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Materials Challenges in ZnO/Conjugated Polymer Photovoltaic Devices

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Sandia and NREL LDRDs, BES core, CINT

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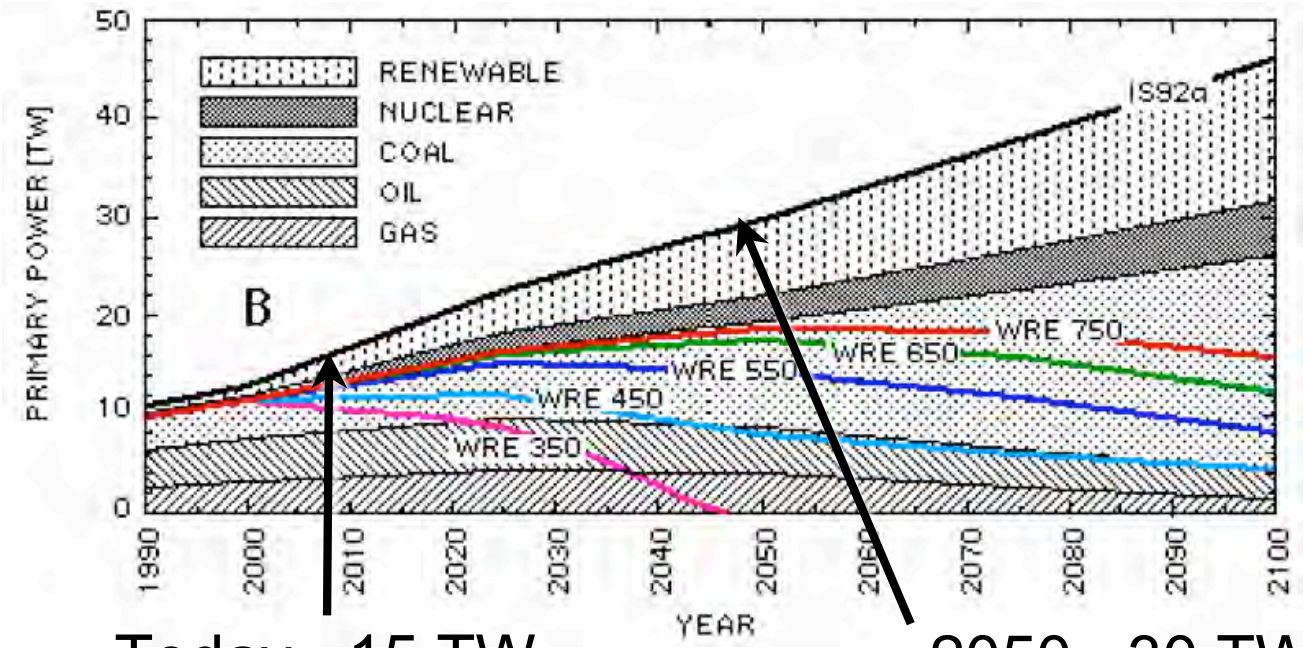
Total Primary Power vs. Year



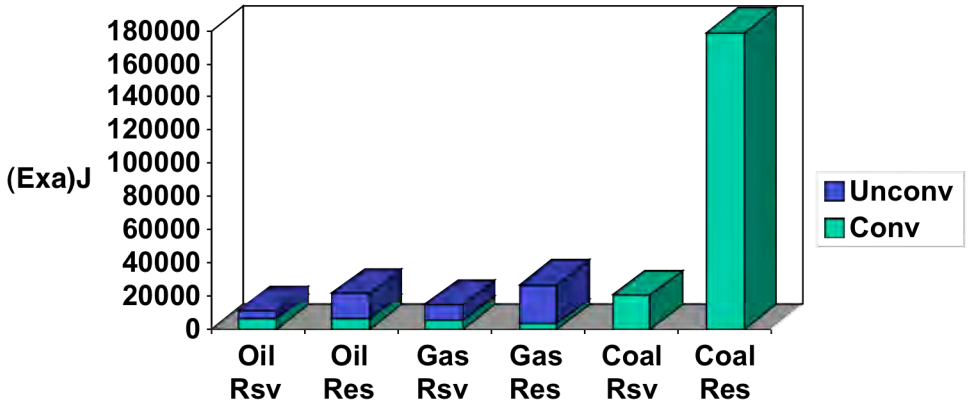
Today ~15 TW

2050 ~30 TW

- US: 5% population; ~ 15% energy production; ~ 1/4 of energy consumption
- From what source will this energy come?
  - Impact on climate change

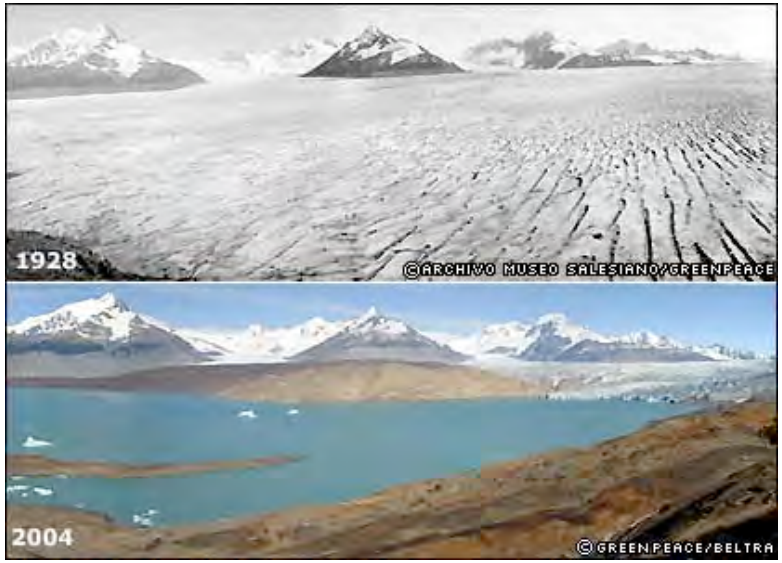
N. Lewis, http://nsl.caltech.edu/energy.html

Environmental Impact

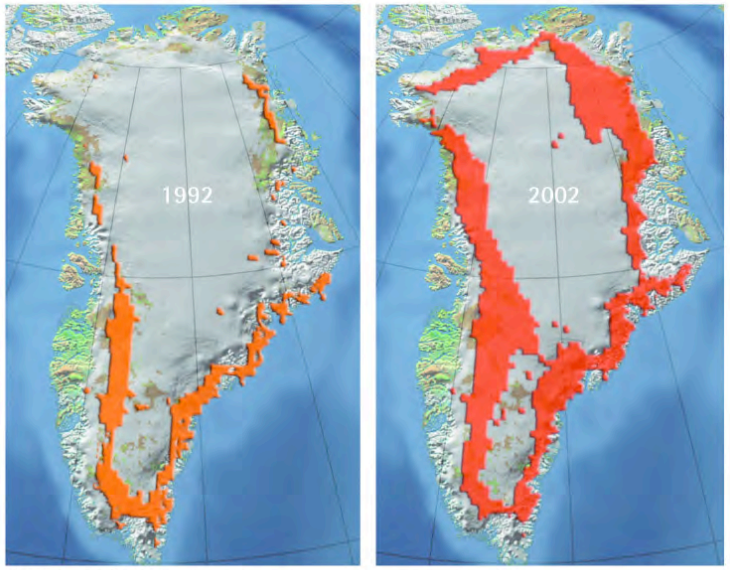


- Oil: 50-150 yr; Gas: 200-600 yr; Coal: 2000 yr
- Bottom line: Abundant, inexpensive energy source based on fossil fuels
- But ….
  - – CO_2 level skyrocketed
  - – Ocean temperature increases
  - – Glacier melting, Coral bleaching
- ***Need carbon-free power now!***

Argentina Upsala Glacier



Greenland Ice Sheet



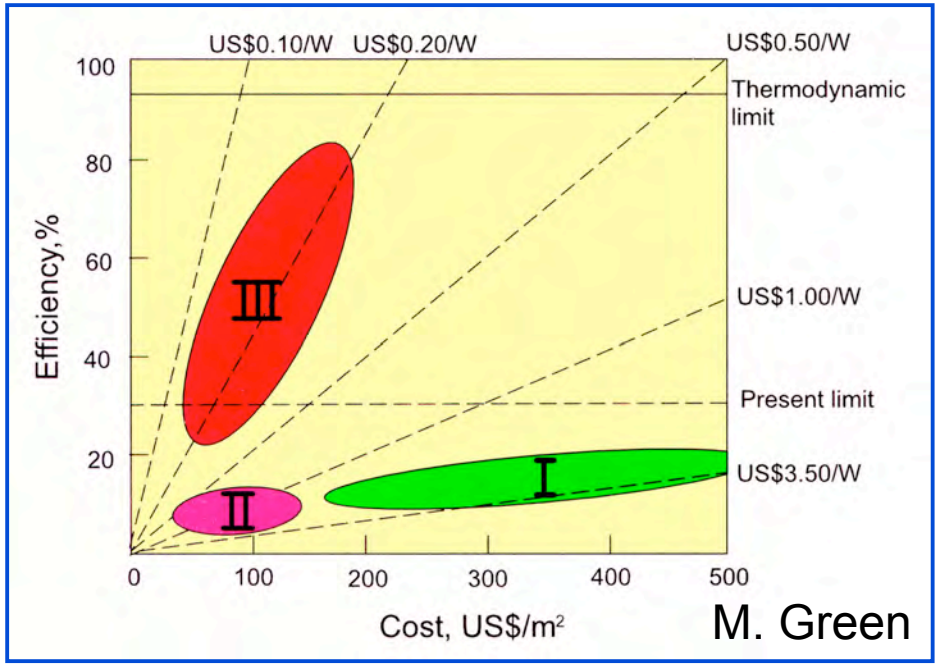
ratories

Promise of Solar Energy

- 1.2×10^5 TW solar energy potential; Other renewables: not enough potential
  - Energy in 1 hr of sunlight ↔ 14 TW for current consumption in a year
  - Generating 20 TW with 10% efficient solar farms requires 0.2% of Globe
- Clean
- Nuclear (fusion & fission)
  - 10 TW = 10,000 GW reactors → a new reactor every other day for the next 50 yrs!
  - Depletion of known reserves after ~ 10 yr

"Problem"

- Coal: 1-4 ¢/kW-hr
- Gas: 2.3-5 ¢/kW-hr
- Oil: 6-8 ¢/kW-hr
- Solar: 20-25 ¢/kW-hr



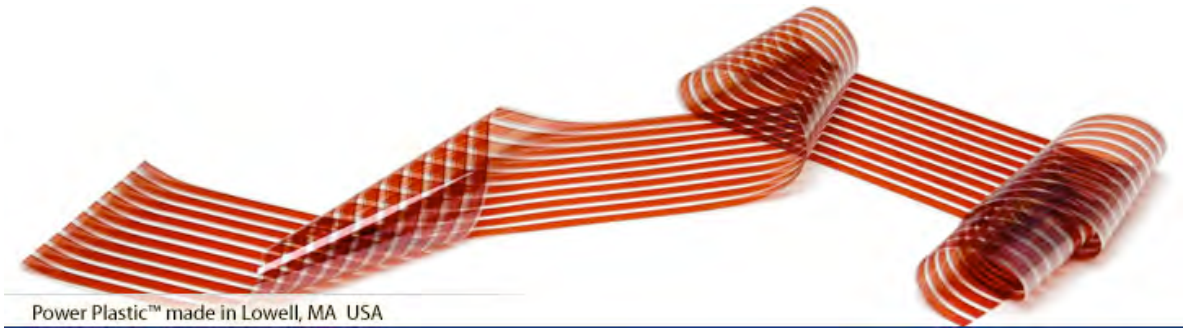
Solar Cells (Photovoltaics)

Basic requirements:

- Light absorption → excitations (e.g. e-h pairs, excitons)
- Carrier separation (e.g. exciton dissociation)
- Carrier transport and collection

Goals of Organic and Hybrid Photovoltaics (OPVs):

- Printed at high speed on flexible substrates
- Using roll-to-roll processing
- Low materials and balance of systems costs
- Near term goal: 5 - 10% efficiency, lifetime 10,000 hrs
- Long term goal: 15% efficiency, lifetime > 3 - 5 yrs

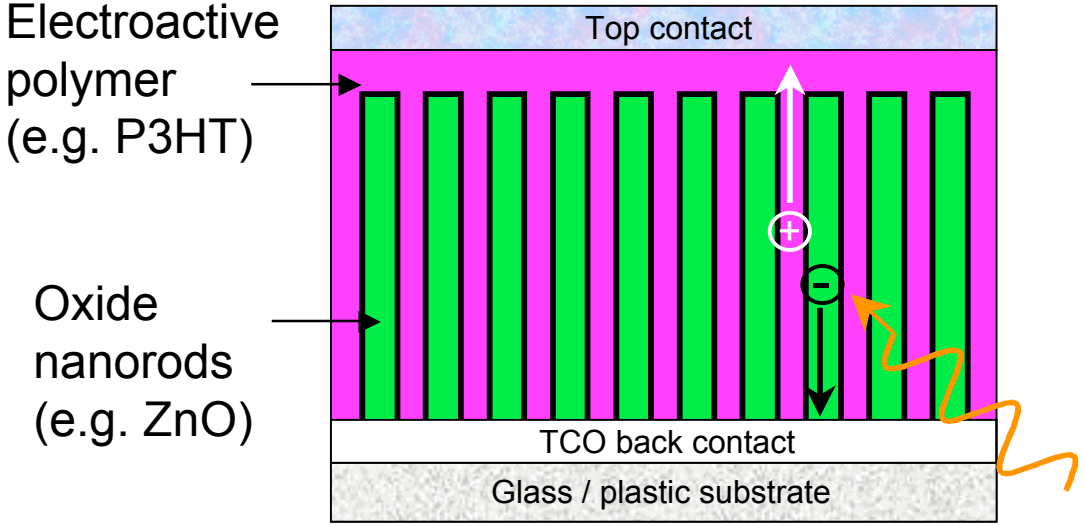


Konarka, http://www.konarka.com

Outline

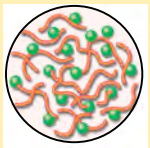
- Nanostructured Oxide - Conjugated Polymer Solar Cells
- Solution Growth of ZnO Nanostructures
  - Control seeding and growth to achieve dense nanorod arrays
  - Using organic modifiers to control morphology
  - Antireflection property vs nanoscale morphology
- Optimize Polymer Infiltration
  - Best device performance to date
  - Device lifetime
- Interfacial Issues
  - ZnO surface processing
  - Polymer morphology at the interface and its impact on device performance
- Oxide Engineering
  - Doping, alloying
  - Core-shell structures

Polymer-Oxide Hybrid Solar Cells



Proposed “ideal structure”

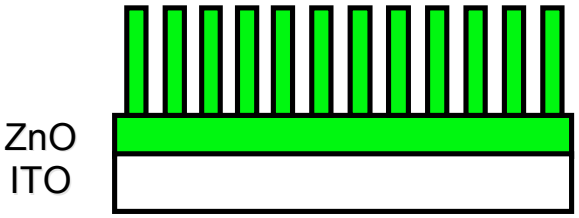
- Replacing PCBM (C60) as electron acceptor/transportor in organic photovoltaics
- Ordered vs. random network in bulk heterojunction



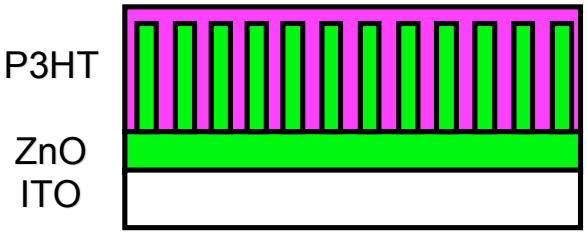
- Advantages of hybrid over pure organic:
  - High electron mobility in crystalline oxides compared to organics
  - Environmental stability
  - Control band alignments through alloying and/or doping of oxides
  - Line of sight conduction path for electrons and holes
  - High interfacial areas, solution processes

Fabrication of Hybrid PV Devices

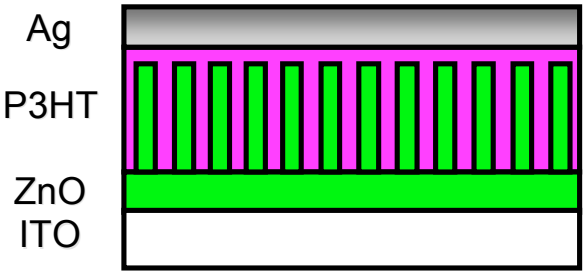
Deposit seed layer on TCO



Fiber growth from dilute aqueous solution



Infiltrate polymer among oxide nanostructures



Deposit top contact

- Challenges:
  - ZnO nanorod spacing must match exciton diffusion length (~10 nm)
  - Complete polymer infiltration while maintaining crystallinity (hole mobility)
  - Efficient charge transfer at P3HT-ZnO interface

Solution Growth of ZnO Nanostructures

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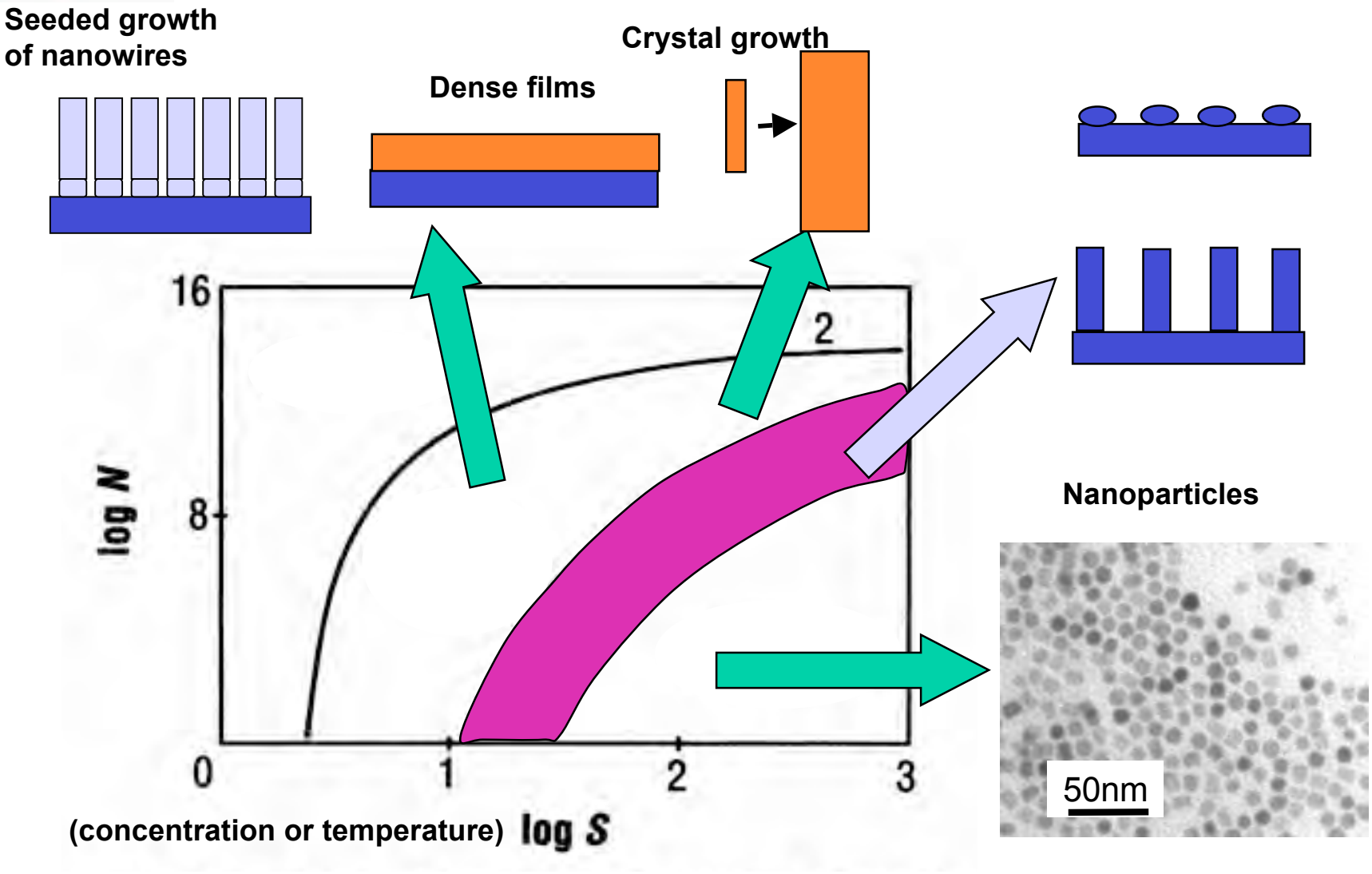
Solubility Diagram for Controlled Nucleation



Bunker et al. Science, 264, 48, 1993

Controlling ZnO Morphology

Growth:

HMT recipe (pH = 6.5)

L. E. Greene et al., *Nano. Lett.* **5**, 1231 (2005)
Y.-J. Lee et al., *J. Crys. Growth* 304, 80 (2007)

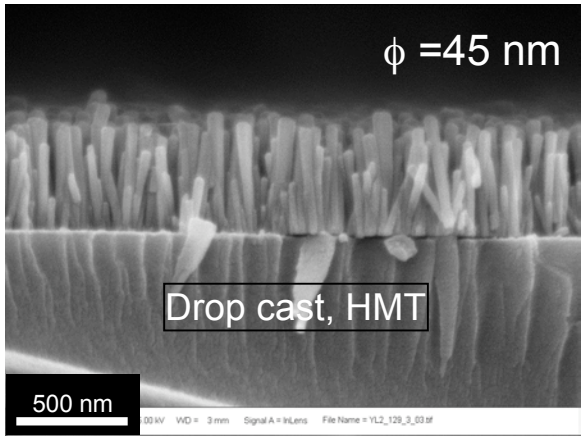
NaOH recipe (pH = 13.2)

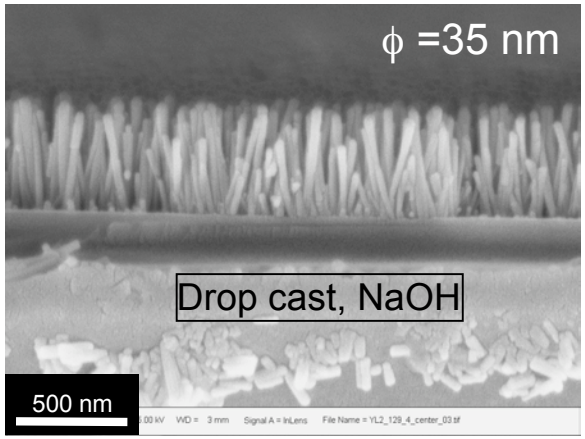
C. L. Peterson et al., *Langmuir* **20**, 5114 (2004)
D.C. Olson et al., *Thin Solid Films* **496**, 26 (2006)

Seeding:

Drop cast (Ordered)

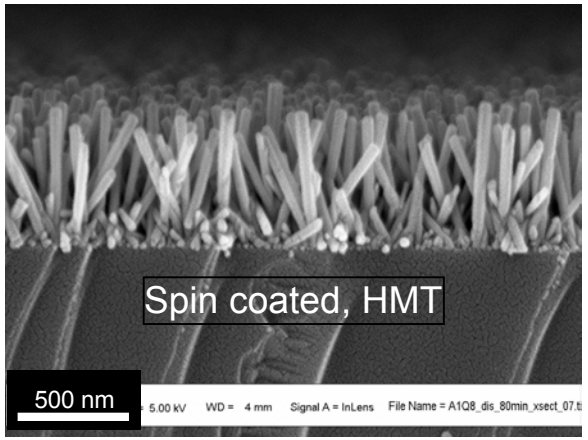
L. E. Greene et al., *Nano. Lett.* **5**, 1231 (2005)

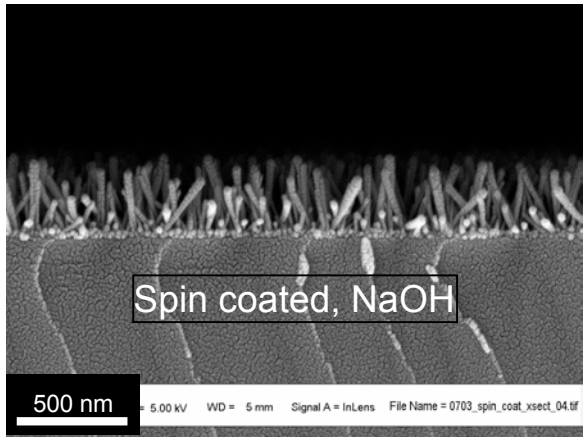




Spin coated (Disordered)

D.C. Olson et al., *Thin Solid Films* **496**, 26 (2006)





- Seed layer controls rod alignment
- Growth chemistry controls rod diameter
- Growth time controls rod length

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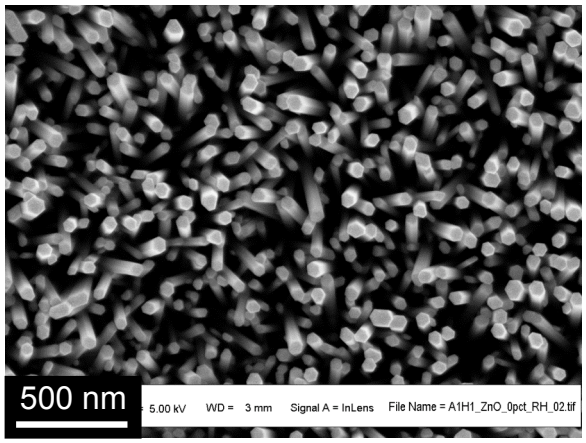
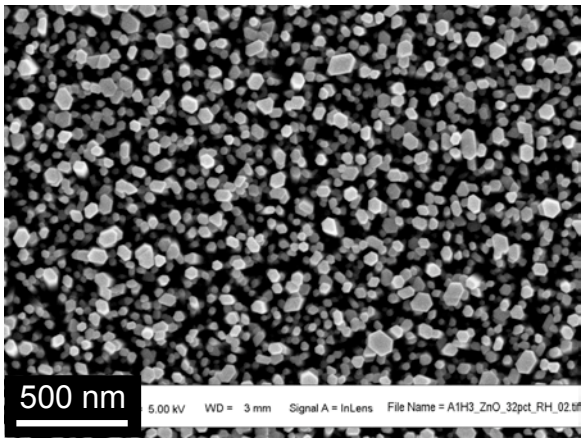
Humidity during Seeding Affects NR Growth

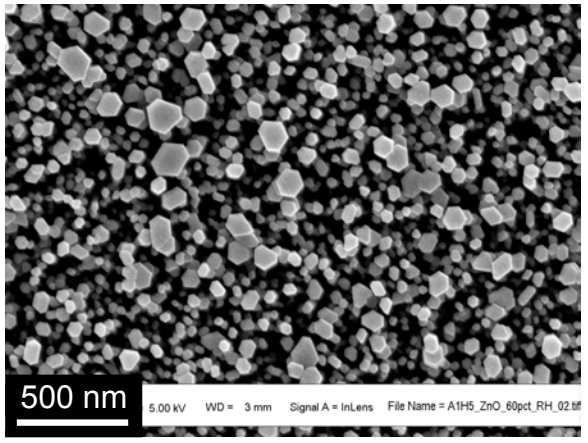
•Y. Lee, et. al. J. Crys. Growth 304, 80 (2007)



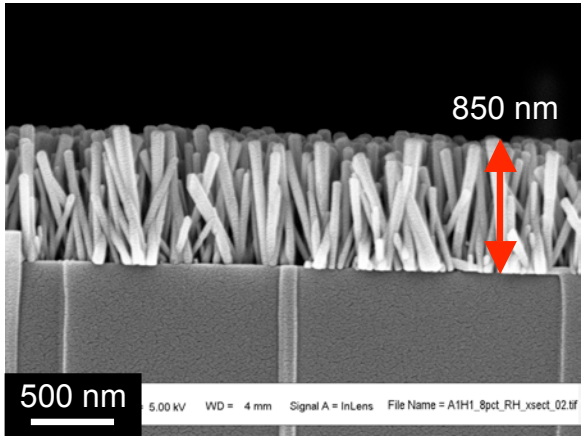
8% RH

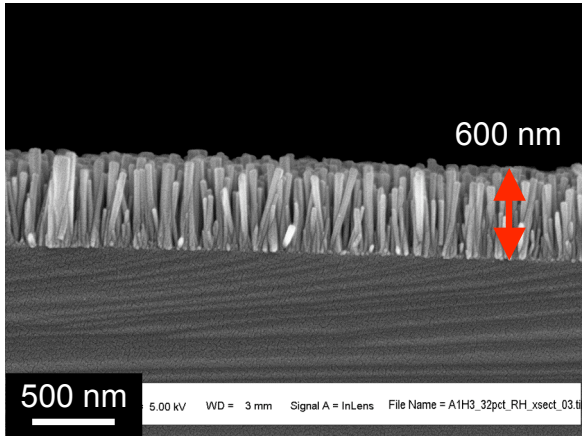


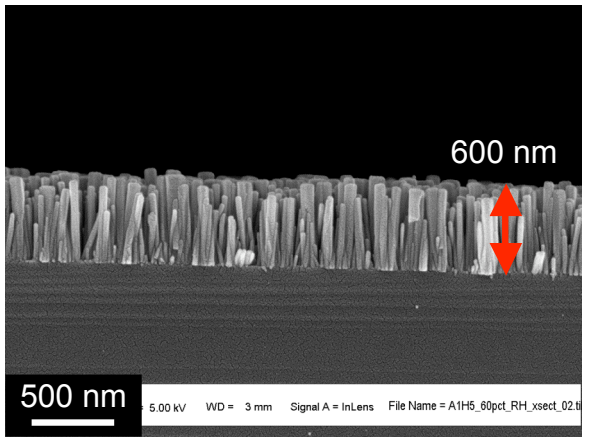
32% RH



60% RH



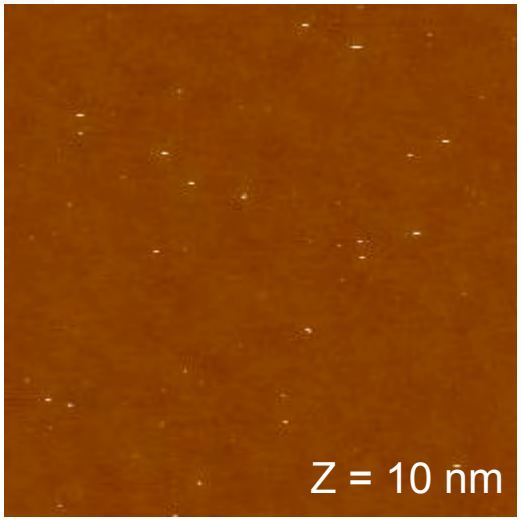




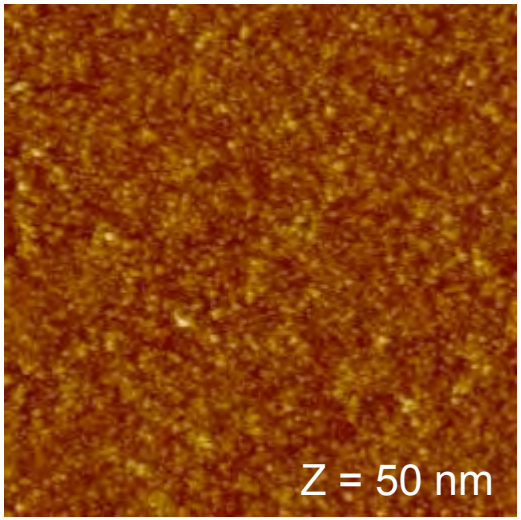
- Decreased rod diameter and film thickness at RH ≥ 20%
- Increased rod alignment and packing density at RH ≥ 20%
- Increased polydispersity in rod diameter and length at RH ≥ 60%

Origin of Alignment: Seed Density

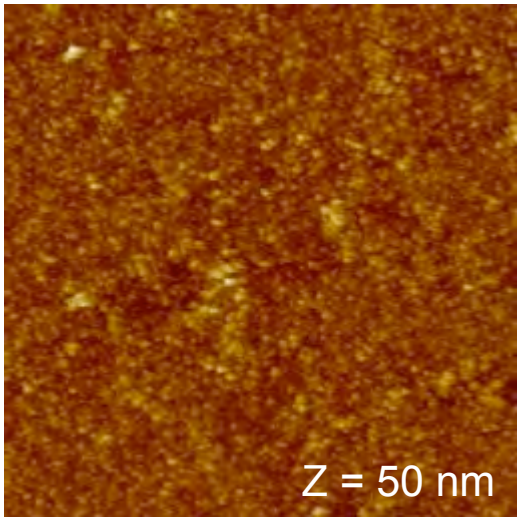
AFM images
5 μm x 5 μm



8% RH



32% RH



60% RH

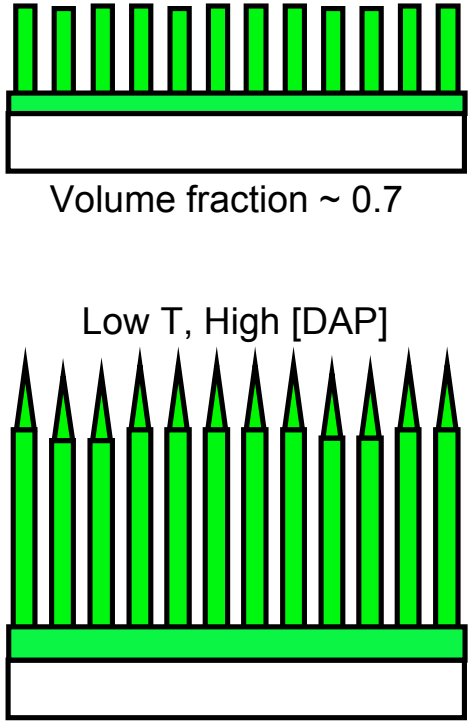
RH (%)	Contact angle (deg)	Roughness (nm)
8	11 ± 2	0.17 ± 0.03
32	73 ± 1	2.96 ± 0.13
60	78 ± 2	2.86 ± 0.34
Bare Si	6 ± 3	0.32 ± 0.13

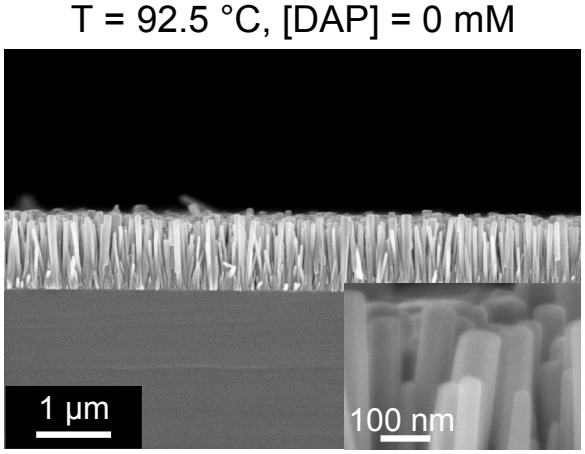
H_2O from atmosphere is required to convert $Zn(OAc)_2$ into a EtOH-insoluble form

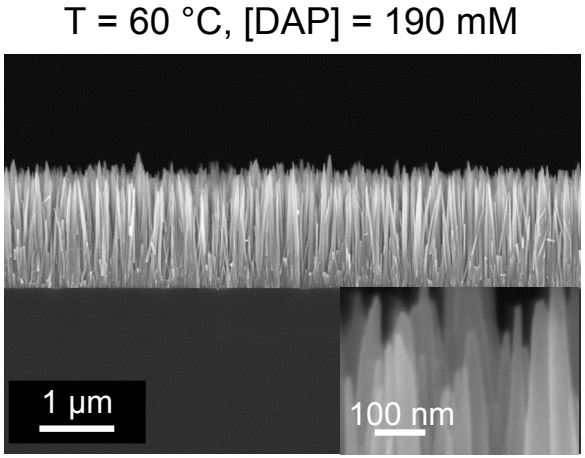
Varying Nanorod Array Morphology

1. Seed substrate

2. Deposit NRA





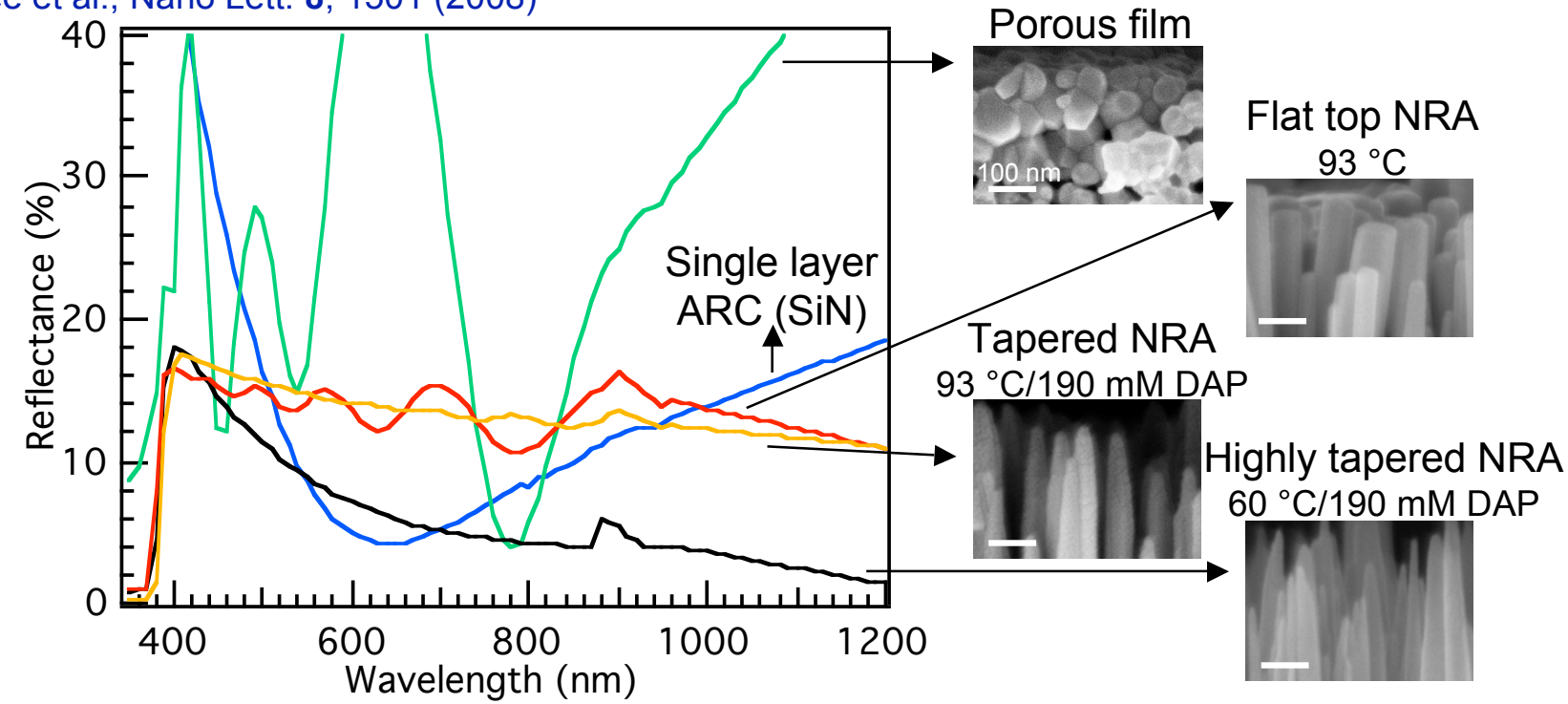


- T. F. Sounart et al., *Adv. Func. Mat.* **16**, 335 (2006)
- Y.-J. Lee et al., Cryst. Growth Des. **8**, 2036 (2008)

How does NRA morphology affect antireflection coating (ARC) performance?

ARC Performance Depend on Nanostructure Morphology

Y.-J. Lee et al., Nano Lett. **8**, 1501 (2008)

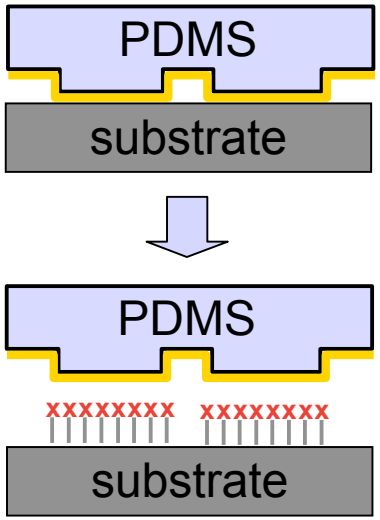


Sample	R_w (%)
SLARC	7.8
Porous film	30.3
Flat top NRA	12.2
Tapered NRA	13.6
High tapered NRA	6.6

- NRA has more broadband suppression of reflectance vs. SLARC
- Alignment of pores significantly decreases reflectance
- Highly tapered NRA leads to better performance than SLARC

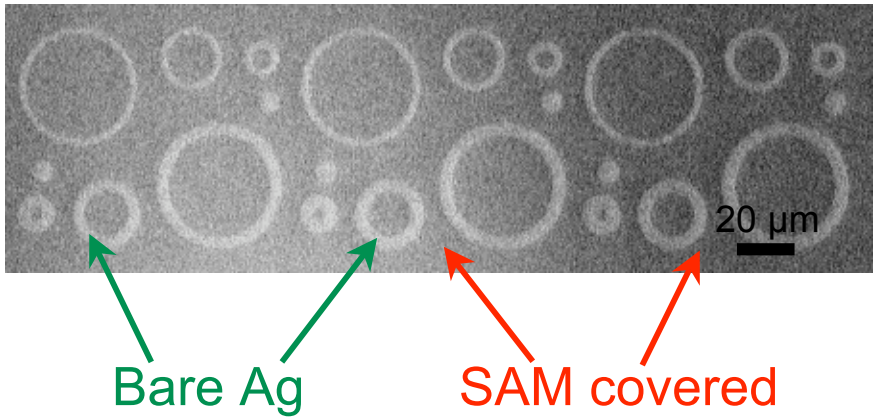
Selective Growth using Organic Templates

Microcontact Printing



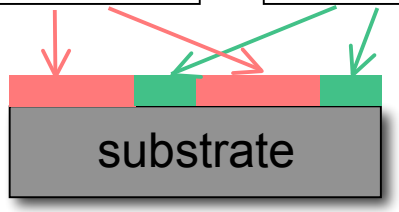
$HSC_{10}H_{20}COOH$
$HSC_{15}H_{30}CH_3$

Nano Lett 5, 83 (2005)



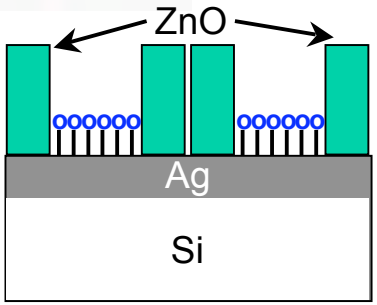
SAM:
High energy regions
little/no nucleation

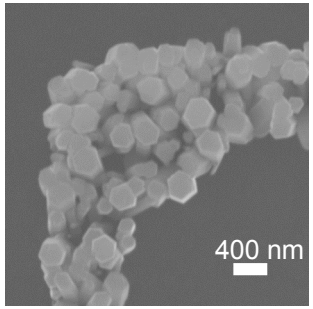
Bare Ag:
Low energy regions
Favor crystal nucleation

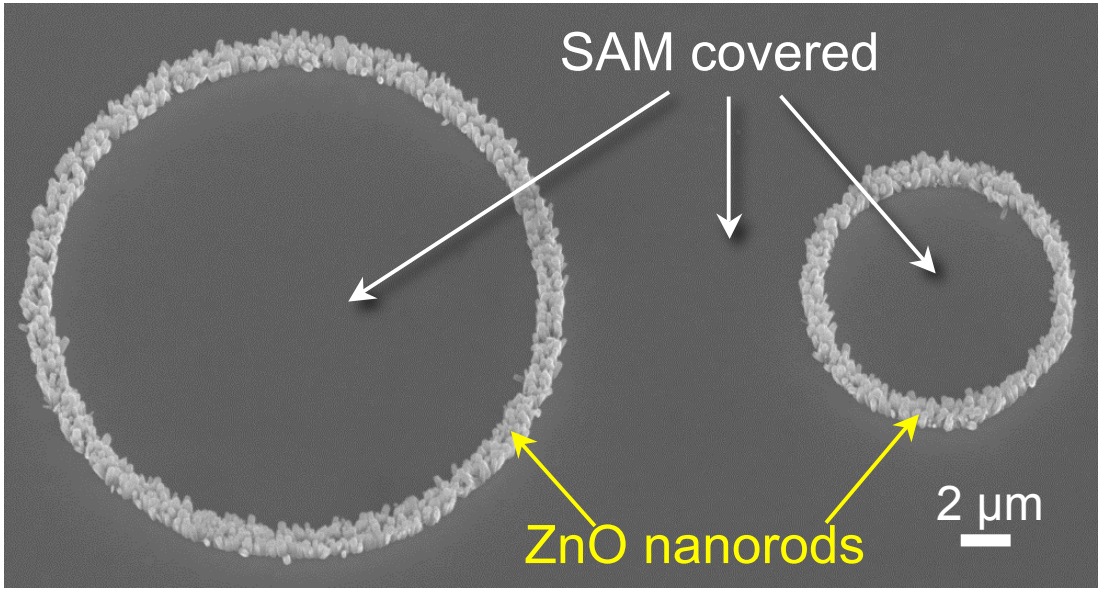


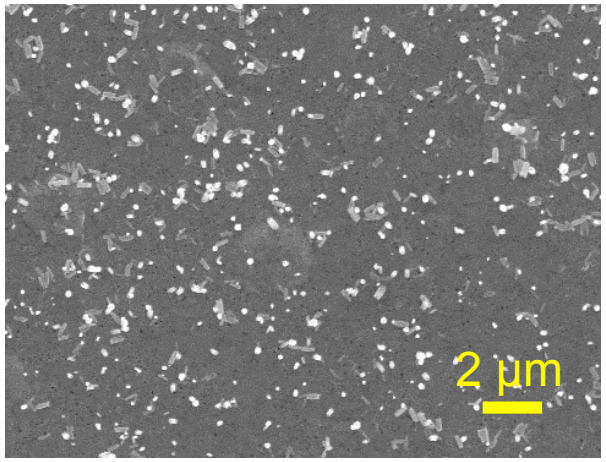
Nano Lett 5, 83 (2005)

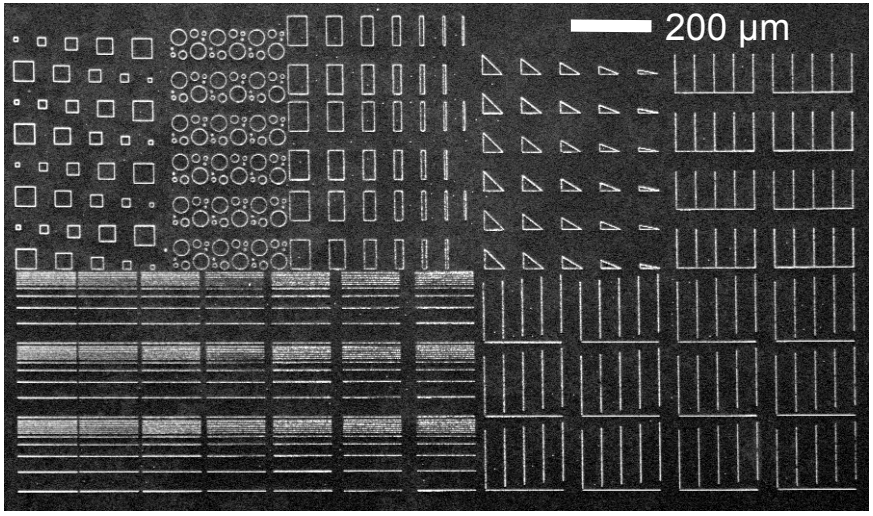
Selective ZnO Growth on Ag











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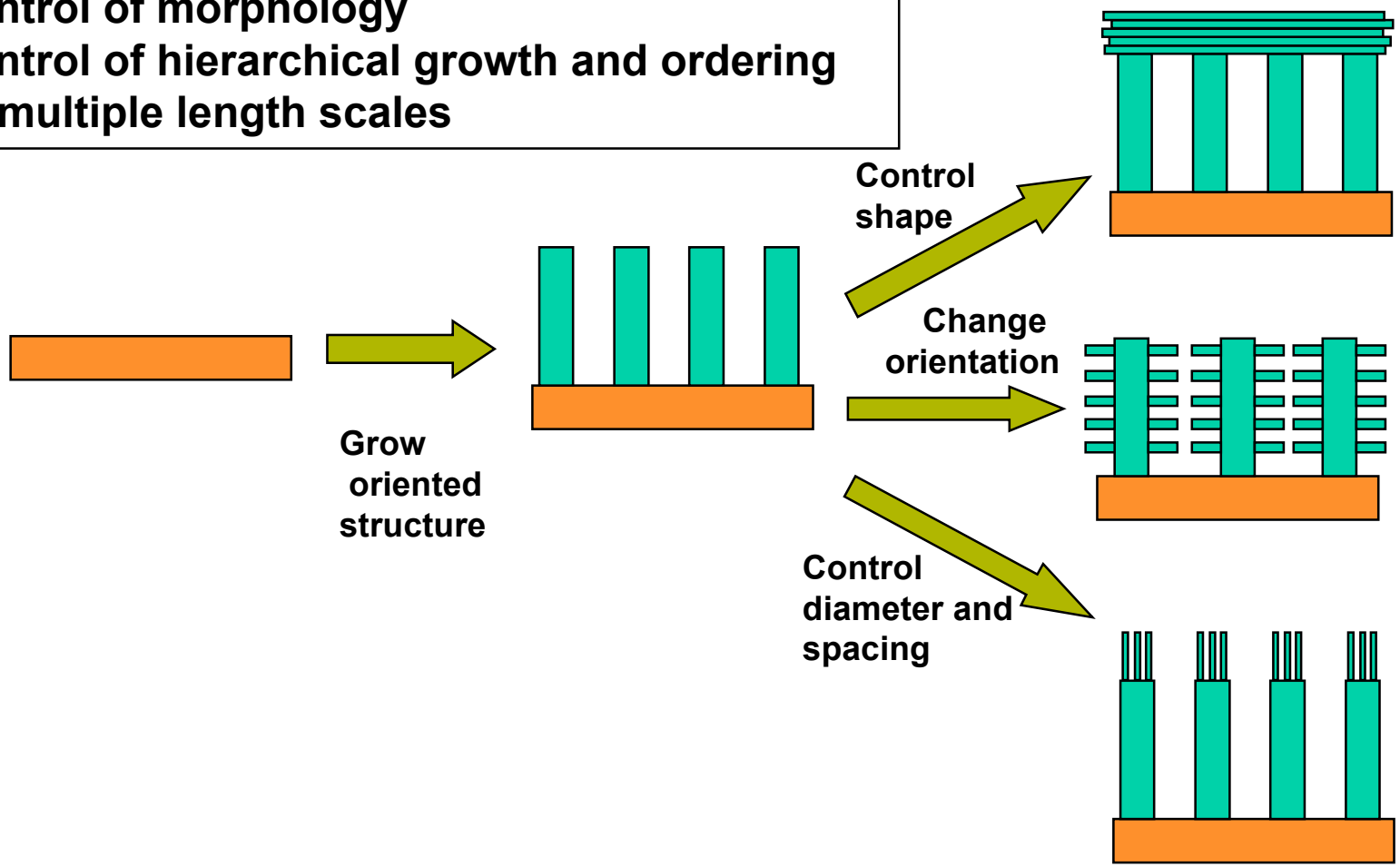
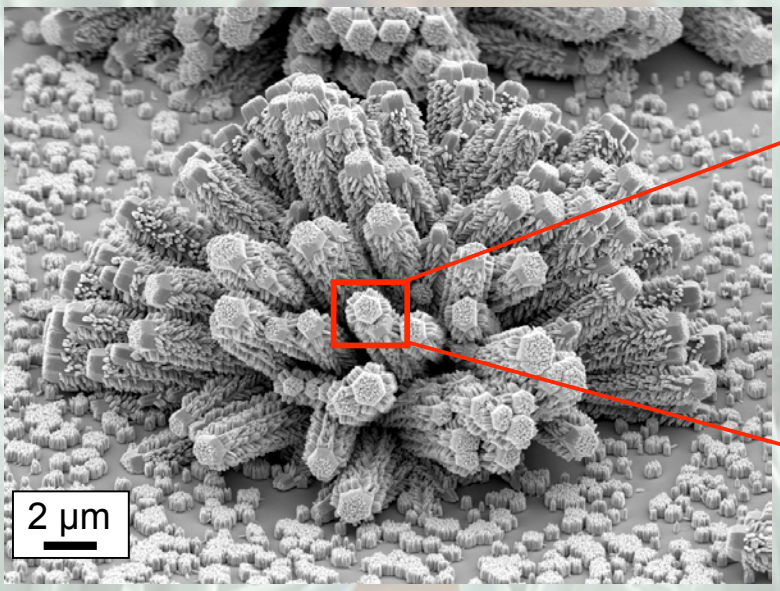
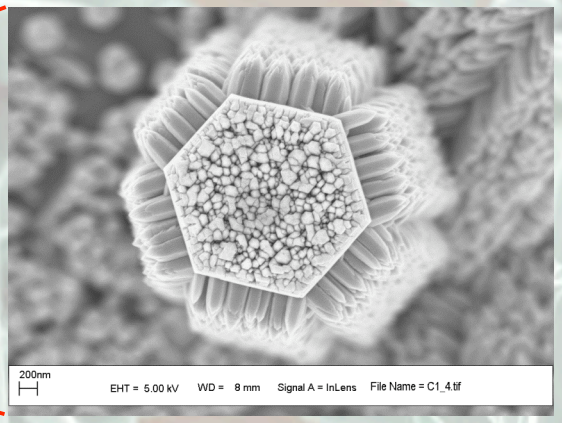
Growth of Complex Nanostructures through Controlled Chemical Synthesis

1. Control of nucleation, growth and orientation
2. Control of morphology
3. Control of hierarchical growth and ordering on multiple length scales

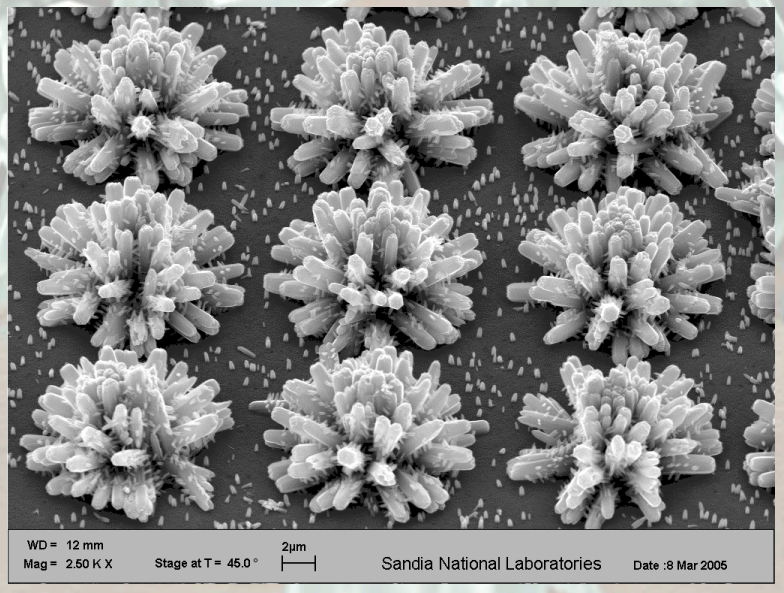


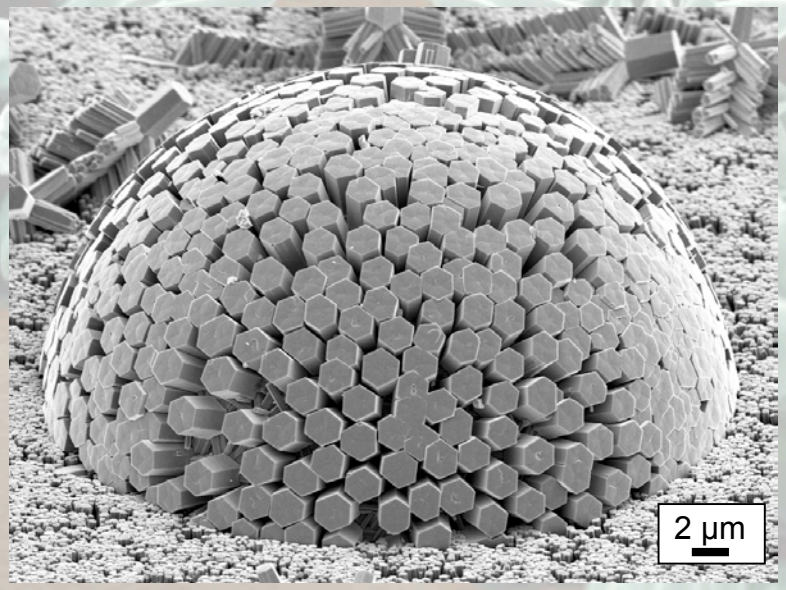
Growth Modifier + Multistage Growth





- J. W. Hsu, et. al. Nano Lett. 5, 83 (2005)
- T. Sounart, et. al. Adv. Func. Mater. 16, 335 (2006)





Optimization of Polymer Infiltration

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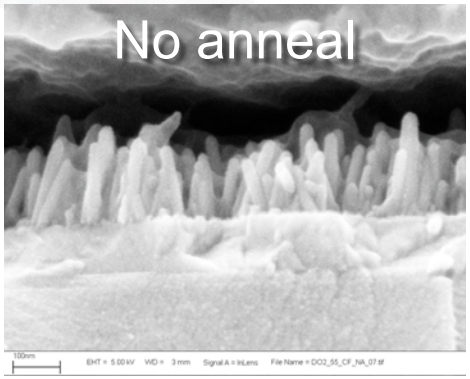
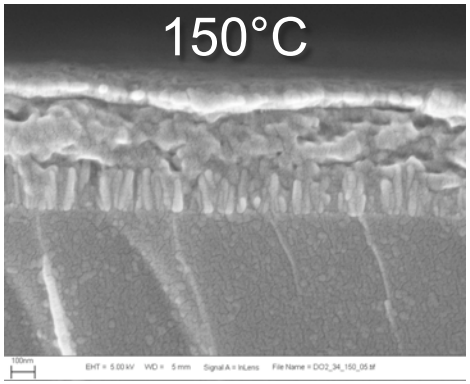
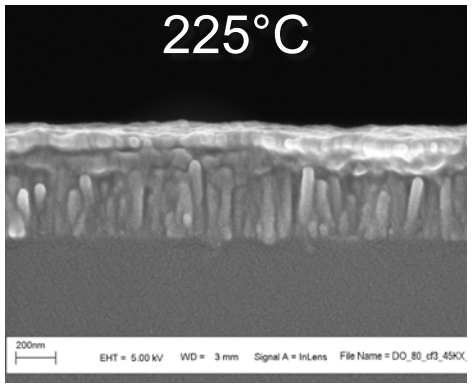
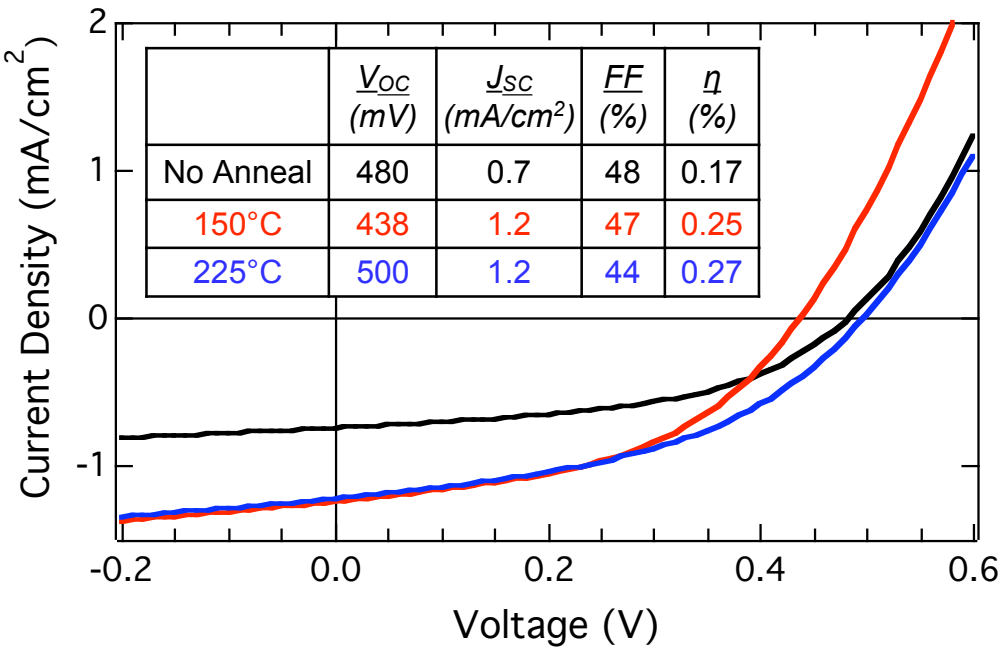
Heating Enhances Polymer Infiltration









	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF (%)	η (%)
No Anneal	480	0.7	48	0.17
150°C	438	1.2	47	0.25
225°C	500	1.2	44	0.27

- Polymer infiltration is greatly improved with annealing, which is reflected in the J_{SC}
- Dichlorobenzene is a better solvent than chloroform for infiltration; annealing provided additional enhancement

- D. C. Olson, et. al. J. Phys. Chem. C 111, 16640 (2007)

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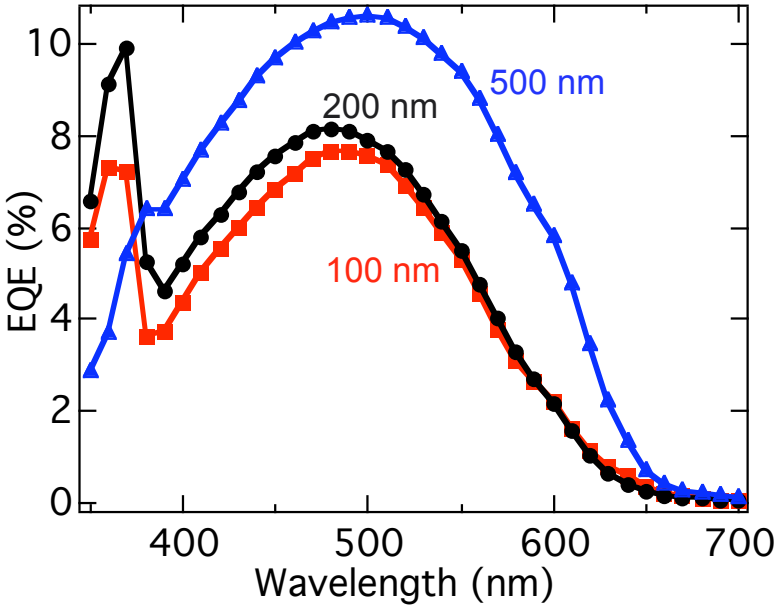
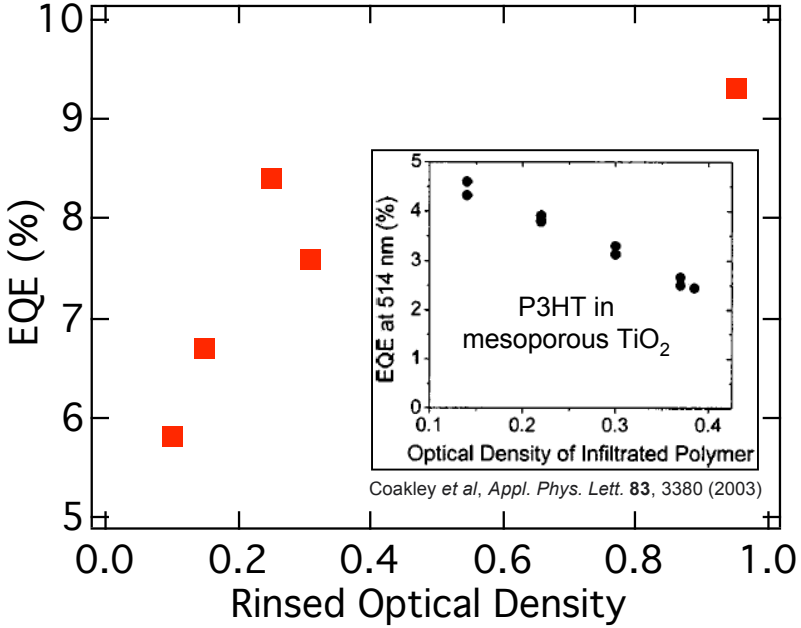
EQE Increases with Rod Length

EQE Spectra



Maximum EQE

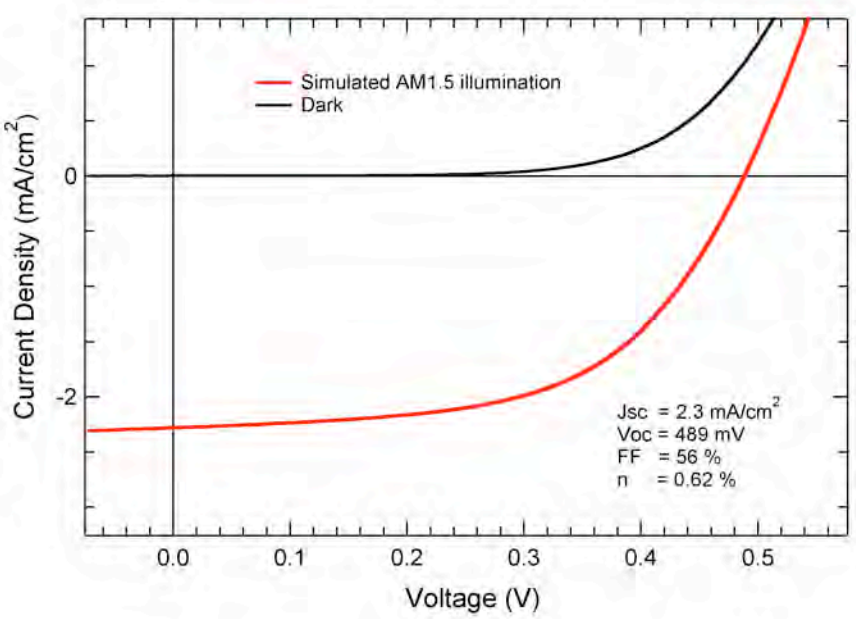


Coakley *et al*, *Appl. Phys. Lett.* **83**, 3380 (2003)

- Improvement in EQE with nanorod length/amount of polymer
- Opposite trend compared to P3HT in mesoporous TiO_2
- Hole transport apparently not an issue

- D. C. Olson, et. al. J. Phys. Chem. C 111, 16640 (2007)

Devices Do NOT Degrade in Air



J_{sc} = 2.3 mA/cm^2

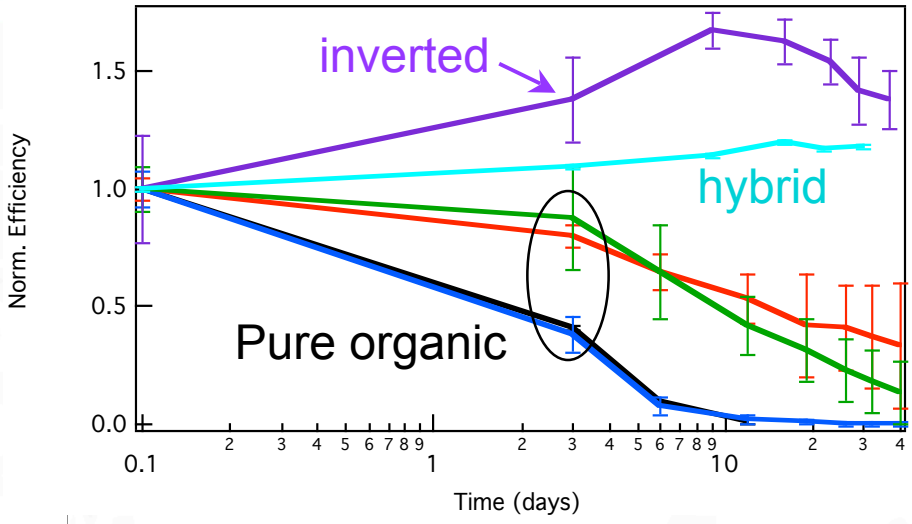
V_{oc} = 489 mV

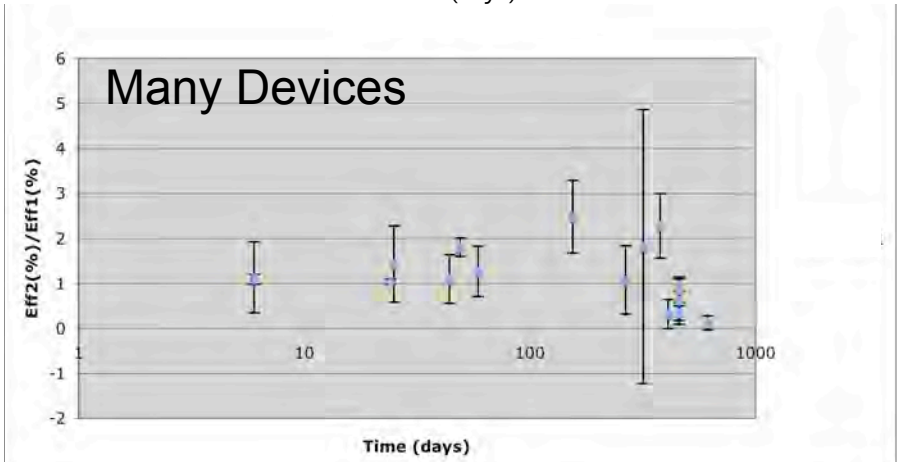
FF = 56%

η = 0.62 %

Not the highest efficiency
But they don't degrade!

Shelf Lifetime Study





Still works after 1 year!

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Interfacial Issues

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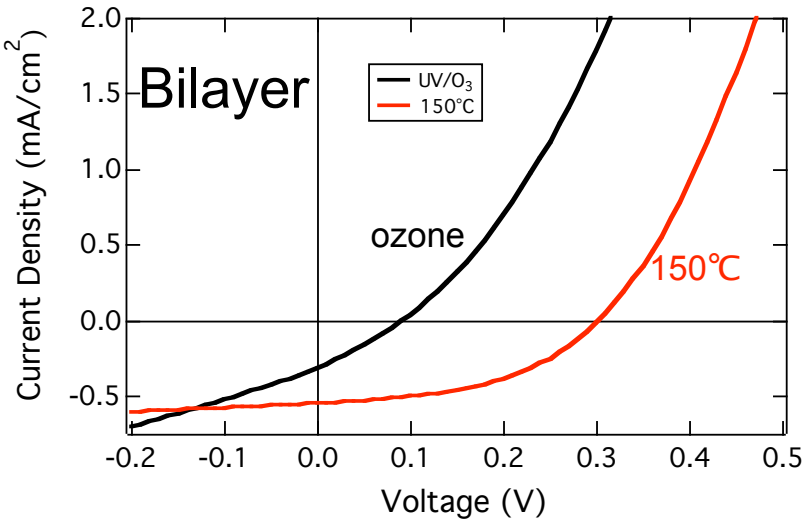
ZnO Surface Treatments Affect Device Performance

- Prior to polymer deposition, the ZnO are treated by:
  - UV ozone, 20 min.
  - Drying @ 150°C in air for 30 min.
- After ZnO treatment
  - Work function of ZnO is larger for the ozone treatment
  - No change in P3HT absorption spectra or infiltration

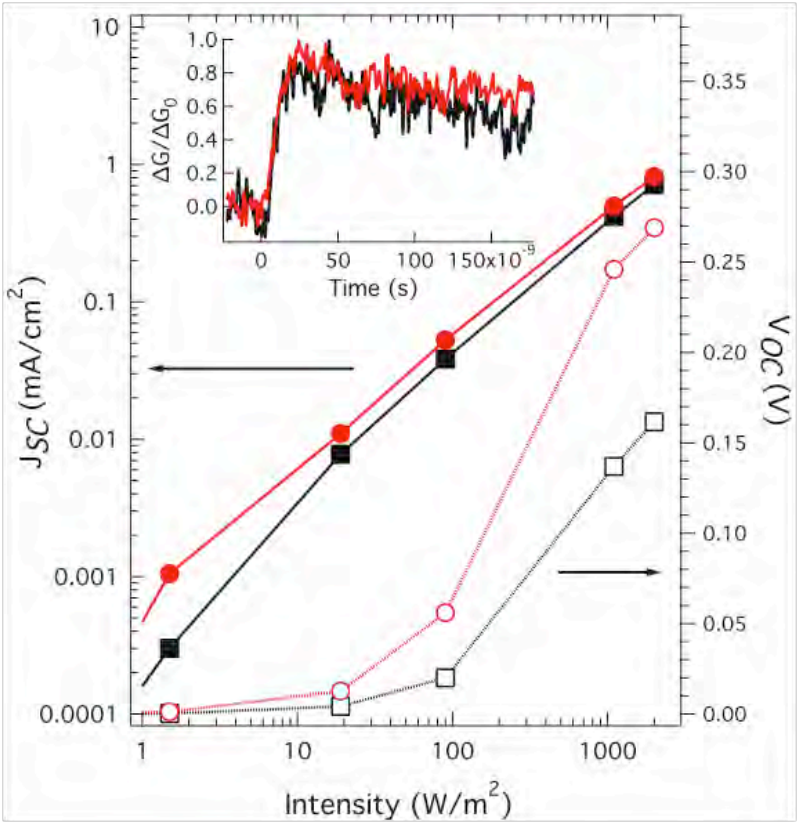


	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF (%)	η (%)
UV/O_3	100	0.31	26	0.01
150°C	310	0.55	46	0.08

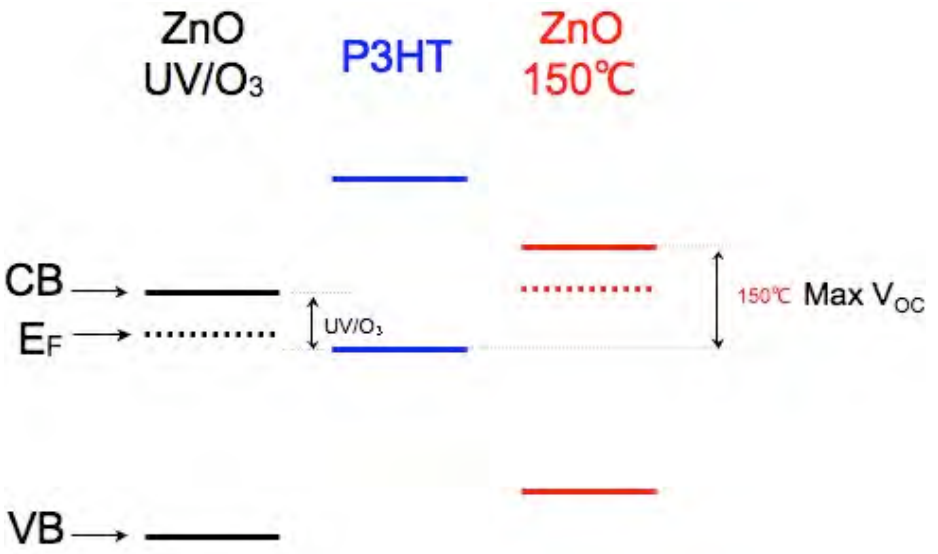
D. C. Olson, J. Phys. Chem. C, 10.1021/jp802626u

- Ozone treatment: Decreased V_{OC}, J_{SC}, FF, & η
- Device performance sensitive to interfacial treatment

Interfacial Dipoles



- Same intensity dependence for J_{sc} and V_{oc}
- Same dynamics in TRMC
- Power ~1 for J_{sc}: monomolecular recombination



- Most likely due to shift in band alignment at the interface
- Interfacial dipoles?
- Collaboration with Kuech (UW-Madison) to understand interfacial dipoles

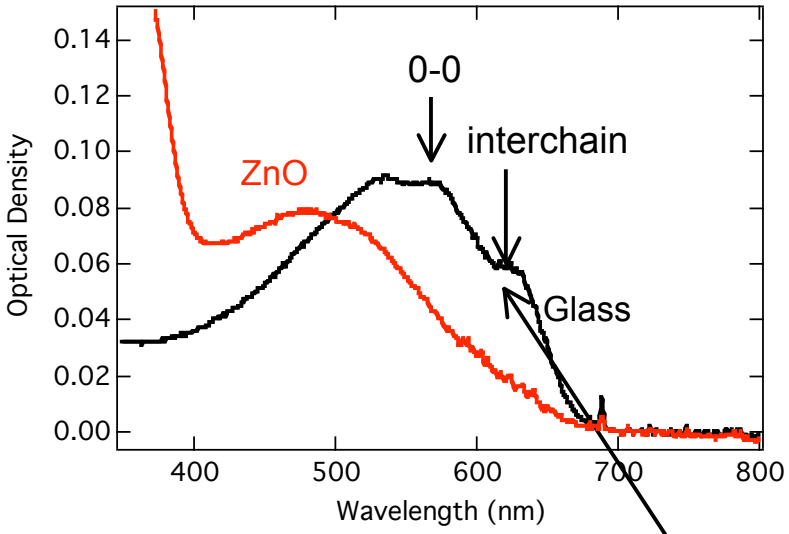
D. C. Olson, J. Phys. Chem. C, 112, 9544 (2008)

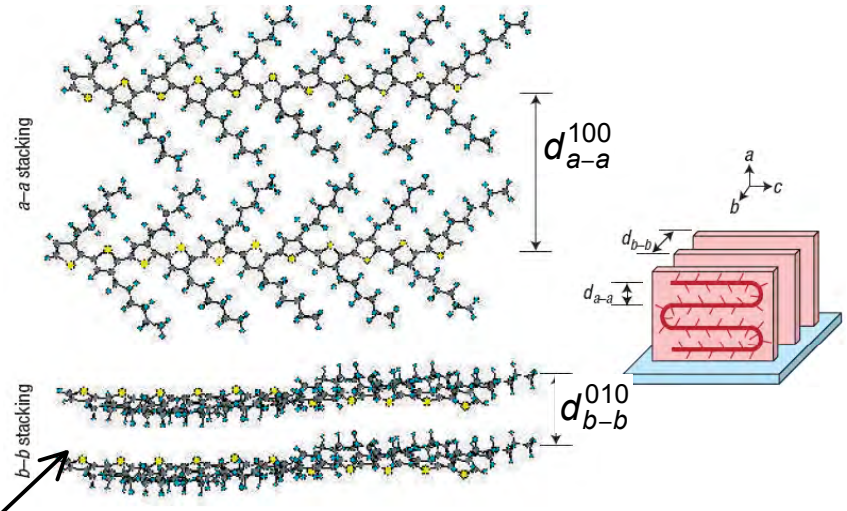
Disordered Polymer at ZnO Interface

- When P3HT is deposited on ZnO, the absorption and photoluminescence is blue shifted

*Kim *et al*, Nature Materials, **5**, 197

< 10 nm P3HT

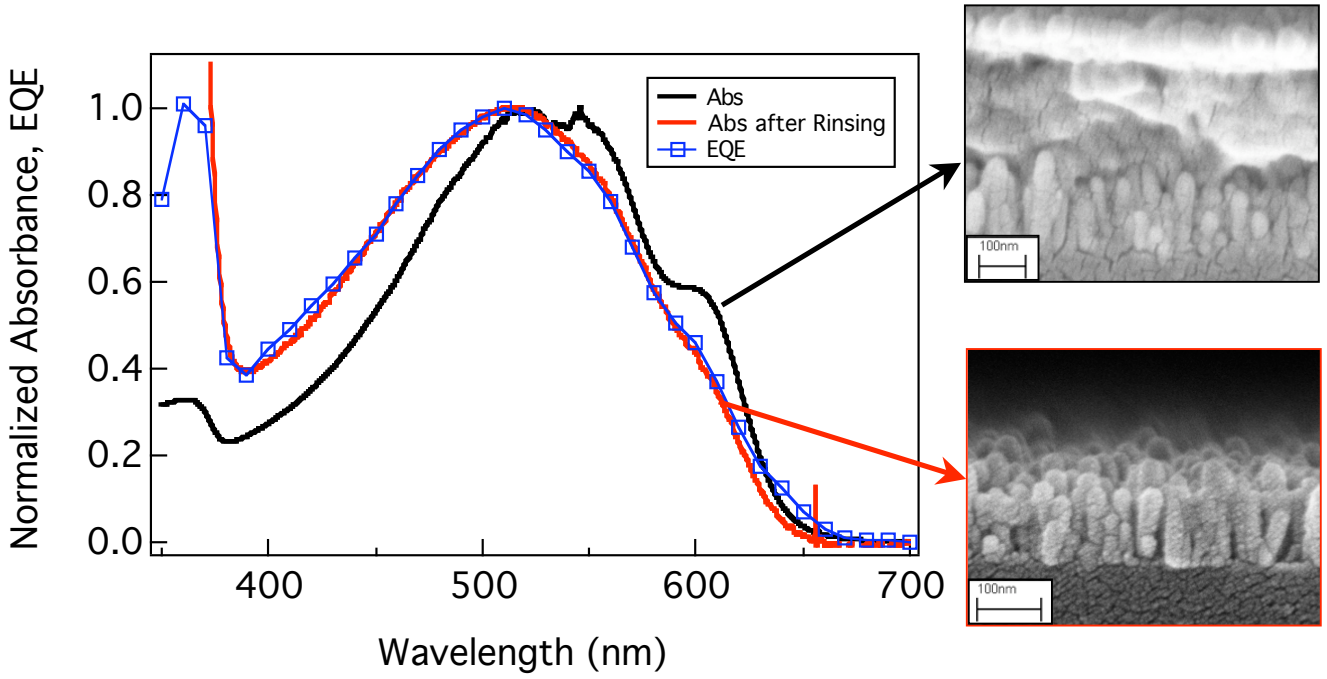




Related to π-π stacking

- Suggesting P3HT is disordered at the ZnO interface
- Blue shift is not observed on glass, quartz, Al_2O_3, TiO_2, ITO, or single crystal ZnO, I.e. surface effect

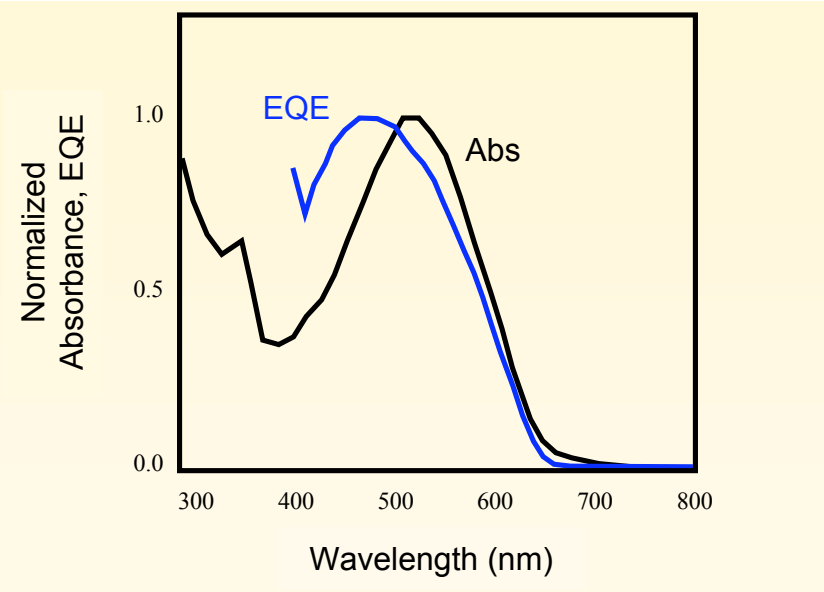
Impact on Solar Cells



- EQE spectra are also blue shifted compared to bulk absorption, but identical to the absorption spectra after top P3HT layer is rinsed off → infiltrated polymer is disordered
- EQE is sensitive to interfacial P3HT only, due to small exciton diffusion length (~ 5 nm)
- P3HT in the critical interfacial region is disordered, leading to...
  - Lower absorption
  - Impede exciton diffusion
  - Lower hole mobility

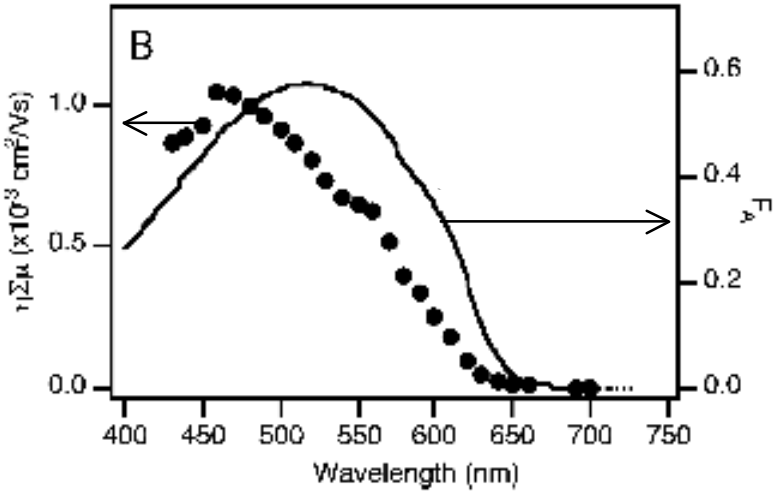
Blue Shift also Seen in Other Works

Absorbance vs. EQE



Beek *et al*, *Adv. Funct. Mater.*, **16**, 1112

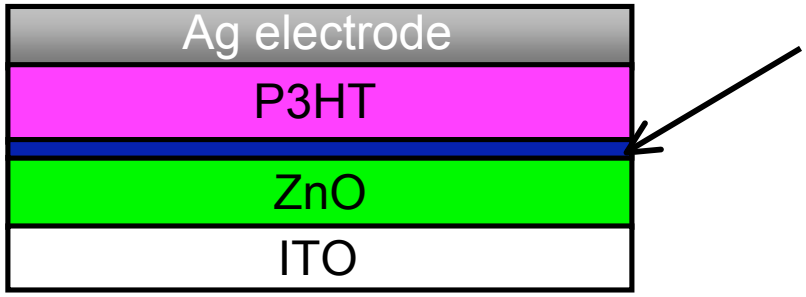
Microwave Conductivity Action Spectra



Quist *et al*, *J. Phys. Chem. B*, **110**, 10315

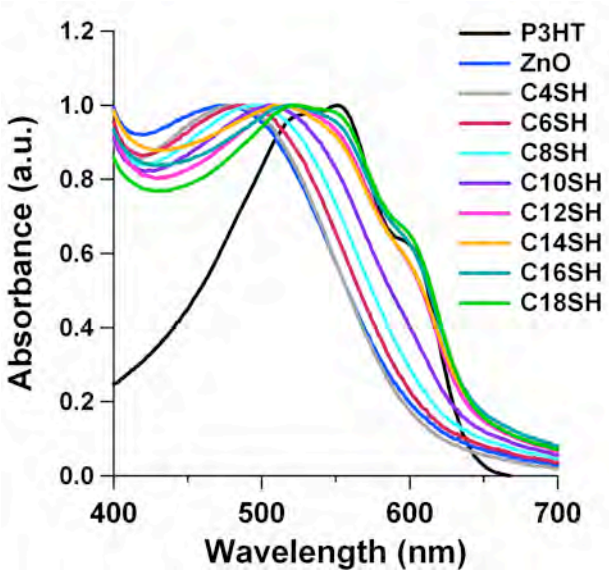
- Blue shift in EQE compared to bulk absorption of P3HT/ZnO nanoparticle devices
- EQE is blue shifted in bilayer devices, therefore it is not due to polymer confinement between rods
- Change in surface chemistry, electron transfer, or exciton dissociation processes

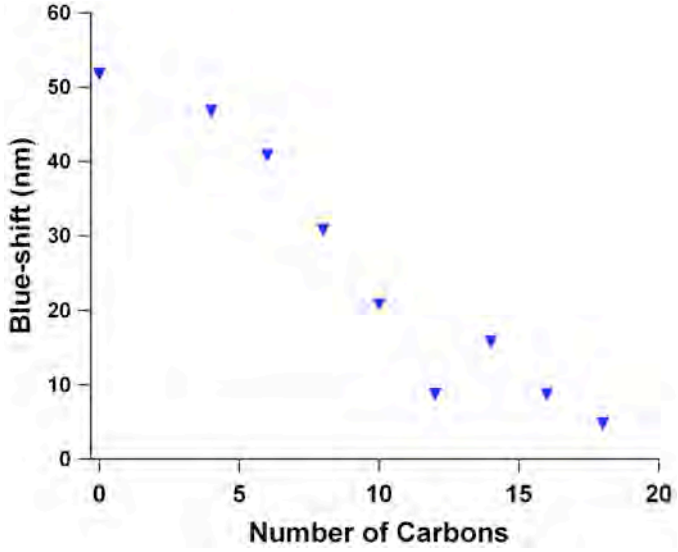
Interface Modification



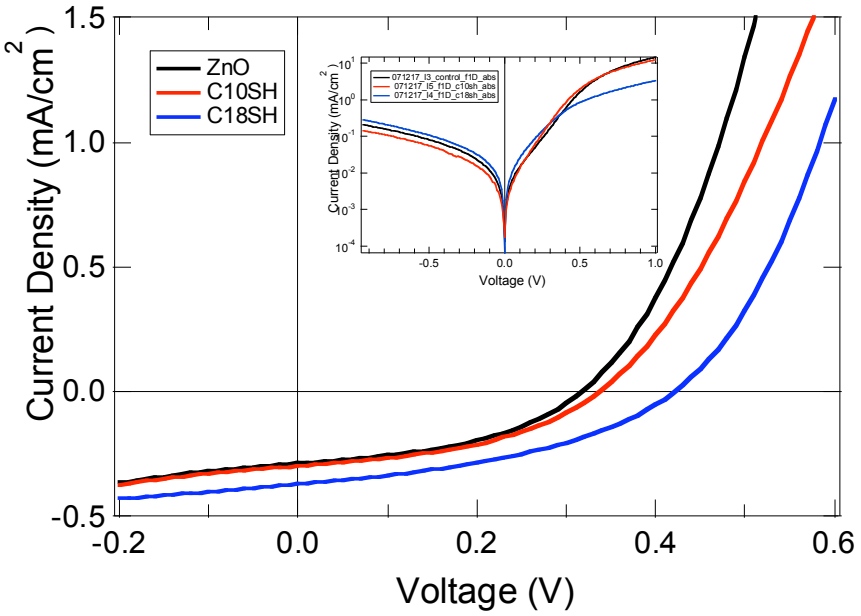
- Organic (molecular layer): catechol, dye, dopamine, C60, alkanethiol
- Inorganic (ALD): AlO_x, ZnO, TiO_x
- Use bilayer for model study

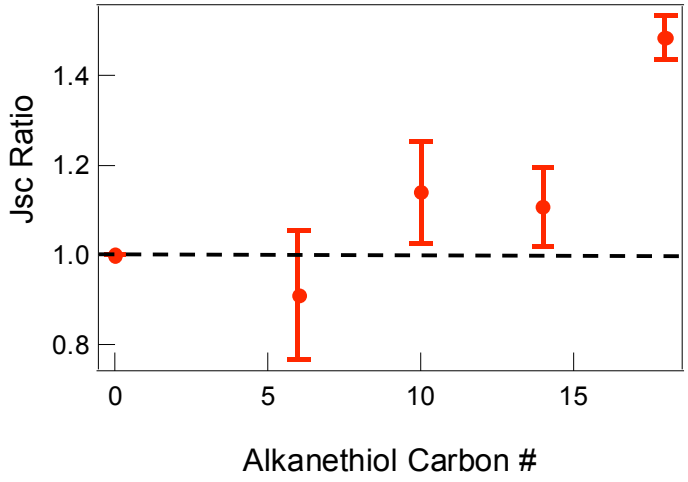
Alkanethiol:$CH_3(CH_2)_nSH$





Bilayer Devices with Alkanethiol Modification





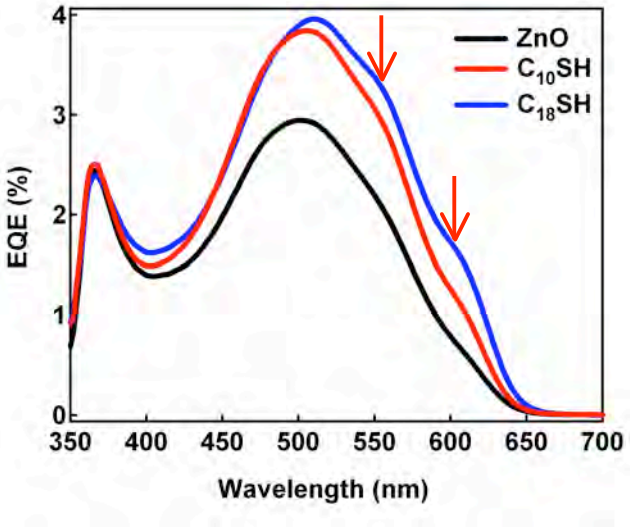
Sample	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF(%)	η(%)	R_{shunt} (kΩ cm^2)	R_{series} (Ωcm^2)
ZnO	317	0.288	43	0.040	4.9	68.9
$C_{10}SH$	337	0.300	43	0.043	3.0	81.5
$C_{18}SH$	422	0.372	40	0.063	2.3	303

- Series resistance increases for longer thiols. (Alkanethiol is insulating.)
- J_{sc} increases for longer thiols!

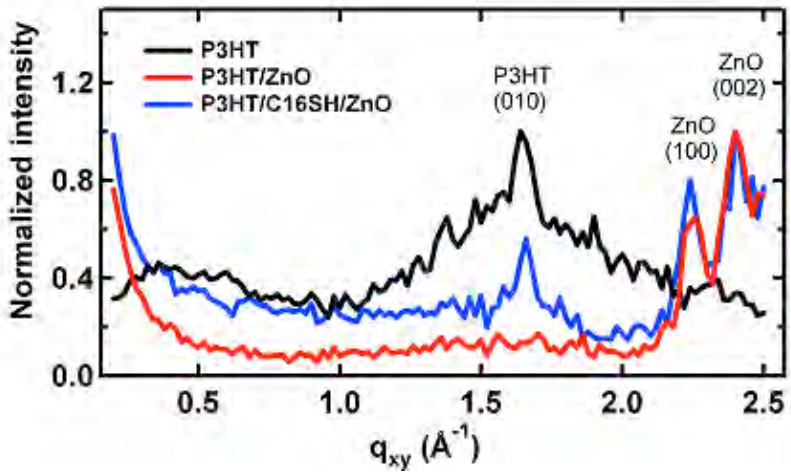
T. C. Monson, Adv. Mater. In press

Alkanethiol Induces Polymer Crystallinity

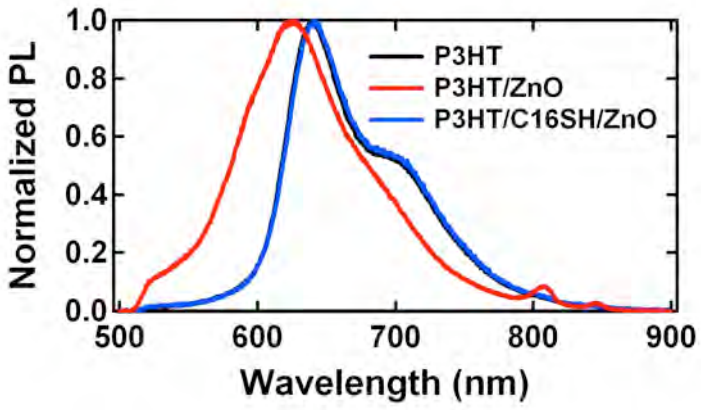
EQE Spectra



Grazing Incidence X-ray Diffraction



PL Spectra

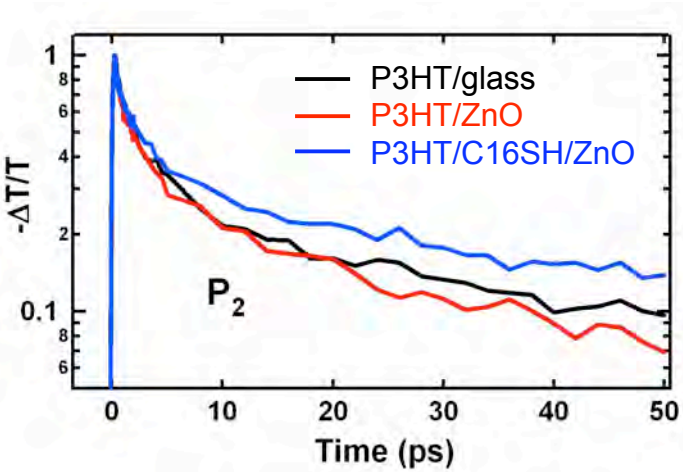


- EQE spectra clearly display interchain features (red arrows) and less blue shift. Have not seen these shoulders with any other interfacial modifications
- Absorption spectra show the same features
- PL spectra are red shifted and identical to neat P3HT on glass
- GIXD clearly show (010) diffraction peak associated with interchain spacing

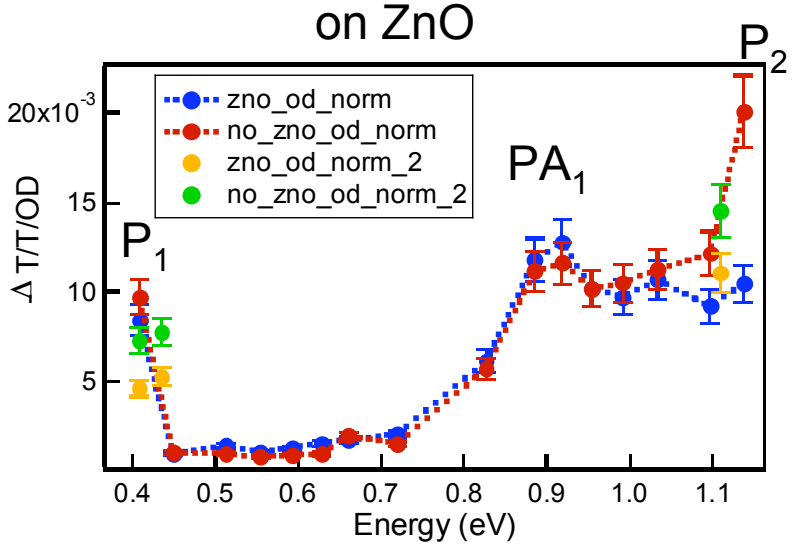
Photoexcition Dynamics at ps

- Transient photoinduced absoprtion
  - Pump at 550 nm
  - Probe from 1090 to 3034 nm
  - 150 fs resolution
- Probing the photoexcited states at very early time
- Use thin films without electrodes

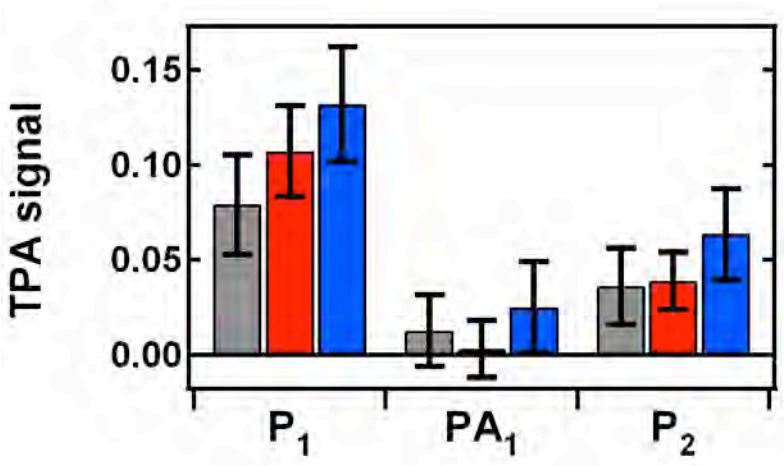
Decay dynamics for polarons



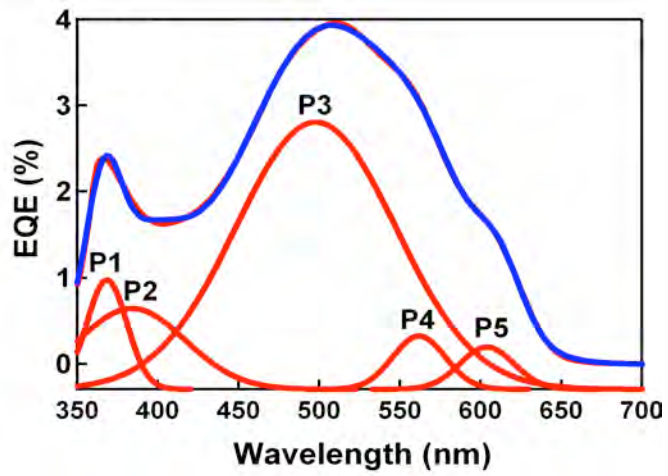
t = 0 transient absorption spectra for 19 nm P3HT film on glass vs on ZnO

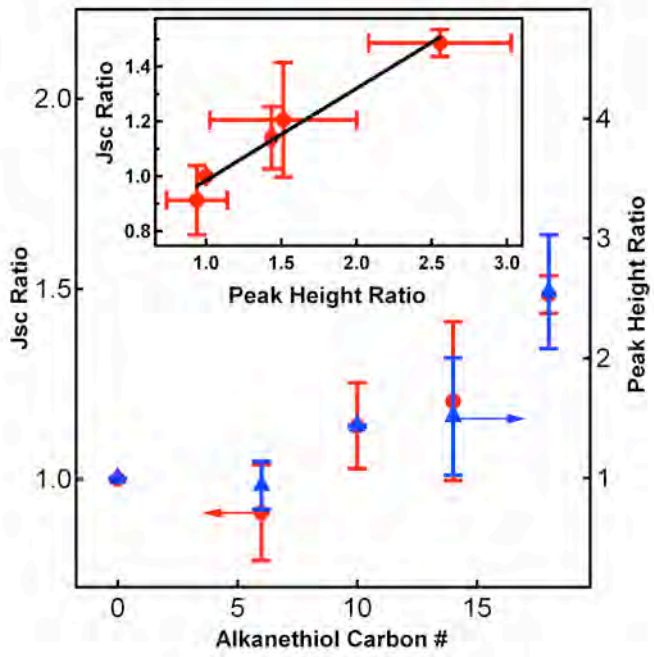


Long-lived signals for different surfaces



Crystalline Polymer Increases J_{sc}





- Alkanethiol SAM "restore" crystallinity in P3HT on ZnO
- While the alkanethiol layer creates a charge transport barrier (higher series resistance), it increases J_{sc}.
- J_{sc} increase directly correlates with the interchain contribution (P4 & P5).
- Photoexcited species on this modified ZnO surface are longer lived, suggesting reduced recombination.
- Enhanced hole mobility reduced carrier recombination compensate for electron tunneling barrier.

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Oxide Engineering

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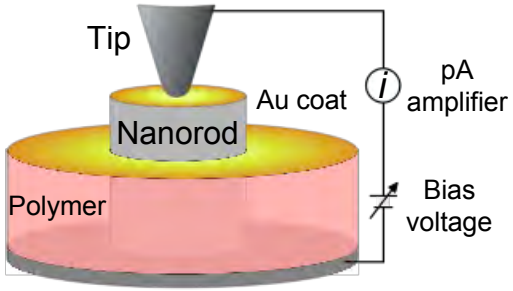
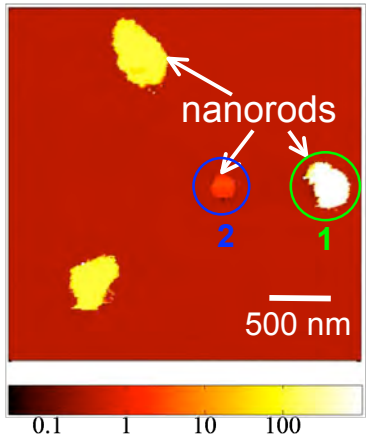
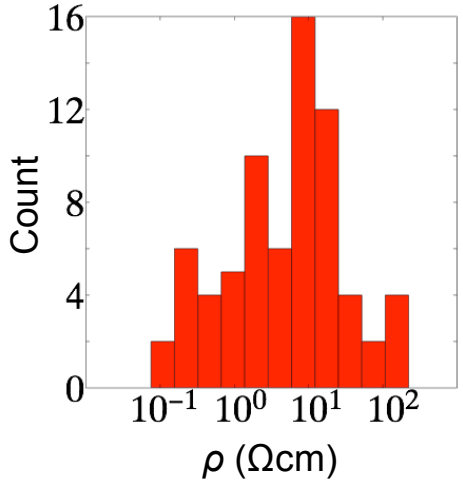
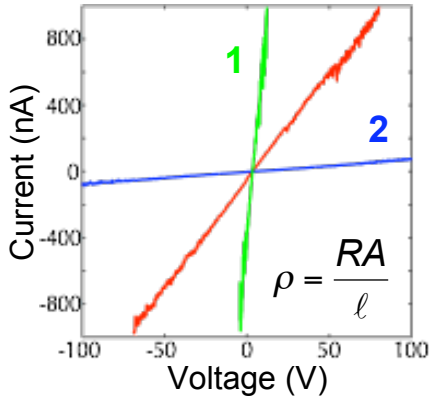
Motivation for Doping ZnO Nanorods

- Conducting AFM measurements reveal a large variation in resistivity amount nanorods grown at the same time on the same substrate.
- ρ vary from 0.1 to 155 Ωcm
- Not related to physical dimensions
- Occurs among rods less than 1 μm apart









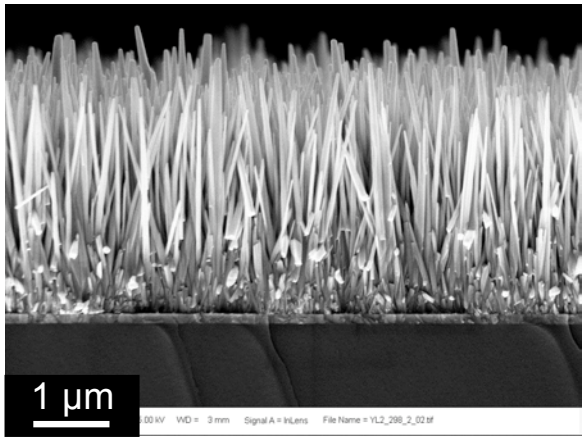
Scrymgeour & Hsu, Nano Lett. **8**, 2204 (2008)

Cause: uncontrolled incorporation of defects or impurities
Solution: Intentional doping; In:ZnO, Al:ZnO, Ga:ZnO

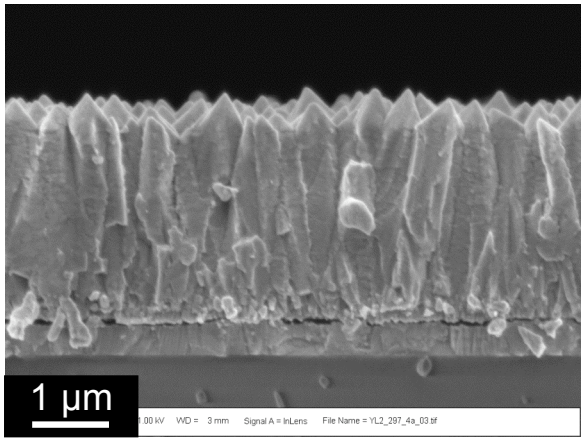
Ga Doping: Growth

- Ga ions are very soluable at pH13 for any codeposition
- 1,3-diaminopropane (DAP) allows Zn, Ga to dissolve at pH = 11; However, interactions between DAP and metal ions increases complexity
- Use $Ga(NO_3)_3$ as Ga source
- At 2.5 mM Ga, long tapered NRA is formed similar to undoped ZnO; At 25 mM Ga, NRA length decreases and nanorods fuse together
  - 25 mM $Zn(NO_3)_2$, 25 mM methenamine, 190 mM 1,3-diaminopropane, x mM $Ga(NO_3)_3$
  - Grow at 92.5 °C for 1 hr

x = 2.5 mM



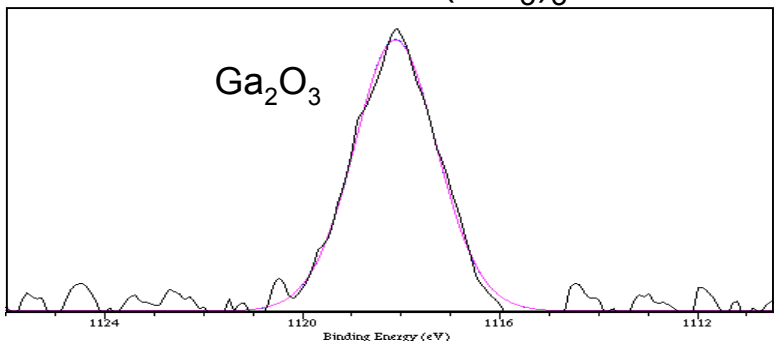
x = 25 mM



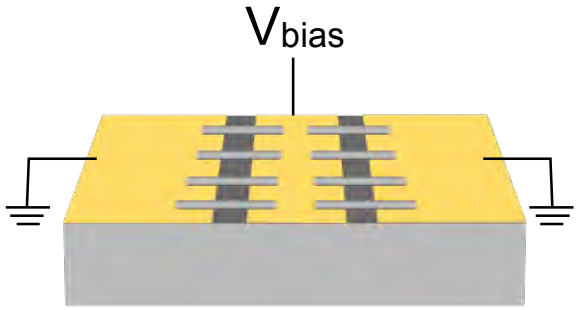
Ga Doping: Chemical & Electrical

- Use XPS to determine Ga concentration
- Position of Ga 2p peak suggests an Ga_2O_3 composition
- 0.3% Ga in ZnO for 2.5 mM Ga solution

2.5 mM $Ga(NO_3)_3$

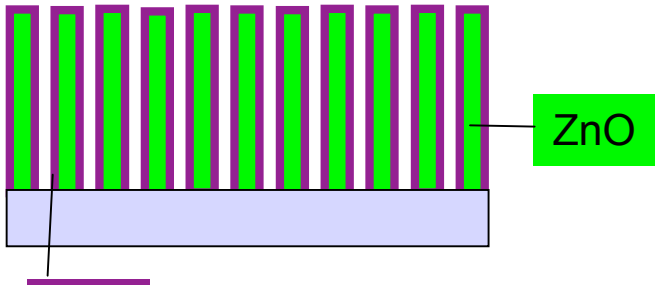


- Use coplanar waveguide to measure the ac conductivity of nanorod arrays
- Nanorods deposited using dielectriphoresis
- 40% decrease in resistance in Ga:ZnO compared to undoped ZnO nanorods

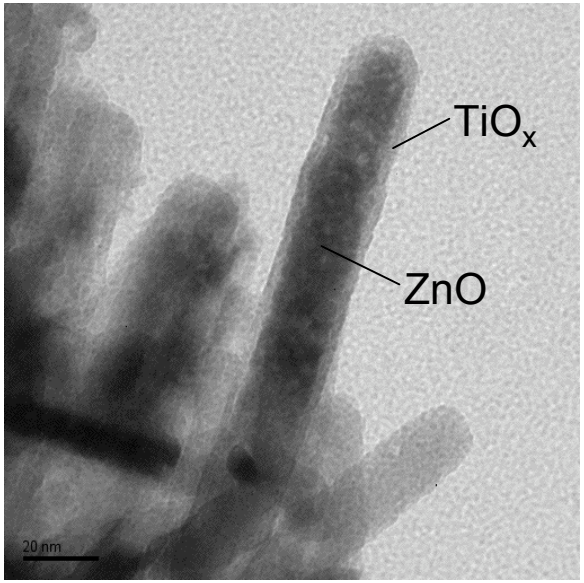


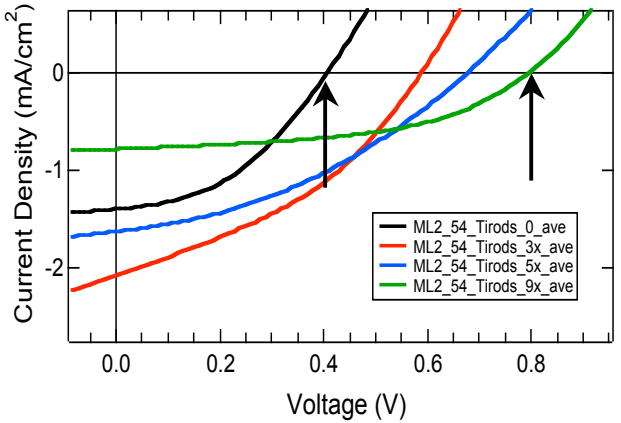
	C_c (x10^{-16} F)	R_{nr} (Ω)
ZnO - DAP	**1.65**	**1761.2**
Ga doped ZnO	**1.61**	**980.0**

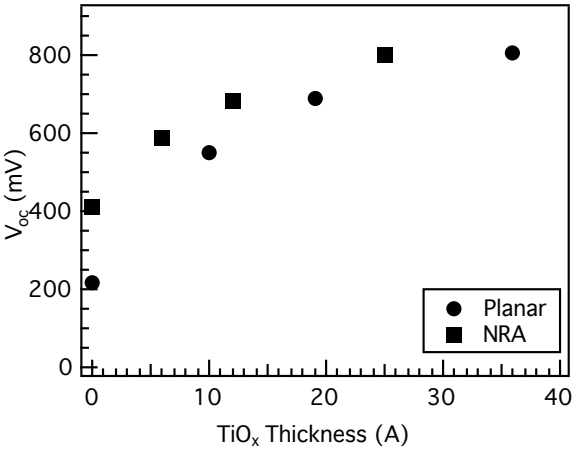
ZnO-TiO_x Core-Shell Nanostructures



- Conformally deposited by ALD or sol gel methods
- Thin: 0.5 to 4 nm
- Amorphous by XRD







- TiO_x coating increases V_{oc}, but decreases J_{sc}
- Current efforts: crystallization to increase conductivity

Summary & Future Directions

- Excellent control in nanostructured oxide growth
  - Achieve dense nanorod arrays
  - Broad band antireflection coating for Si by optimize nanorod shape and length
- Successful infiltration of P3HT & show hole transport is not a limiting factor
  - Best nanorod device achieve 0.6% power conversion efficiency
  - Device shelf lifetime is over 1 year
- Interfacial modification to improve solar cell performance
  - Interfacial processing has dramatic impact on device performance
  - Controlling interfacial polymer morphology is critical
- Future directions:
  - Understand better the requirement for exciton dissociation at the interface
  - Band alignment engineering