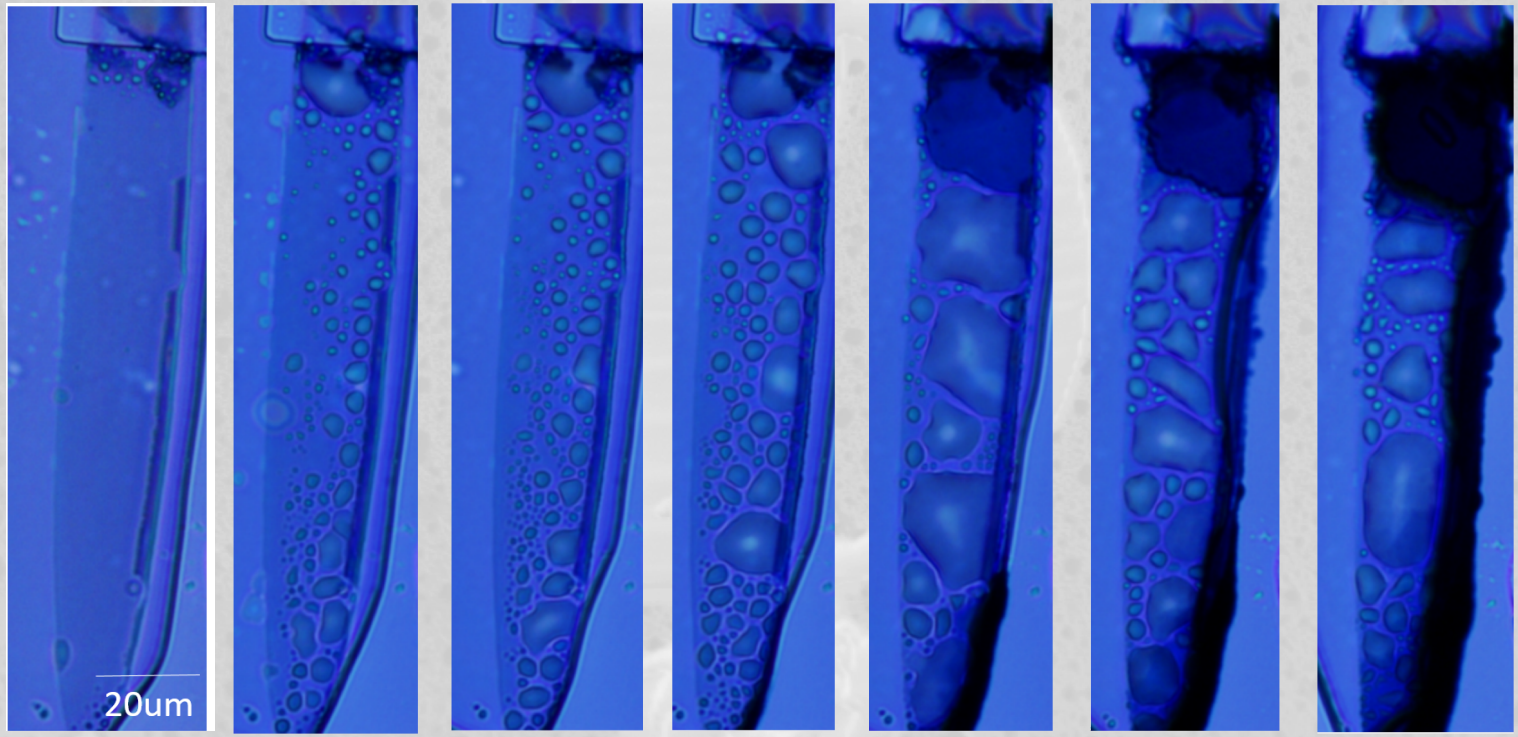


Time - 105 s

Mag = 2.67 K X 1 µm WD = 4.9 mm EHT = 5.00 kV Signal A = InLens ESB Grid = 500 V Date :20 Oct 2011 Time :16:36:18
Auriga 60-39-95 FIB Imaging = SEM Noise Reduction = Line Int. Done FIB Probe = 30KV:50pA System Vacuum = 1.38e-006 mbar

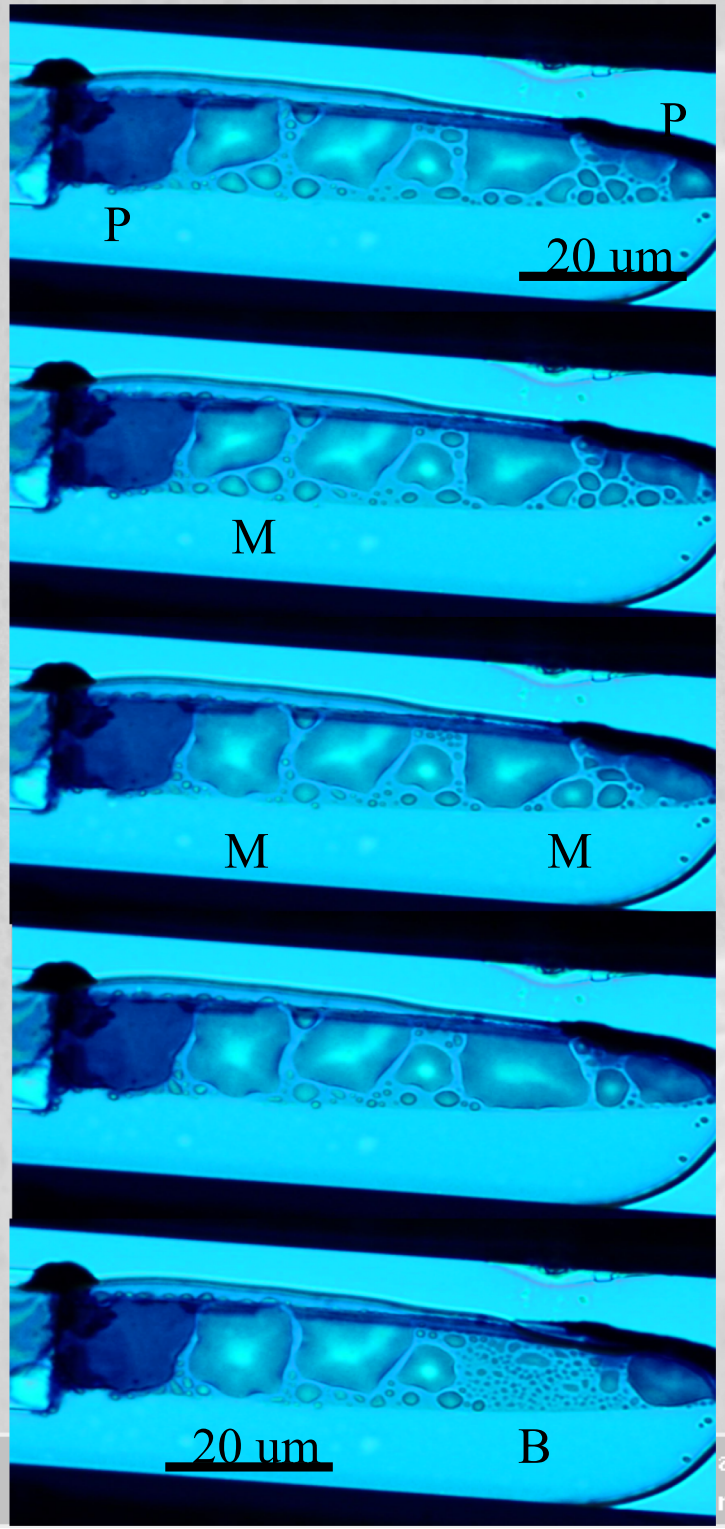
Potentiostatic Conditions

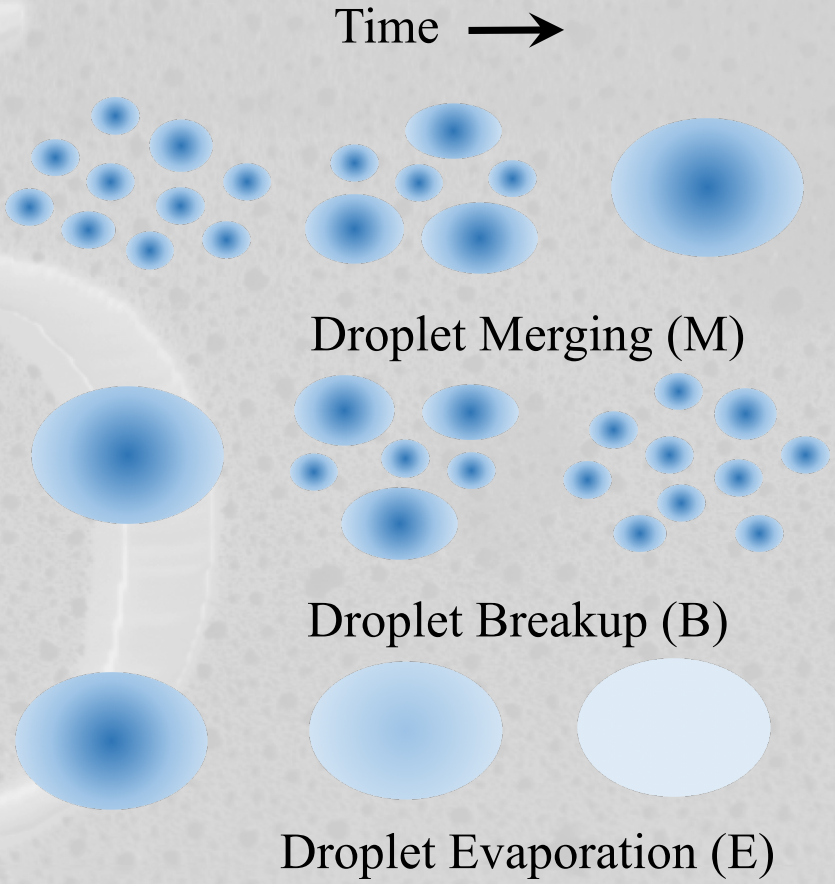
Transmitted Light, +1.2 V, ~250 nA current



Initial droplets are translucent (PEDOT oligomers), liquid-like (breakup)
Final film is dark (PEDOT), solid-like (stable)

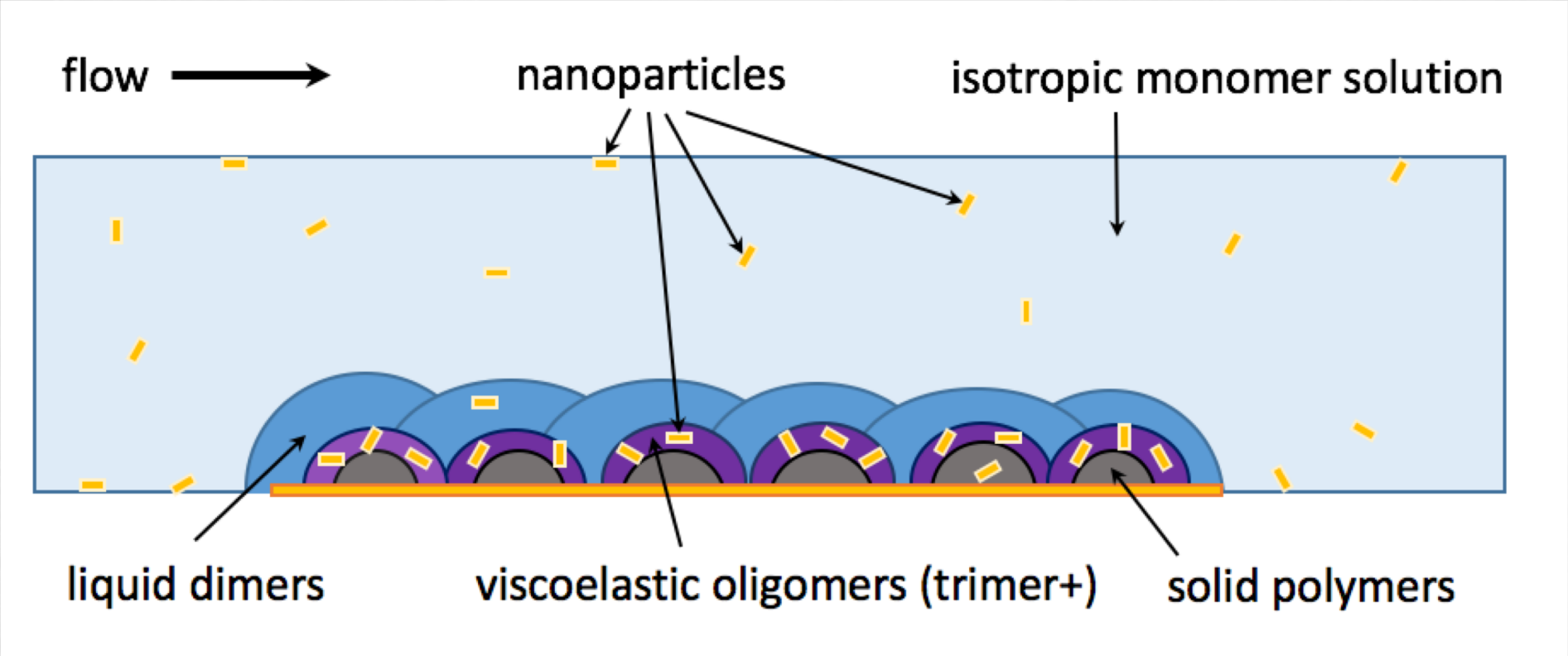
Mag = 2.67 K X 1 µm WD = 4.9 mm EHT = 5.00 kV Signal A = InLens ESB Grid = 500 V Date :20 Oct 2011 Time :16:36:18
Auriga 60-39-95 FIB Imaging = SEM Noise Reduction = Line Int. Done FIB Probe = 30KV:50pA System Vacuum = 1.38e-006 mbar





Schematic diagram of the processes of droplet merging (M), droplet break-up (B), and droplet evaporation (E). These events are seen during imaging of liquid-like oligomer droplets formed during intermediate stages of the deposition, but are not seen in the solid, sessile PEDOT polymer films.

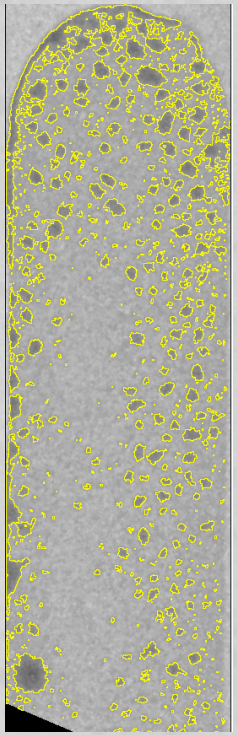
Mag = 2.67 K X 1 µm
Auriga 60-39-95
al A = InLens ESB Grid = 500 V Date :20 Oct 2011 Time :16:36:18
ne Int. Done FIB Probe = 30KV:50pA System Vacuum = 1.38e-006 mbar



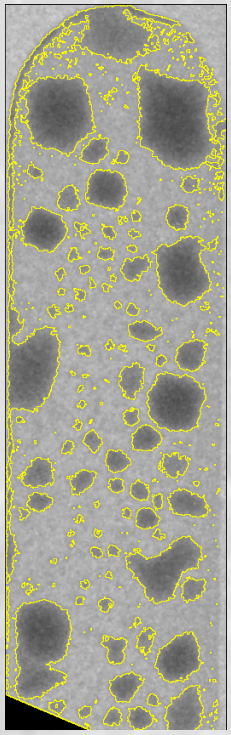
Schematic of the hypothesized variations in the interaction of solid nanoparticles suspended in a flowing isotropic monomer solution with the products of an electrochemical polymerization reaction depositing on a solid surface. The initial liquid droplets form primarily from EDOT dimers that should have relatively weak interactions with the solid nanoparticles. The intermediate components (trimers and higher MW oligomers) will be viscoelastic and thus appear "sticky" to the particles, causing them to be trapped as they flow by, much as the mucus inside the nasal cavity and lungs traps unwanted contaminants. The final PEDOT polymer product will be solid, again resulting in relatively weak interactions that will allow the particles to continue to flow past. By examining the nanoparticle-containing solution with the electrodepositing film, we expect to obtain novel information about these complex rheological processes.

Mag = 2.67 K X 1 µm WD = 4.9 mm EHT = 5.00 kV Signal A = InLens ESB Grid = 500 V Date :20 Oct 2011 Time :16:36:18
Auriga 60-39-95 FIB Imaging = SEM Noise Reduction = Line Int. Done FIB Probe = 30KV:50pA System Vacuum = 1.38e-006 mbar

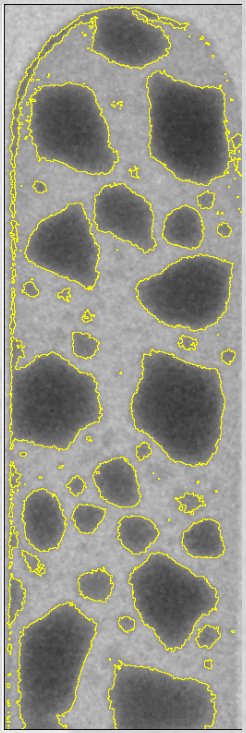
Nucleation and Growth Analysis



Time - 120 s

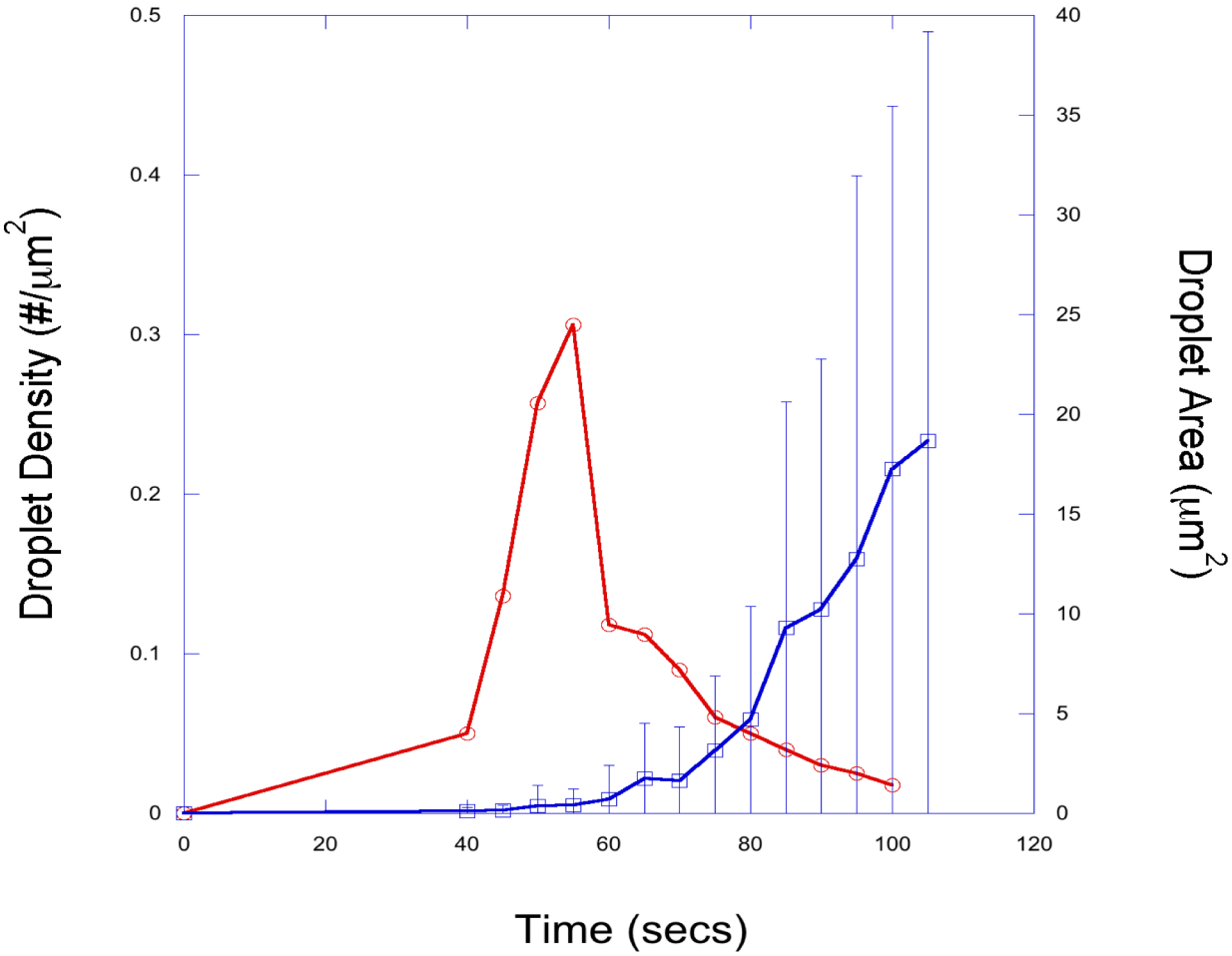


Time- 360 s



Time- 600s

In-situ Deposition of PEDOT: FEI Talos 200C

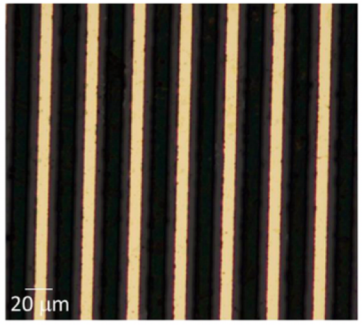


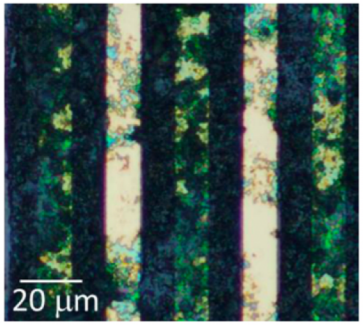
Mag = 2.67 K X 1 μm
Auriga 60-39-95
WD = 4.9 mm
FIB Imaging = SEM
EHT = 5.00 kV
Noise Reduction = Line Int. Done
Signal A = InLens
FIB Probe = 30KV:50pA
ESB Grid = 500 V
System Vacuum = 1.38e-006 mbar
Date :20 Oct 2011 Time :16:36:18

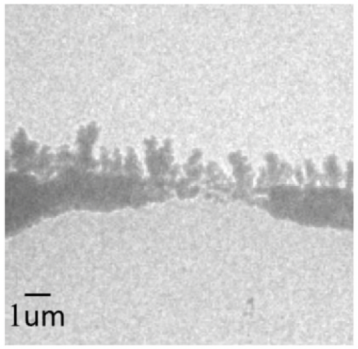
Direct Observations of PEDOT / PDMICA Nanofibril Growth Mechanisms

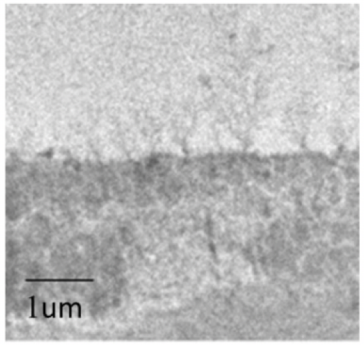
PEDOT-PAA PDMICA PEDOT-PAA PDMICA

Optical

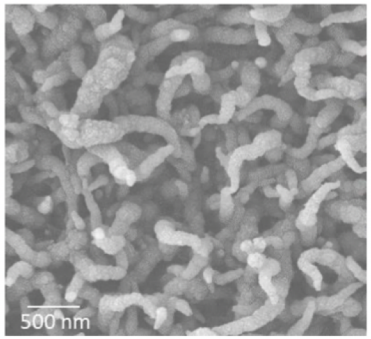


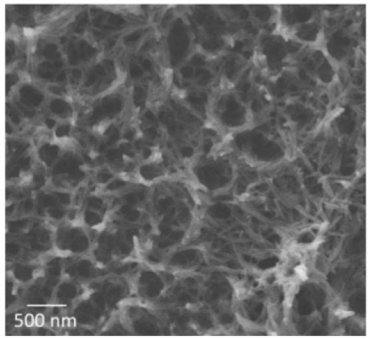


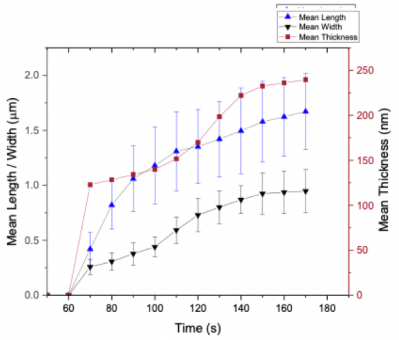


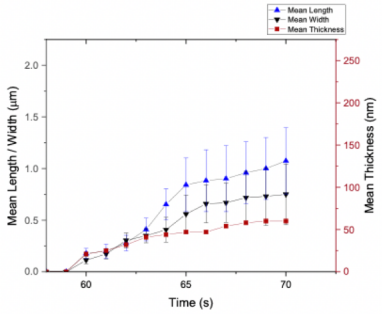


SEM

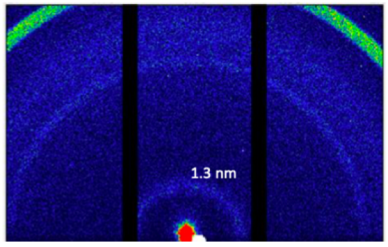


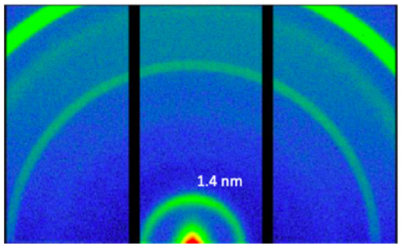


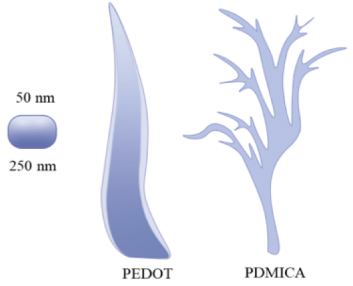




GIWAXS

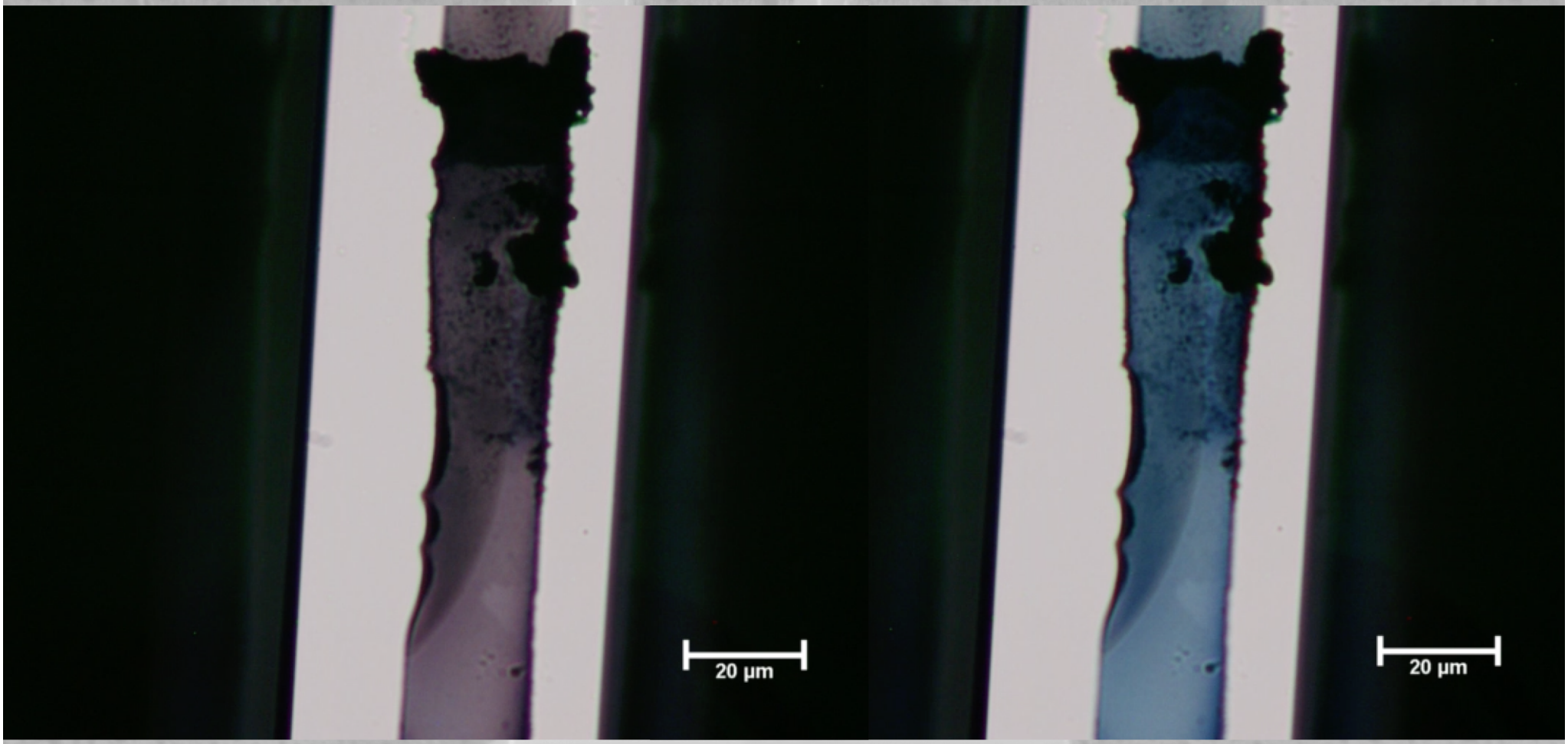






Mag = 2.67 K X 1 µm WD = 4.9 mm EHT = 5.00 kV Signal A = InLens ESB Grid = 500 V Date :20 Oct 2011 Time :16:36:18
Auriga 60-39-95 FIB Imaging = SEM Noise Reduction = Line Int. Done FIB Probe = 30KV:50pA System Vacuum = 1.38e-006 mbar

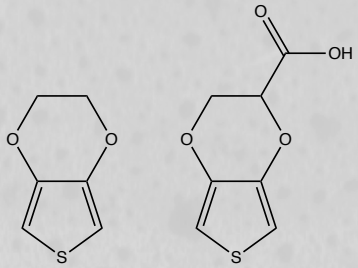
PEDOT: thermochromic switching in external bias during CV



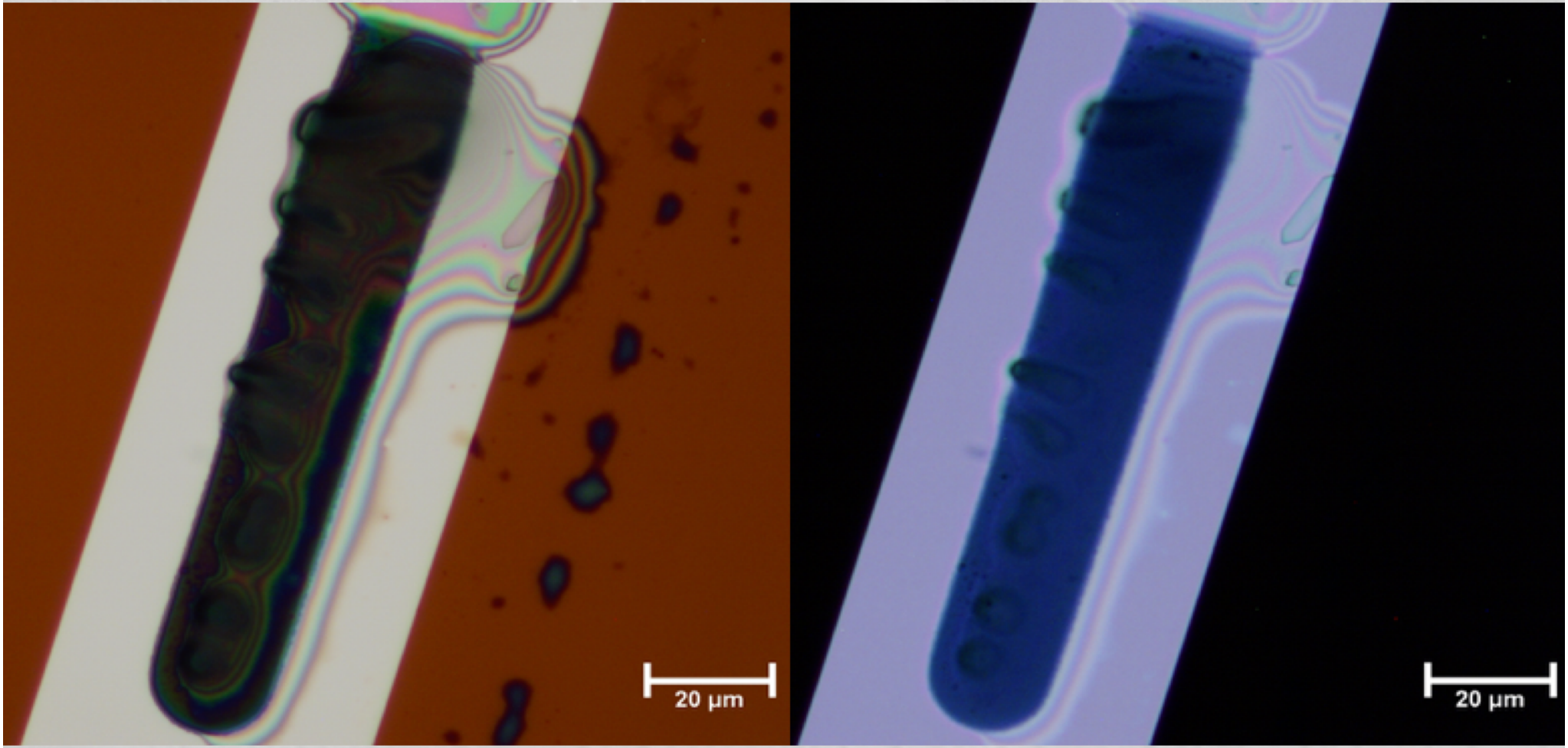
-0.6 Volts (reduced)
non-conductive

+1.2 Volts
(oxidized)
conductive

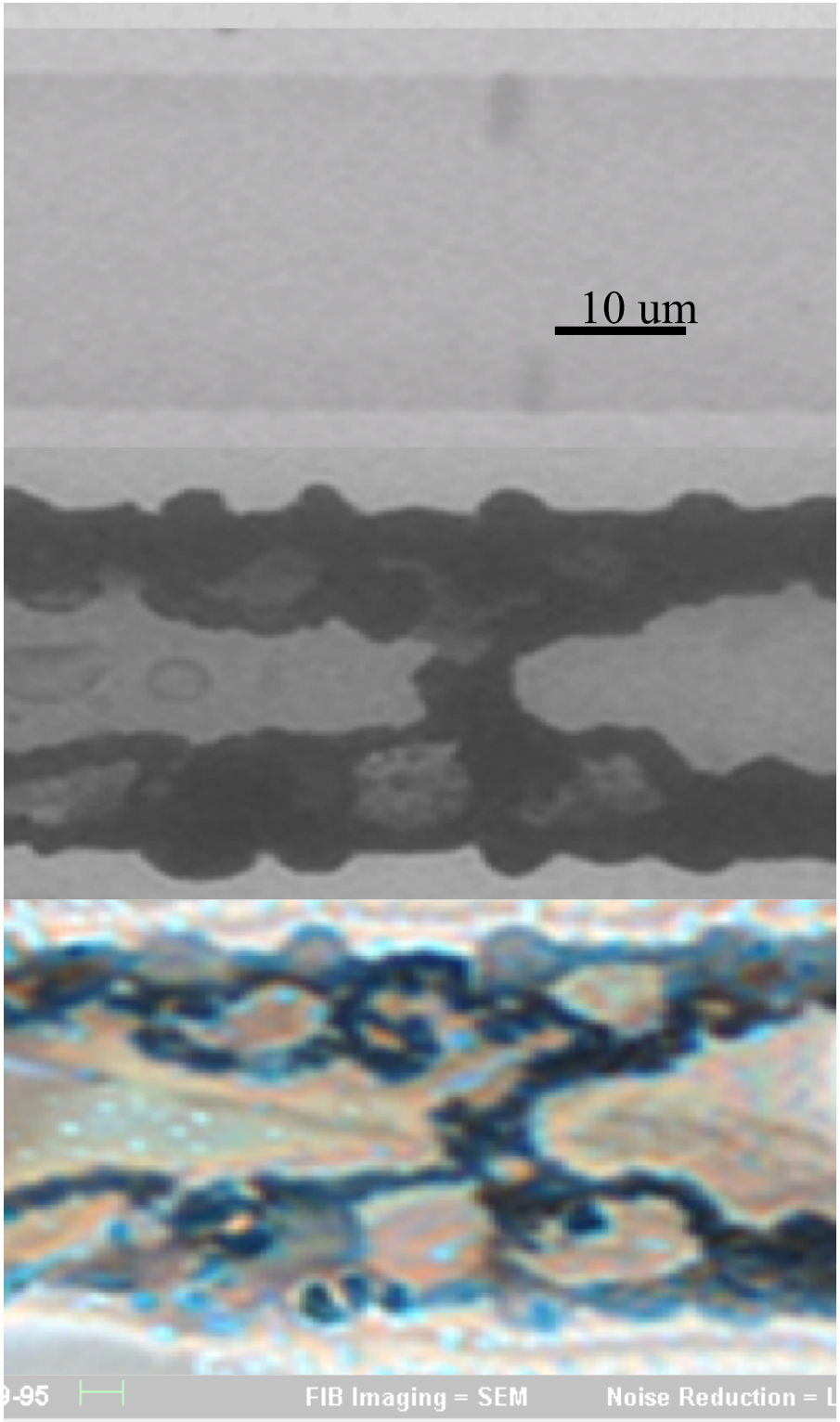
PEDOT-co-EDOT-acid



EDOT EDOT-acid



Mag = 2.67 K X 1 µm
Auriga 60-39-95
WD = 4.9 mm
FIB Imaging = SEM
EHT = 5.00 kV
Noise Reduction = Line Int. Done
Signal A = InLens
FIB Probe = 30KV:50pA
ESB Grid = 500 V
System Vacuum = 1.38e-006 mbar
Date :20 Oct 2011 Time :16:36:18



Bright Field TEM
t=0

Bright Field TEM
t=300 secs of
electrodeposition

Optical Microscopy
t=300 secs of
electrodeposition

EELS : UV/vis Spectroscopy

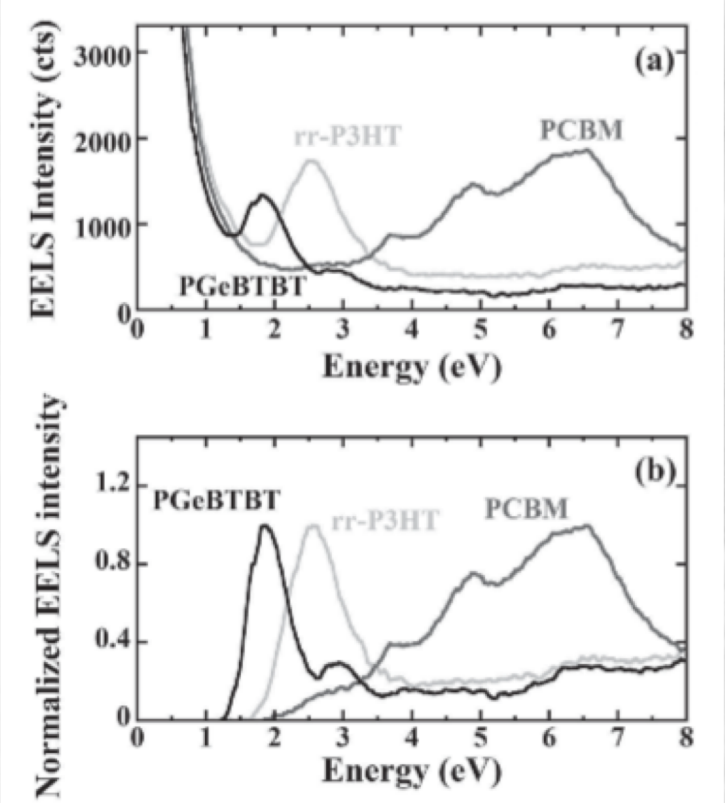


Figure 1. a) Raw EELS data and b) background-subtracted EELS data for rr-P3HT, PCBM, and PGeBTBT neat films. rr-P3HT films were annealed at 150 °C for 12 h to highlight crystalline properties. The background signal due to the zero-loss peak (<2 eV) is modeled as a third-order power law. EELS in (b) are generated by subtracting the background from the spectra in (a). EELS data are normalized by the maximum peak intensity.

Guo et al., "Probing Local Electronic Transitions in Organic Semiconductors through Energy-Loss Spectrum Imaging in the TEM", Adv. Funct. Mat., 25, 6071, (2015) DOI: 10.1002/adfm.201502090

Instrumentation limitations
Beam sensitivity

Mag = 2.67 K X 1 µm WD = 4.9 mm EHT = 5.00 kV Signal A = InLens ESB Grid = 500 V Date :20 Oct 2011 Time :16:36:18
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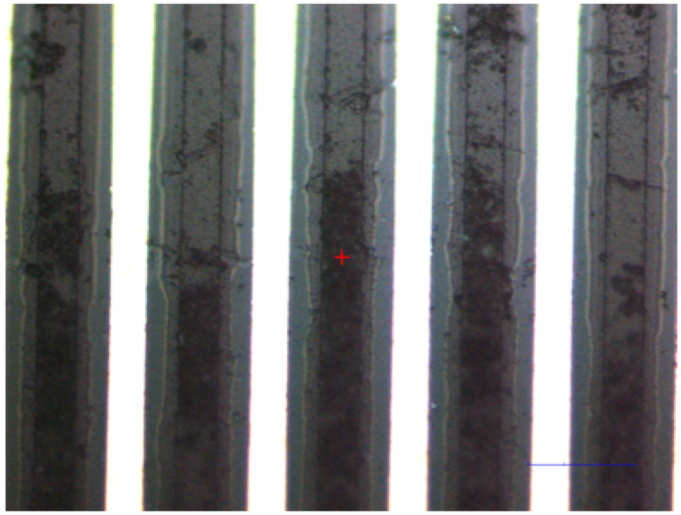
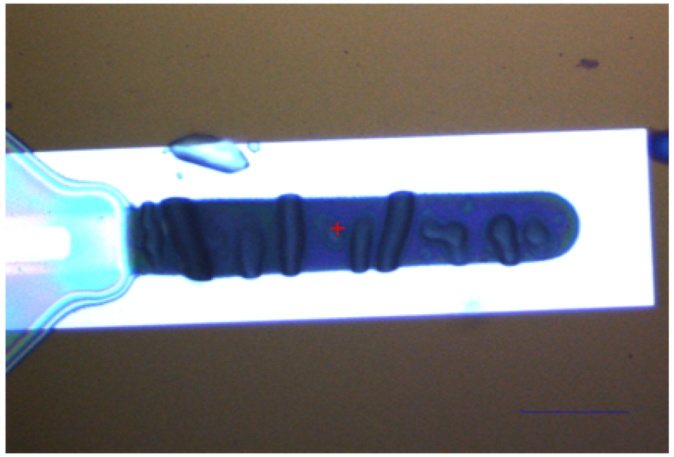
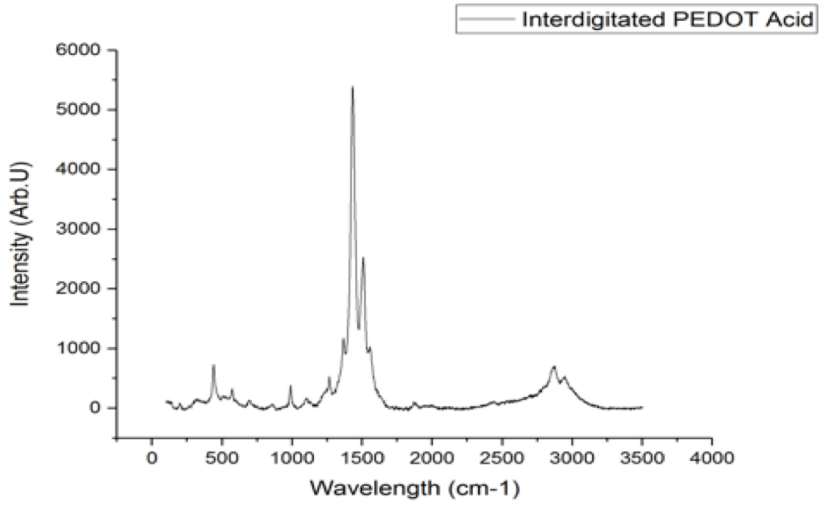
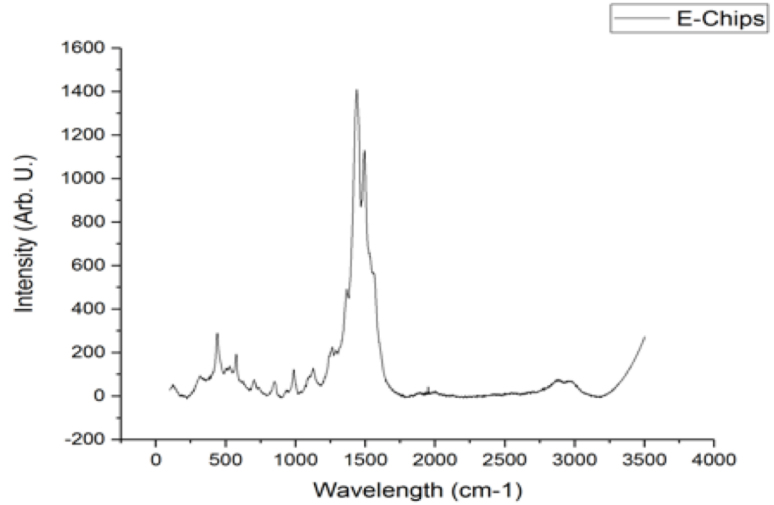
Microfocused Raman









Mag = 2.67 K X 1 µm
Auriga 60-39-95
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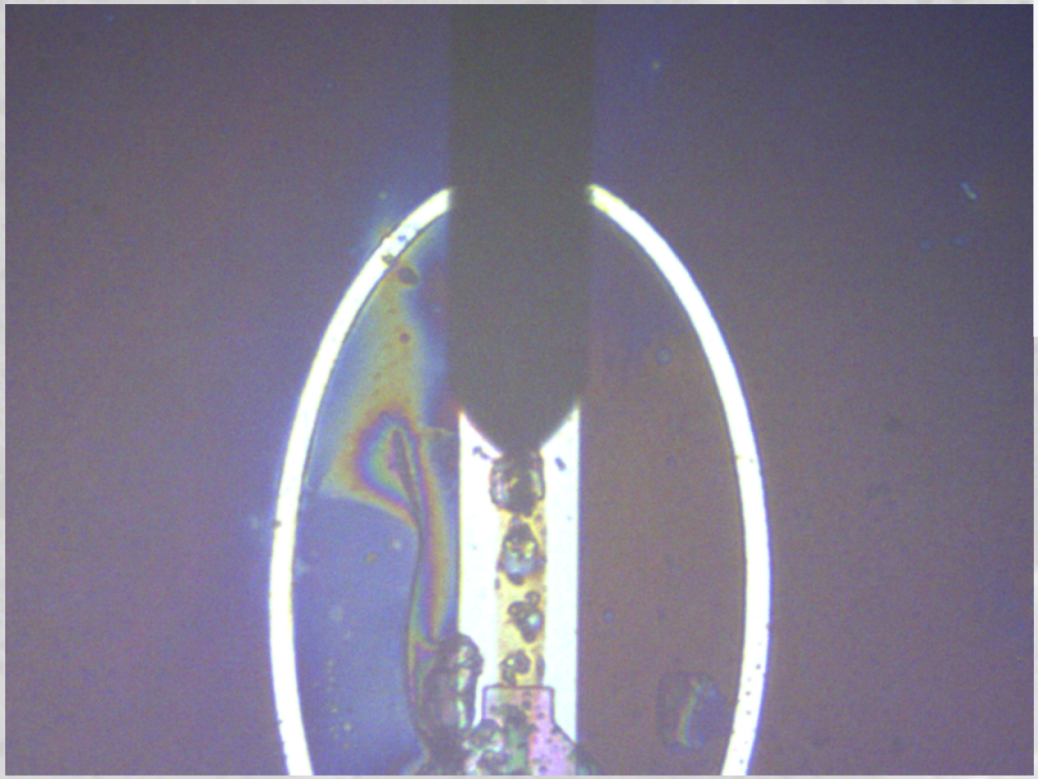
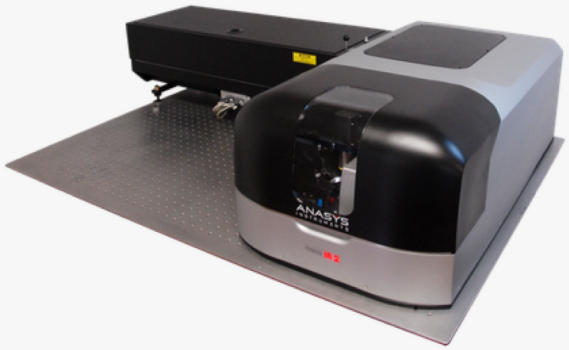
Noise Reduction = Line Int. Done
Signal A = InLens
FIB Probe = 30KV:50pA
ESB Grid = 500 V
System Vacuum = 1.38e-006 mbar
Date :20 Oct 2011 Time :16:36:18

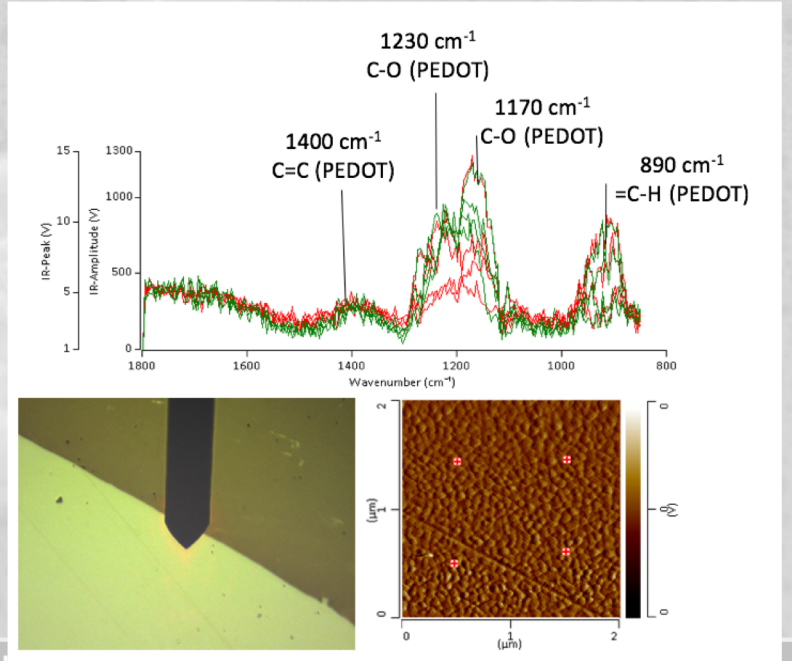
Nano-IR and Nano-Raman



Anasys NanoIR2



- Expands nanoscale IR to a broad range of real world samples
- New resonance enhanced mode enables nanoscale IR on <20nm films
- Rich, interpretable IR spectra
- Powerful, full featured AFM
- Multifunctional measurements including integrated thermal and mechanical property mapping
- Designed and built for productivity and rapid time-to-results



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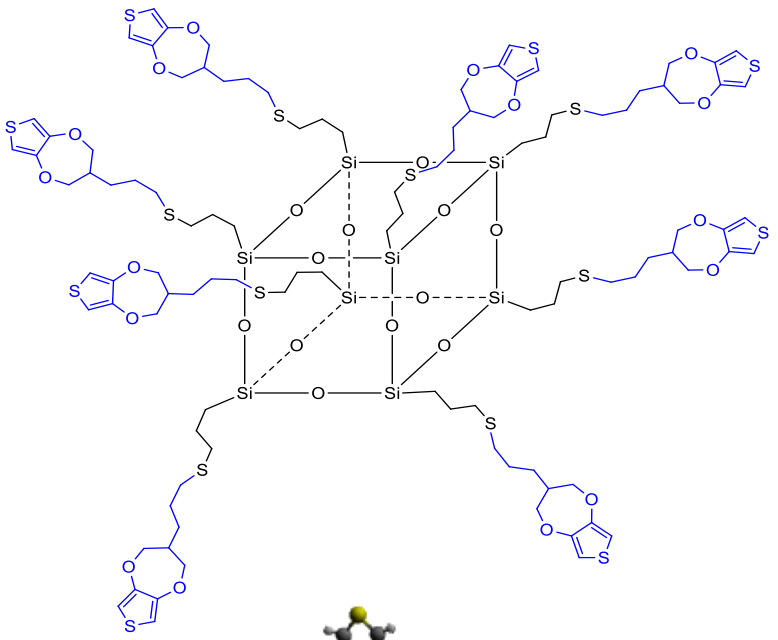
Auriga 60-39-95 FIB Imaging = SEM Noise Reduction = Line Int. Done FIB Probe = 30KV:50pA System Vacuum = 1.38e-006 mbar

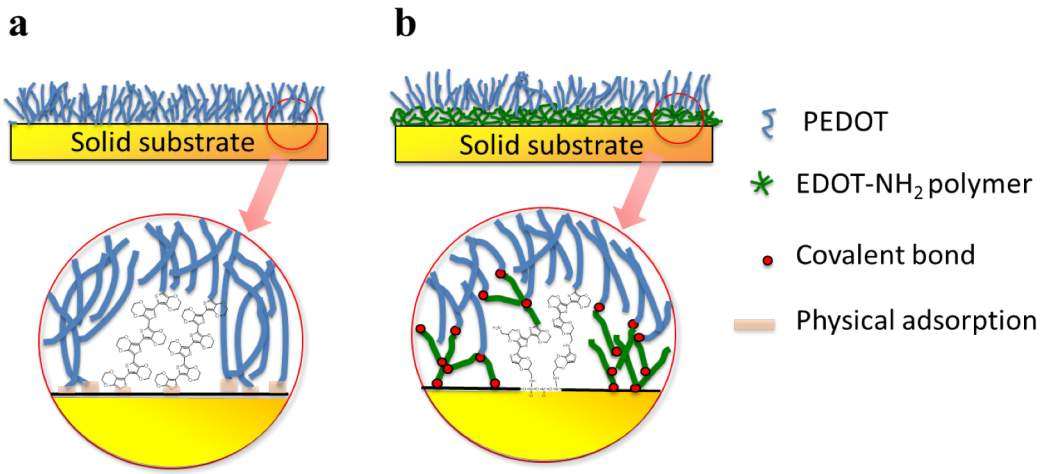
New Materials Design

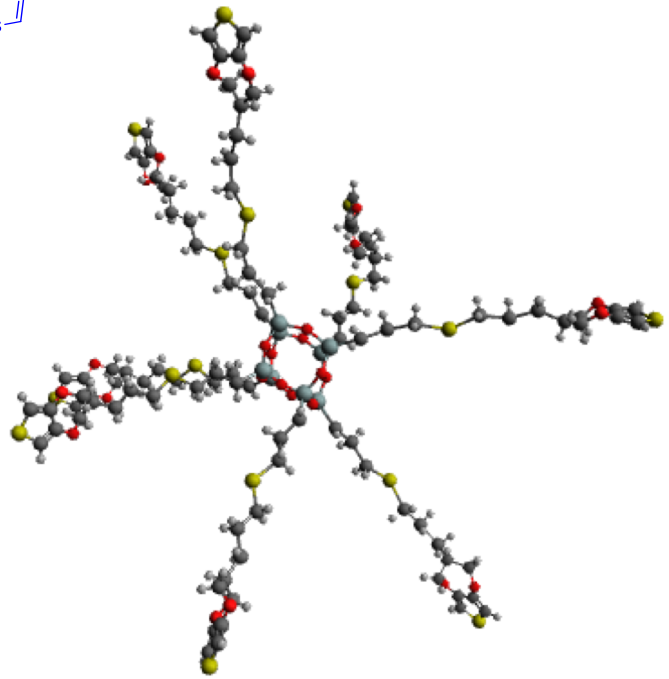
Thiol-ene "click" chemistry:

- POSS-ProDOT cross-linkers
- Alternating Copolymers
- Conjugated Polymer Networks



EDOT-amine: adhesion, transport

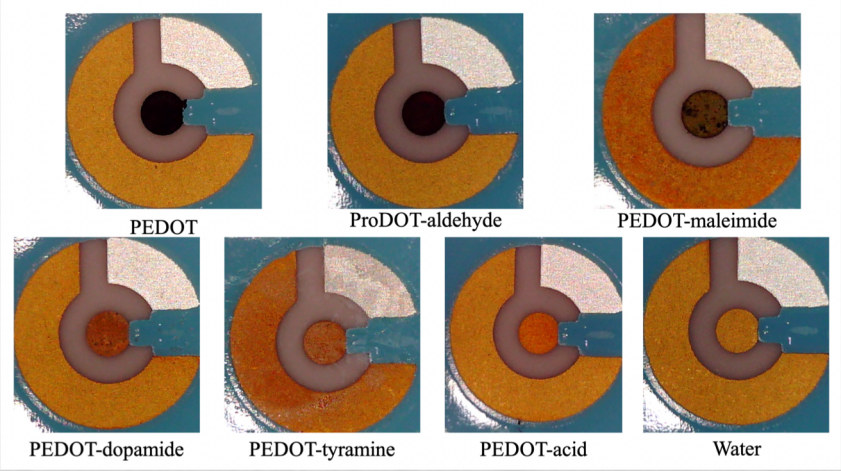


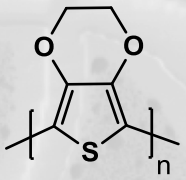


Ouyang, et al., **Science Advances**, 3: e1600448, (2017).

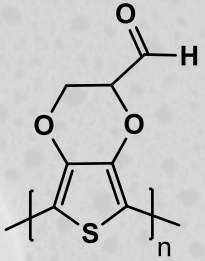
Bin Wei

Functionalized EDOT monomers

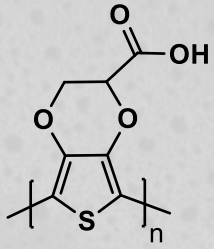




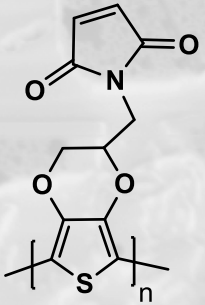
PEDOT



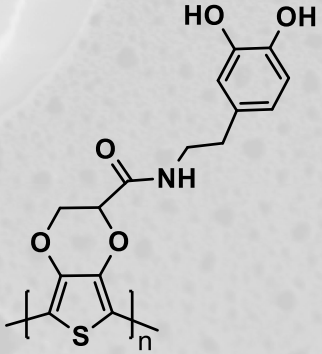
PEDOT-aldehyde



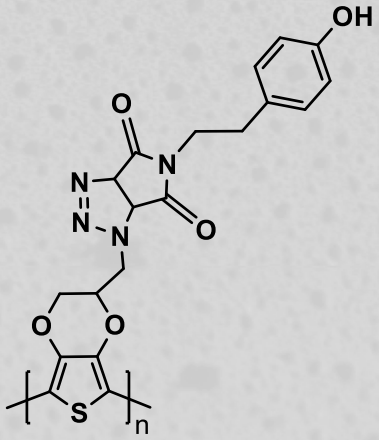
PEDOT-acid



PEDOT-maleimide



PEDOT-dopamide



PEDOT-tyramine

Samadhan Nagane, Peter Sitarik, Yuhang Wu, Quintin Baugh, Shrirang Chhatre, Junghyun Lee, and David C. Martin, "Functionalized Polythiophene Copolymers for Electronic Biomedical Devices", MRS Advances, 1-14, (2020). http://dx.doi.org/10.1557/adv.2020.3

Mag = 2.67 K X 1 µm WD = 4.9 mm EHT = 5.00 kV Signal A = InLens ESB Grid = 500 V Date :20 Oct 2011 Time :16:36:18
Auriga 60-39-95 FIB Imaging = SEM Noise Reduction = Line Int. Done FIB Probe = 30KV:50pA System Vacuum = 1.38e-006 mbar