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Air-Stable ZnO Precursor for Hybrid Bulk Heterojunction Photovoltaic Device

Yun-Ju Lee

Collaborators: David R. Wheeler, Mark A. Rodriguez, Robert J. Davis, Diana L. Moore, Ping Lu, Paula P. Provencio, James A. Voigt, and Julia W. P. Hsu

Sandia National Laboratories, Albuquerque, NM, 87185

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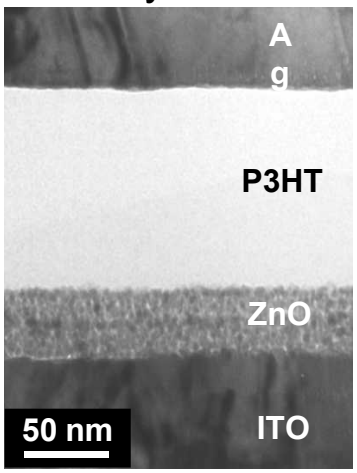
Progress In P3HT-ZnO PVs

P3HT-ZnO bilayer

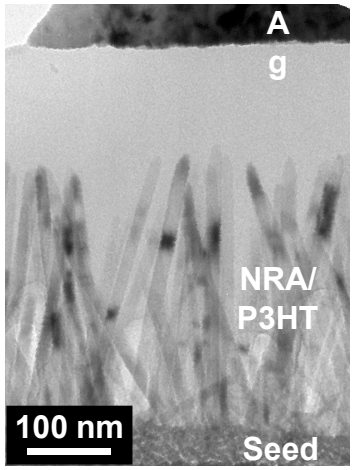
V_{oc} = 440 mV
J_{sc} = 0.37 mA/cm^2
FF = 53%
Eff = 0.09%



Y.-J. Lee et al.,
JPCC **113**, 15778 (2008)

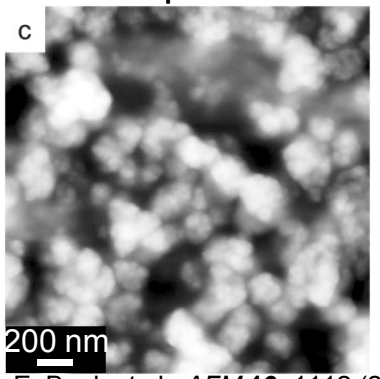
P3HT-ZnO NRA

V_{oc} = 380 mV
J_{sc} = 2.91 mA/cm^2
FF = 50%
Eff = 0.55%



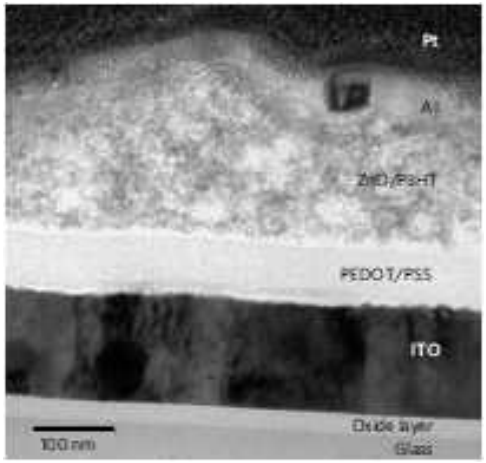
P3HT-ZnO np

V_{oc} = 690 mV
J_{sc} = 2.19 mA/cm^2
FF = 55%
Eff = 0.92%



W. J. E. Beek et al., *AFM* **16**, 1112 (2006)

P3HT-diethylzinc



30 nm

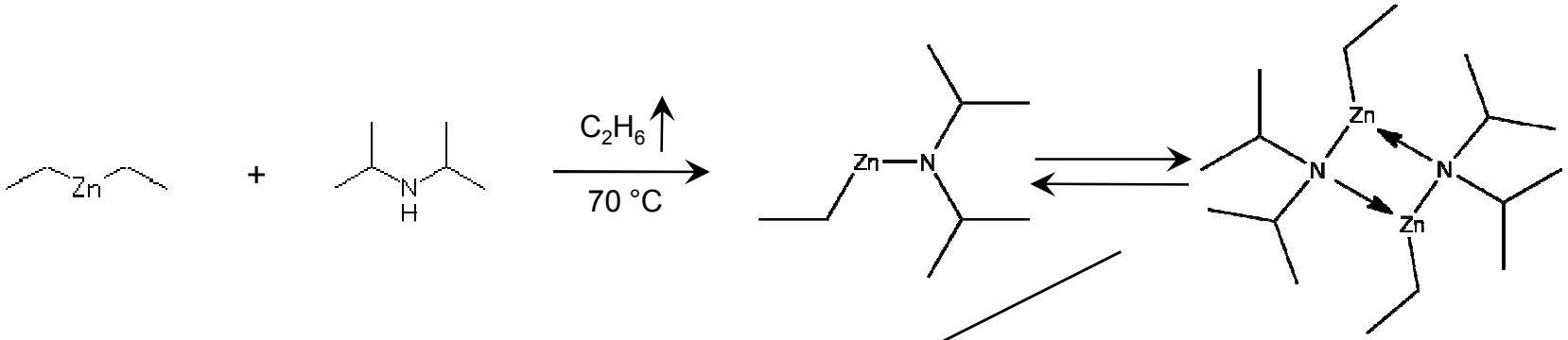
V_{oc} = 750 mV
J_{sc} = 5.20 mA/cm^2
FF = 52%
Eff = 2.0%

S. D. Oosterhaut et al.,
Nat. Mat. **8**, 818 (2009)

- High interfacial area = high J_{sc}, but with increasing process complexity

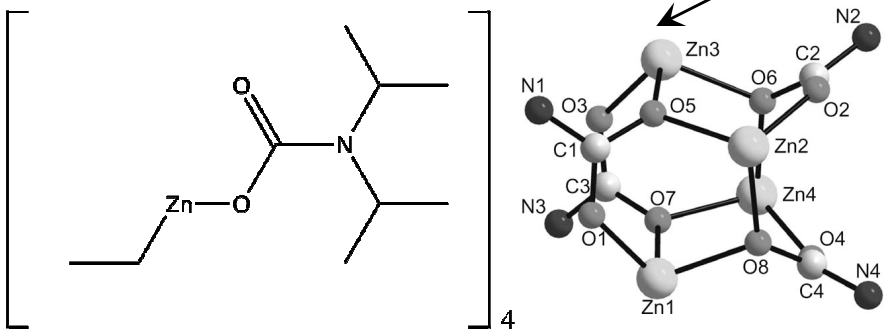
Air-Stable ZnO Precursor

$[EtZn(O_2CN(iPr)_2)]_4$, tetrakis[((diisopropylcarbamoyl)oxy)(ethyl)zinc]

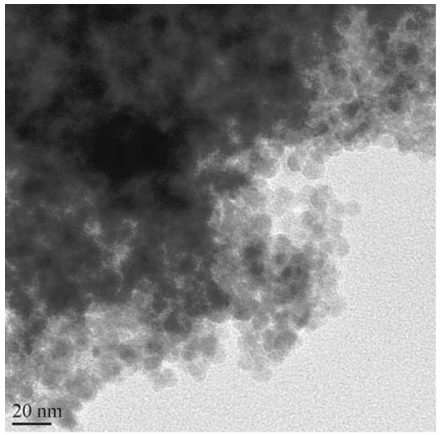


CO_2

Tetramer



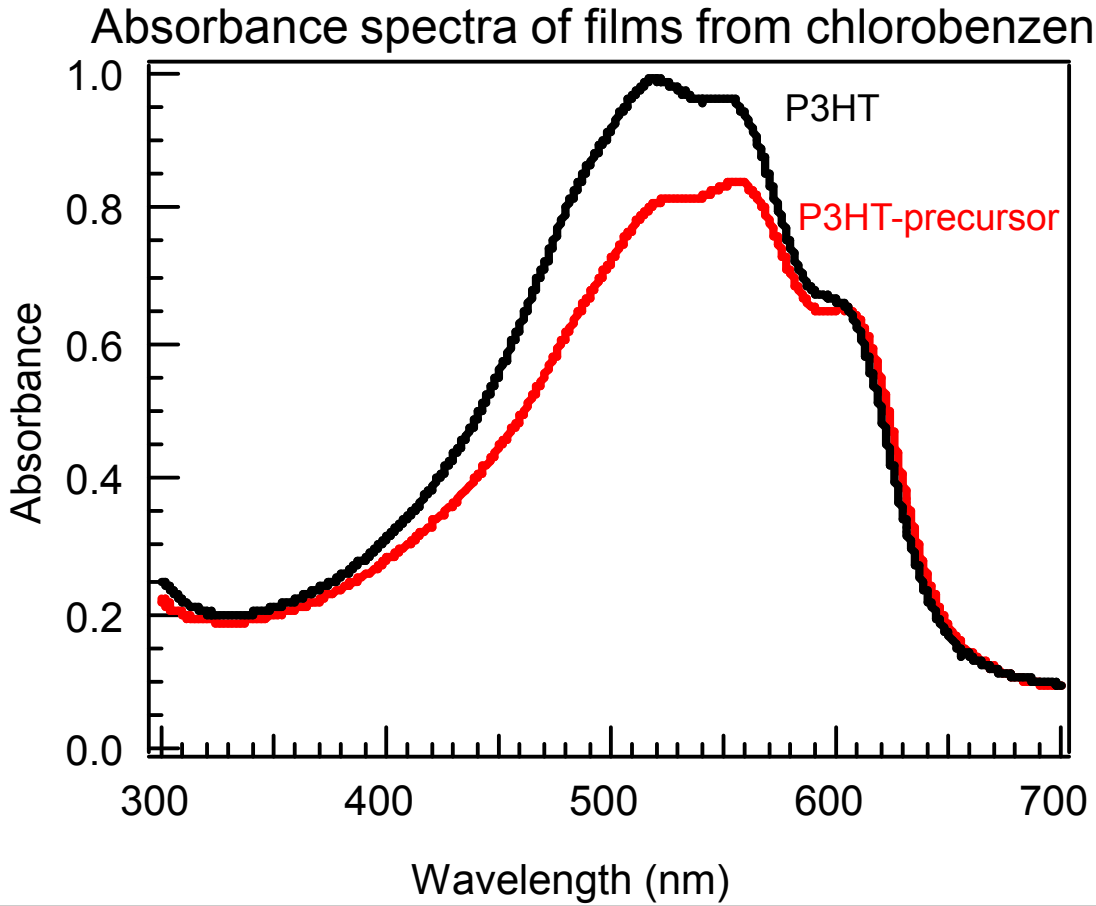
300 °C



D. Domide et al., *Eur. J. Inorg. Chem.* **4**, 3177 (2008)

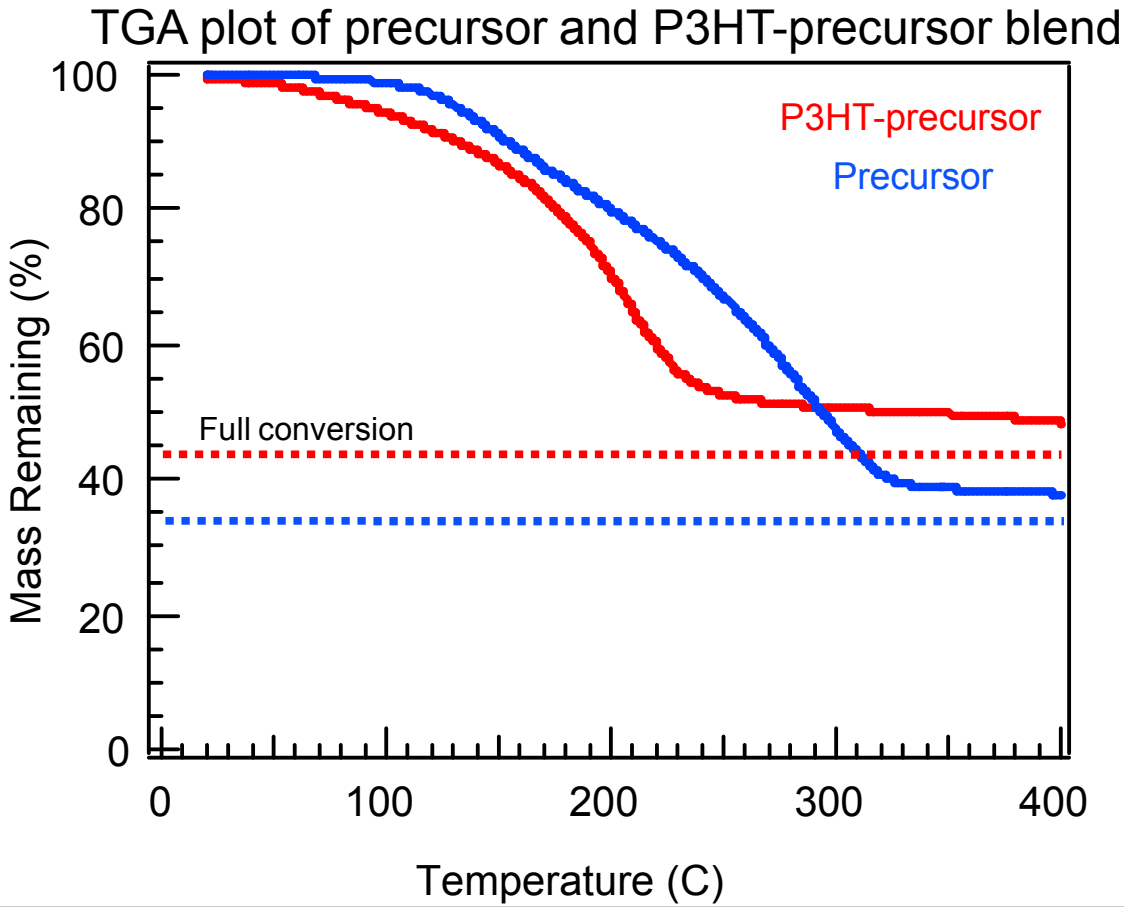
- Air stable ZnO precursor synthesized with high yield (> 95%)
- Processing issue: how to convert to ZnO in presence of P3HT?

Spin Coating of P3HT-Precursor Blend



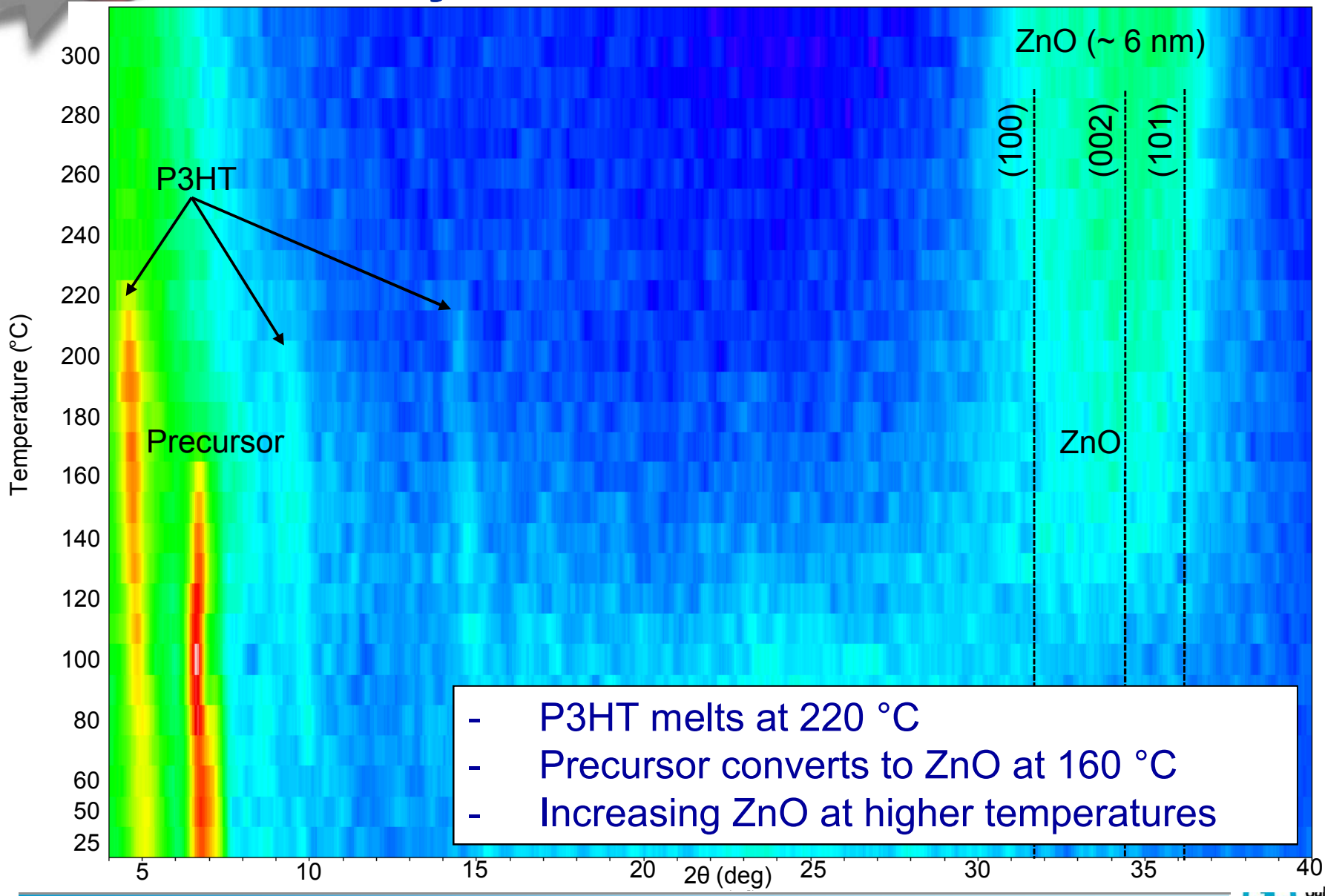
- Precursor soluble in multiple solvents at > 200 mg/mL
- Spin coated films are uniform with possibly greater P3HT crystallinity

TGA Study of ZnO Conversion in Blend



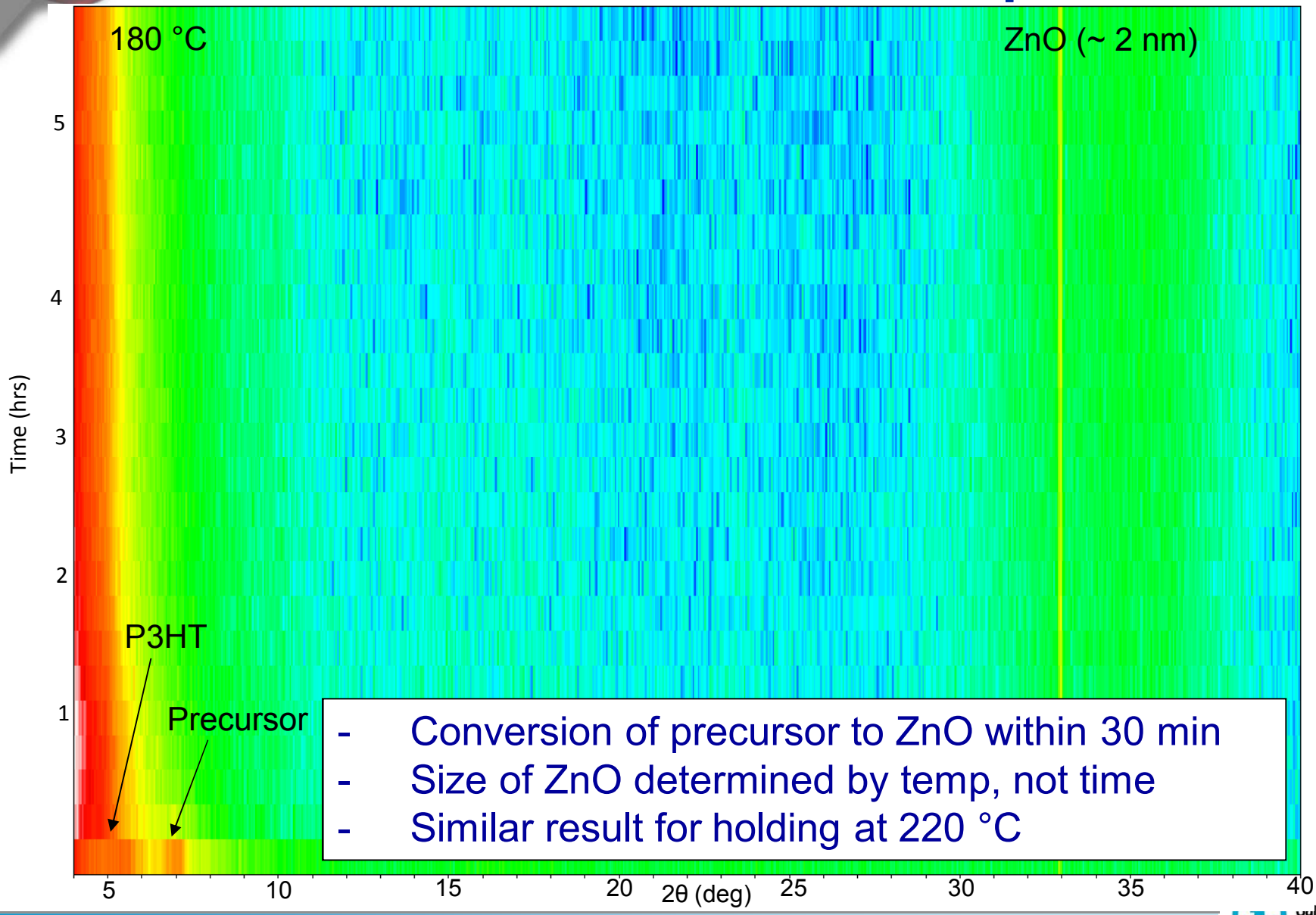
- ~ 90% conversion of precursor by 300 °C
- P3HT does not appear to hinder precursor conversion

XRD Study of ZnO Conversion in Blend



- P3HT melts at 220 °C
- Precursor converts to ZnO at 160 °C
- Increasing ZnO at higher temperatures

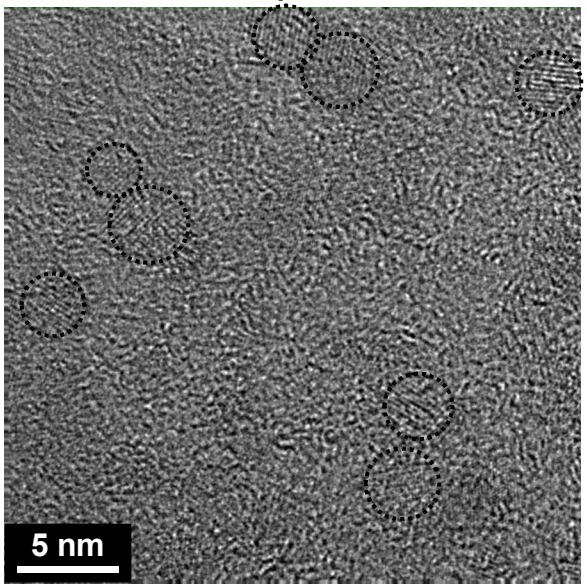
ZnO Conversion at Constant Temperature



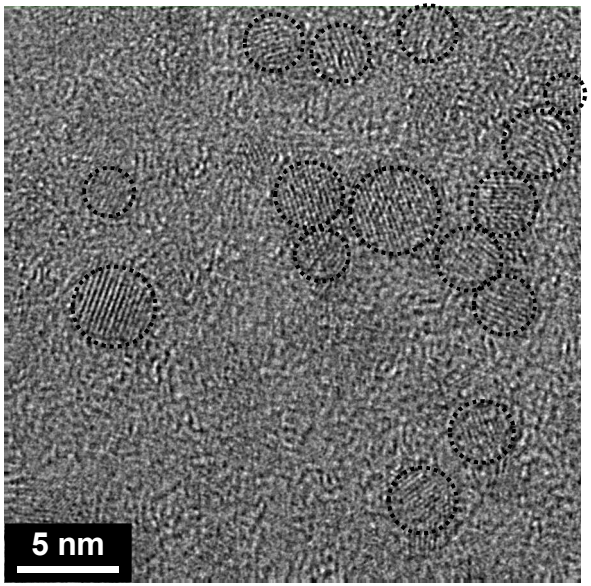
TEM of P3HT-Precursor Blends

10 nm thick films

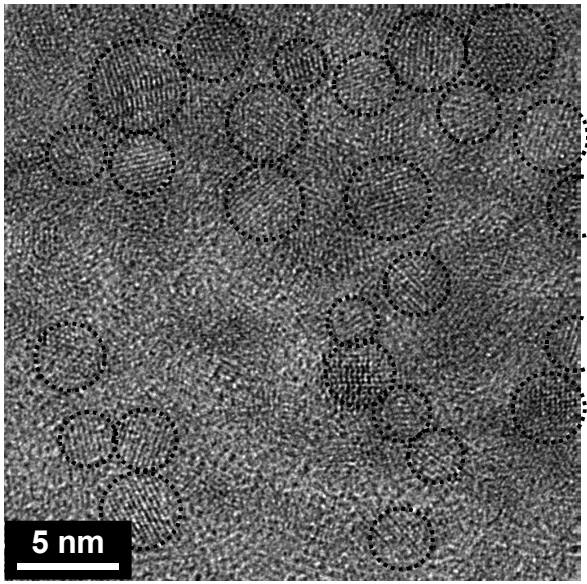
As deposited



180 °C, 15 min

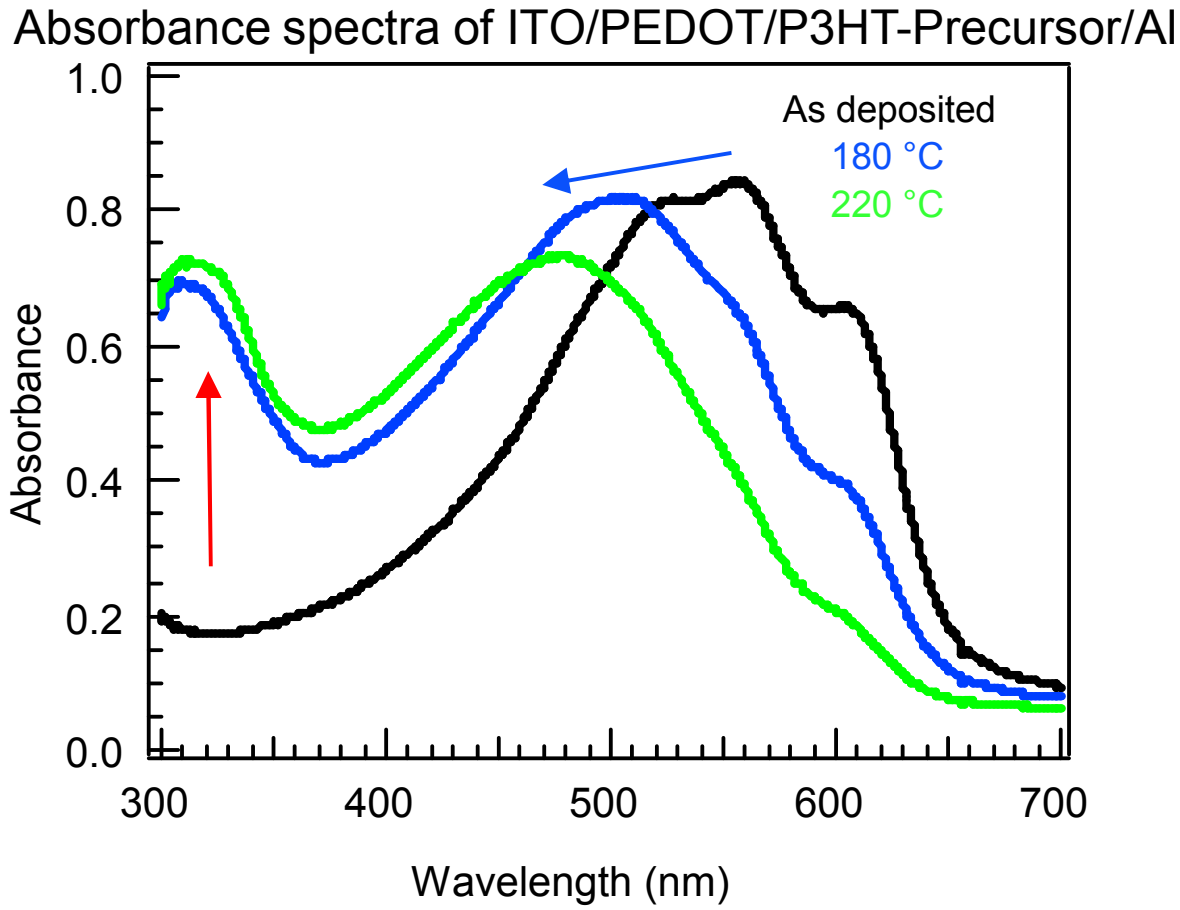


220 °C, 15 min



- Heating increases number and possibly size of nanoparticles
- Surprisingly, unheated sample contains a few nanoparticles
- ZnO nanoparticles appear isolated

Effect of Heating on Optical Properties

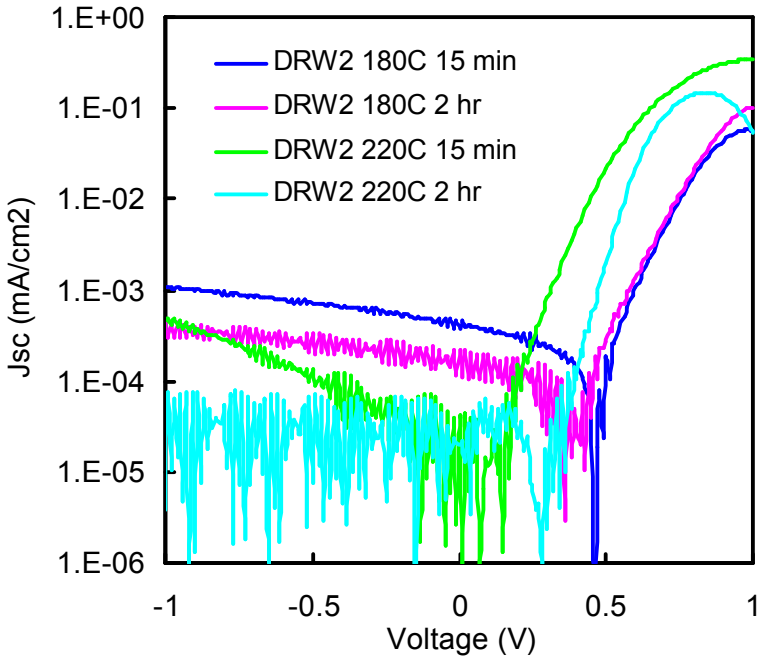


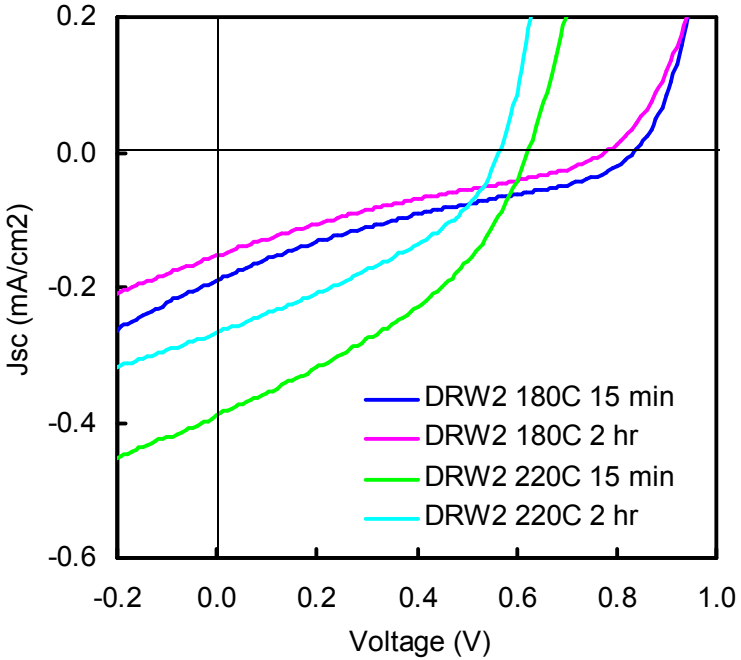
- Heating results in absorbance feature at 350 nm from ZnO
- Heating causes blue shift in P3HT from polymer-ZnO interactions

T. C. Monson et al., *Adv. Mater.* **20**, 4755 (2008)

Performance of P3HT-Precursor Blends

ITO/PEDOT/P3HT-Precursor/Al



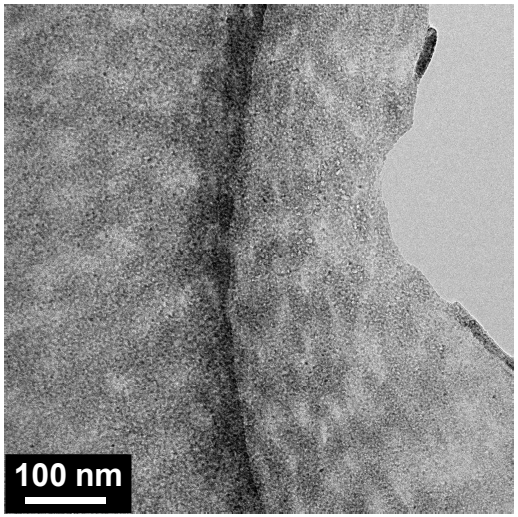


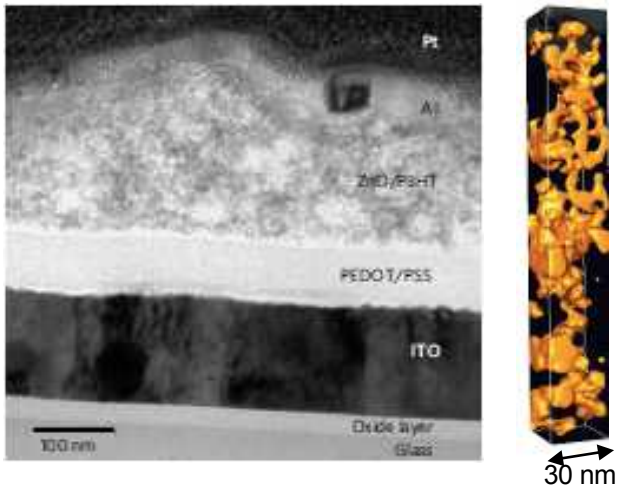
Sample	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	η (%)	Rs (Ωcm^2)
180 °C, 15 min	836	0.19	24.4	0.04	1473
180 °C, 2 hr	779	0.15	23.8	0.03	2057
220 °C, 15 min	623	0.39	37.8	0.09	3175
220 °C, 2 hr	567	0.27	36.4	0.06	5533

- High V_{oc} from quantum confinement
- Low J_{sc} and high R_s from isolation of ZnO
- Room for improvement

Conclusions

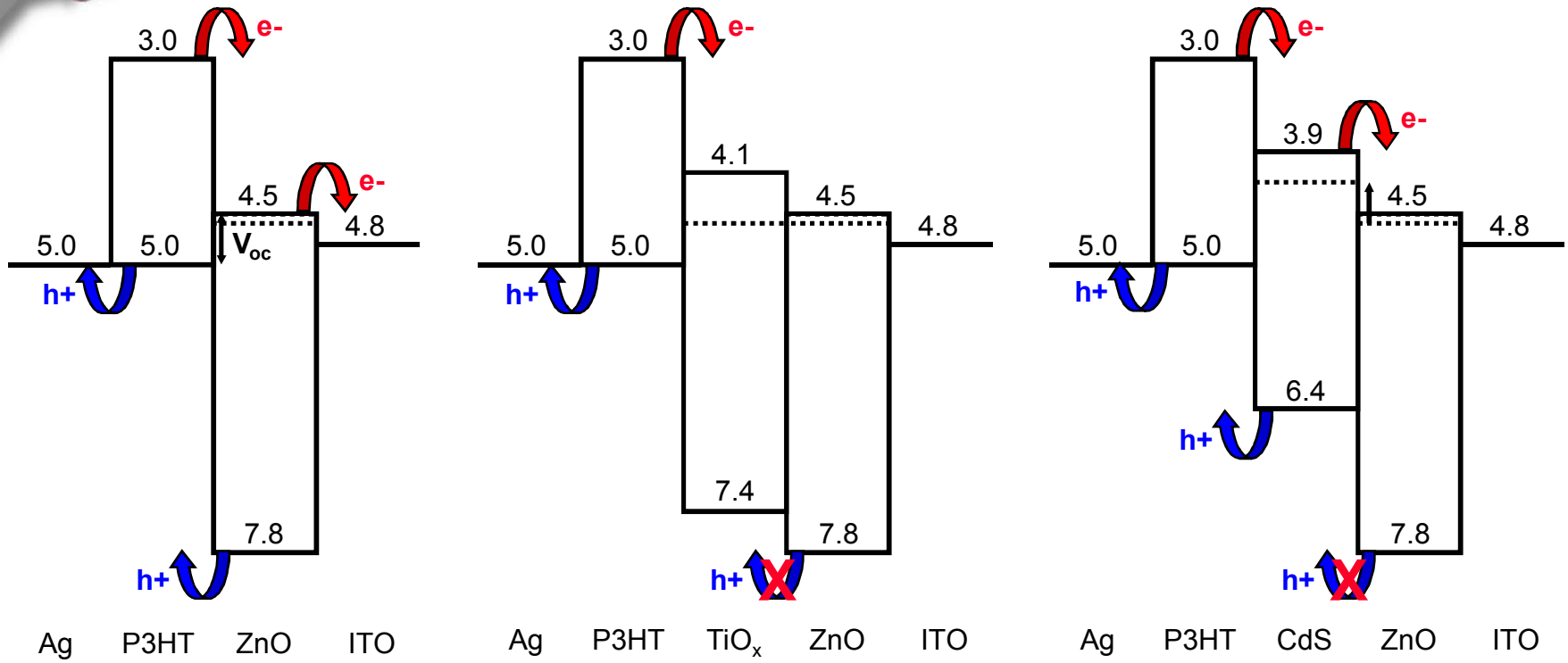
- Air stable ZnO precursor synthesized and blended with P3HT
- Thermal conversion to ZnO studied in detail
  - XRD + in situ heating shows processing window 160 °C - 220 °C
  - Number and size of nanoparticles determined by temperature, not time
  - Conversion to ZnO and interaction with P3HT confirmed with UV-vis
- Initial devices show high V_{oc} but low J_{sc}
  - Possibly caused by high R_s from isolated nanoparticles
  - Modify precursor synthesis and film processing to improve morphology





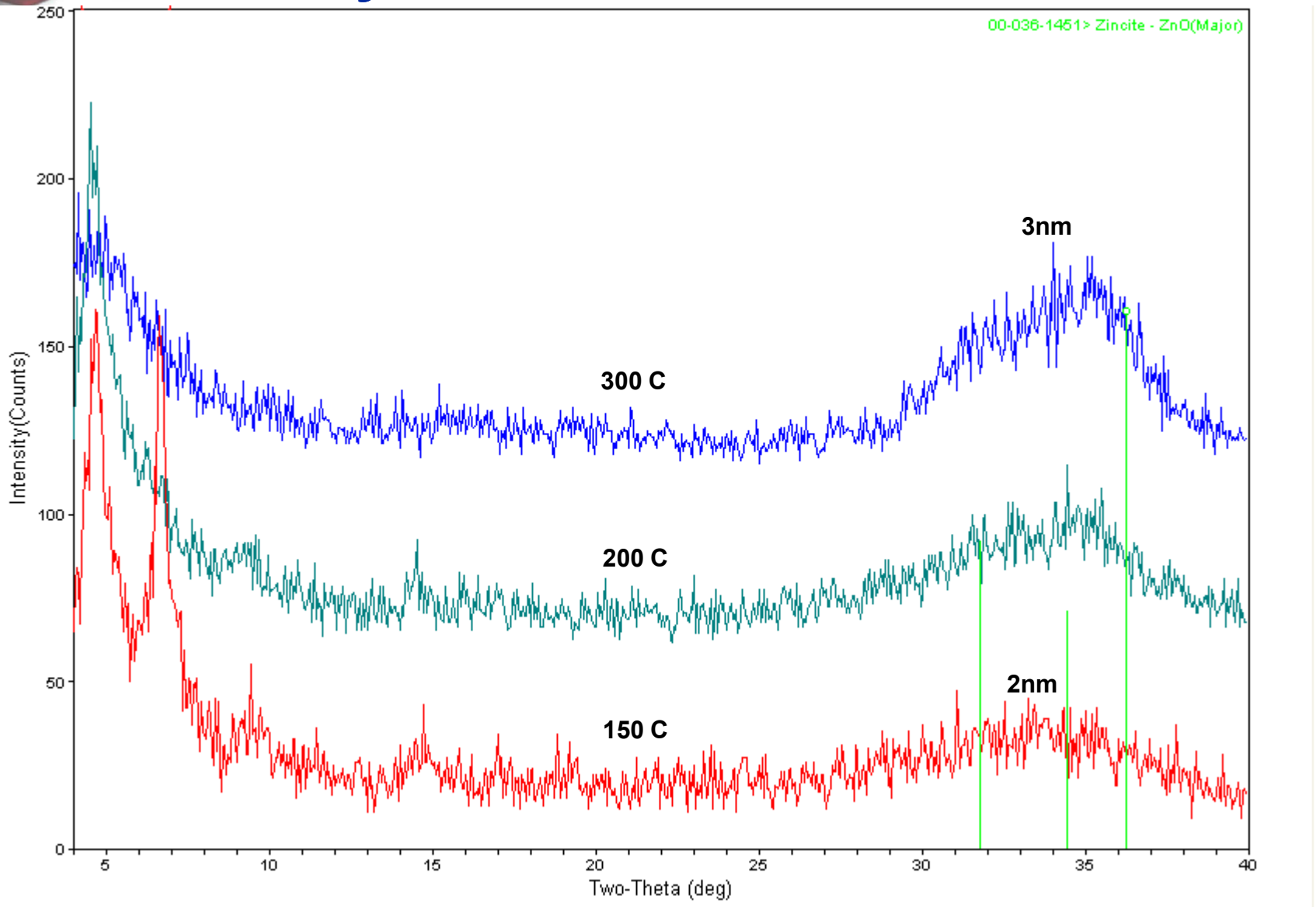
S. D. Oosterhaut et al., *Nat. Mat.* **8**, 818 (2009)

P3HT/Inorganic PV Band Levels

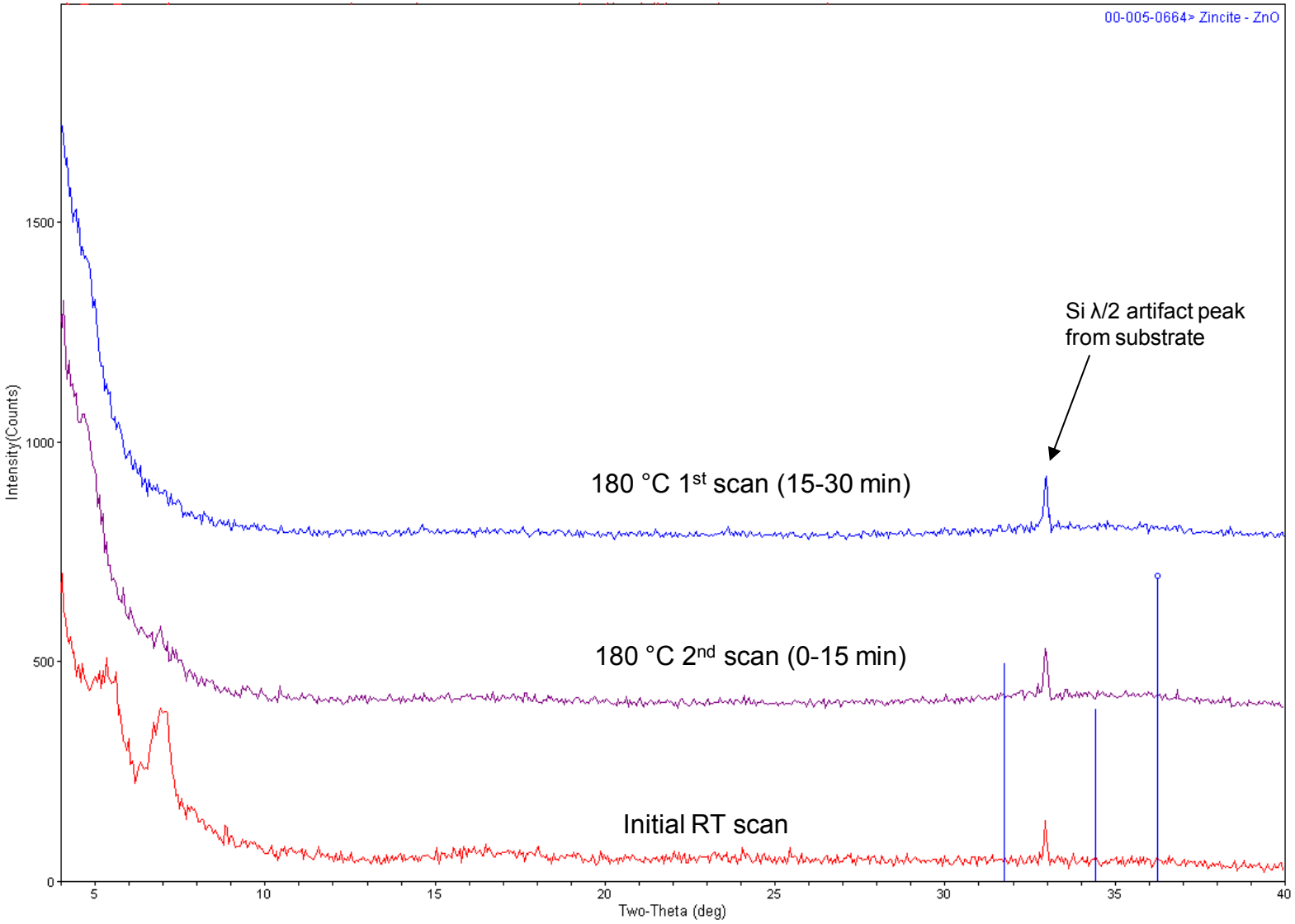


Lin et al., *J. Mat. Chem.* **17**, 9571 (2007)

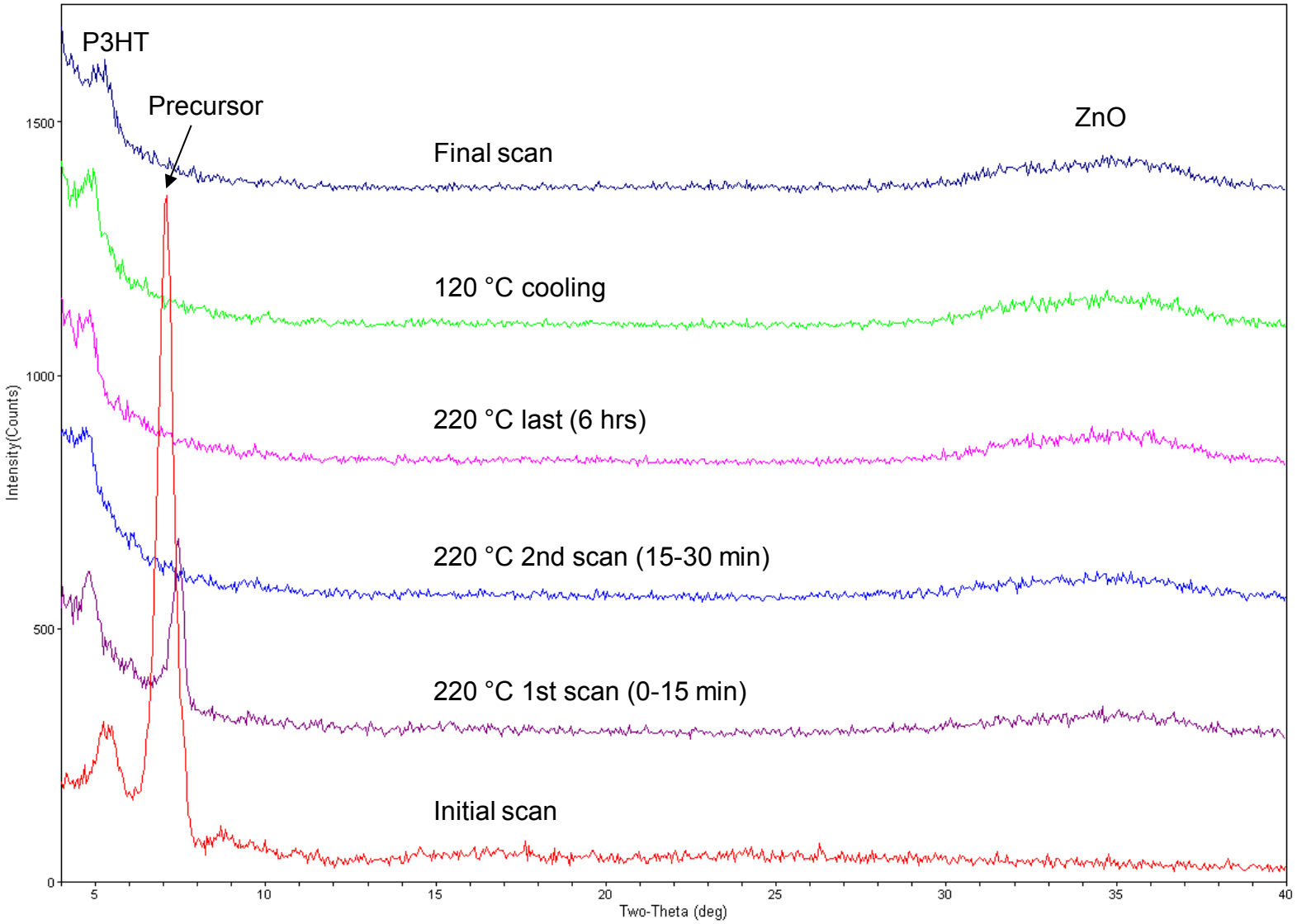
XRD Study of ZnO Conversion in Blend



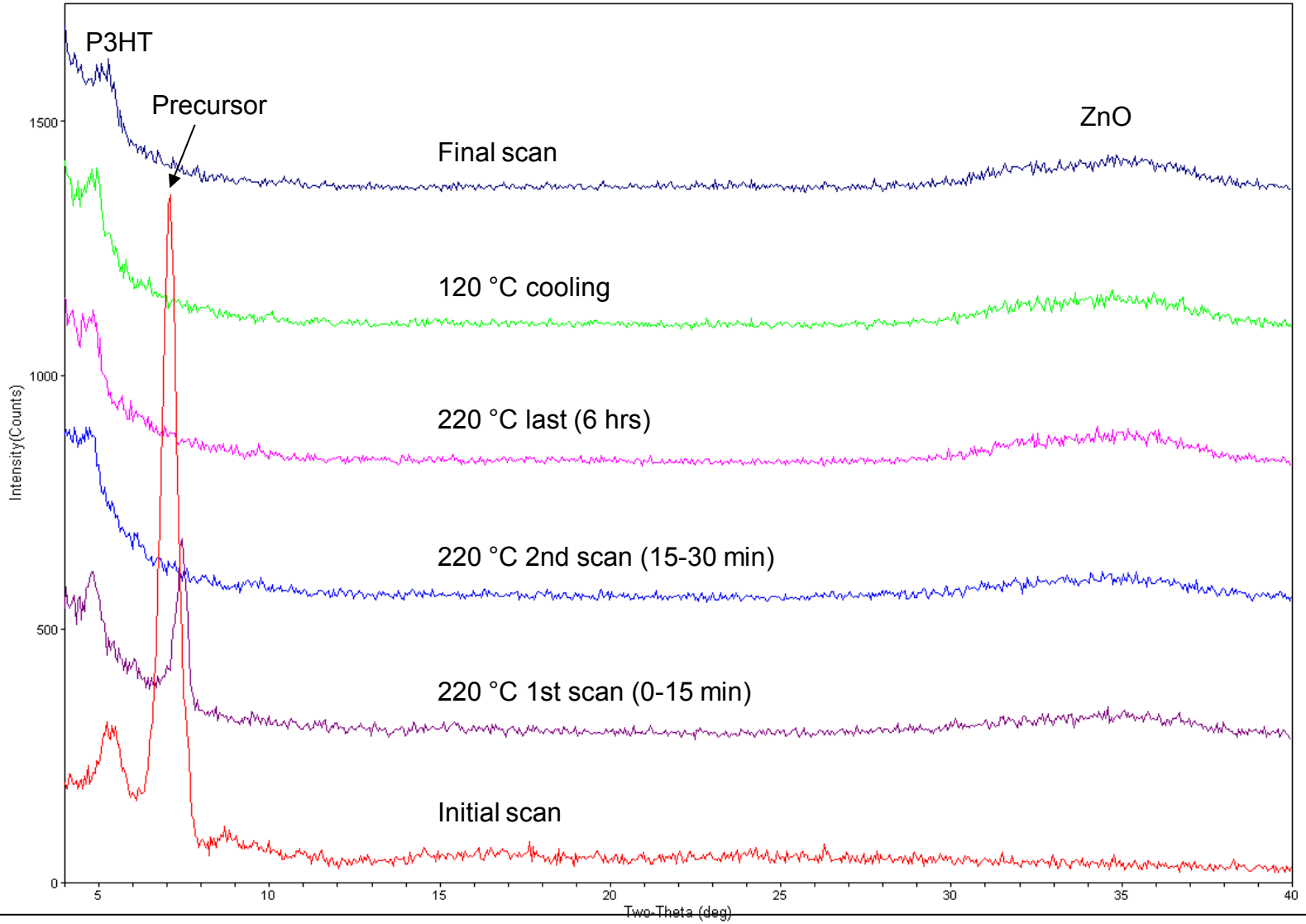
ZnO Conversion at 180 °C



ZnO Conversion at 220 °C

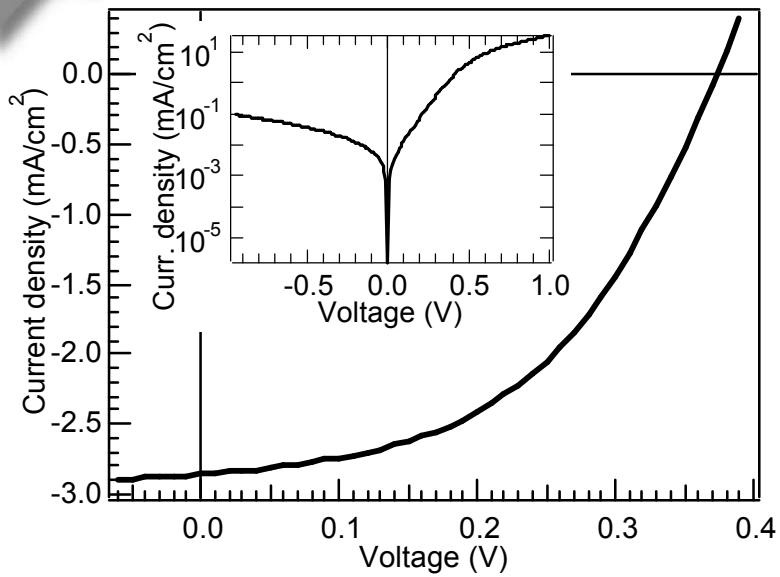


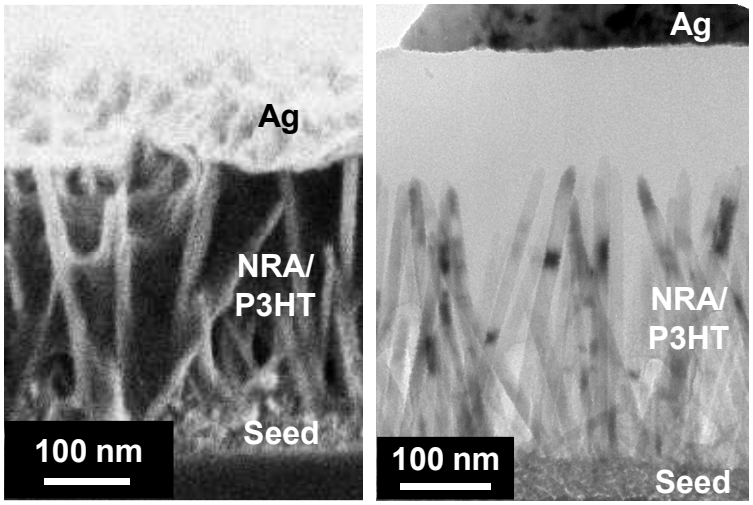
ZnO Conversion at 220 °C



- Precursor converts to ZnO within 15 min

ZnO NRA PV





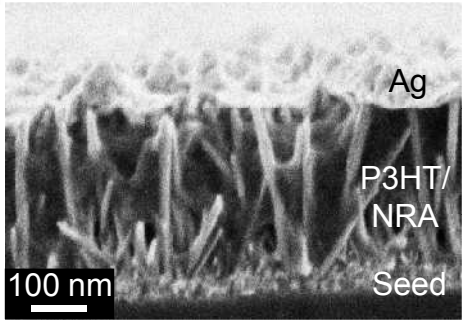
Y.-J. Lee et al., *JPCC* **113**, 15778 (2008)

Sample	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF (%)	Eff (%)
Bilayer	440	0.37	53	0.09
ZnO NRA	380	2.91	50	0.55

- Slower NRA growth rate also leads to less dense NRA
- More P3HT in close proximity to NRA leads to higher J_{sc}

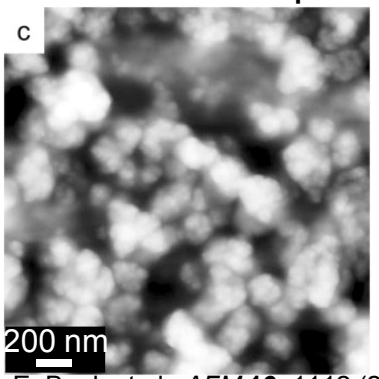
Progress In P3HT-Metal Oxide PVs

P3HT-ZnO NRA



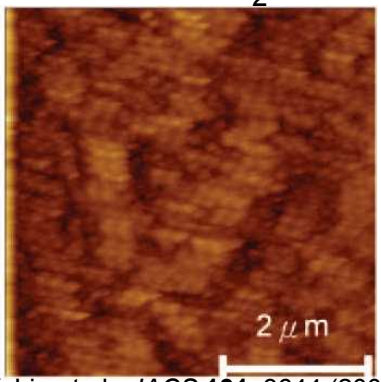
Y.-J. Lee et al., *JPCC* **113**, 15778 (2008)

P3HT-ZnO np



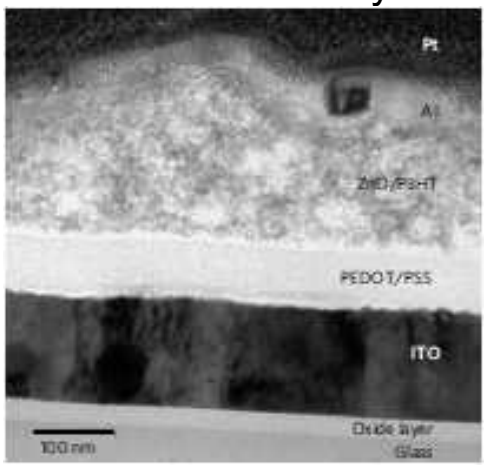
W. J. E. Beek et al., *AFM* **16**, 1112 (2006)

P3HT-TiO_2 nr



Y.-Y. Lin et al., *JACS* **131**, 3644 (2009)

P3HT-diethylzinc



S. D. Oosterhaut et al., *Nat. Mat.* **8**, 818 (2009)

Sample	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF (%)	Eff (%)
P3HT-ZnO Bilayer	440	0.37	53	0.09
P3HT-ZnO NRA	380	2.91	50	0.55
P3HT-ZnO np	690	2.19	55	0.92
P3HT-TiO_2 nr-pyr	690	2.10	62	1.12
P3HT-TiO_2 nr-N3	780	4.33	65	2.20
P3HT-diethylzinc	750	5.20	52	2.0

- D-A energy level offset + quantum confinement = high V_{oc}
- High interfacial area = high J_{sc}, but with increasing process complexity