The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization
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1938-12

Workshop on Nanoscience for Solar Energy Conversion

27 - 29 October 2008

Solid-State Dye-Sensitized Solar Cells: Device Operation, Optimization, Charge Generation Mechanism and Novel Electrodes Structured from Diblock Copolymers

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Understanding loss mechanisms in solid-state dye-sensitized solar cells and diblock copolymer templated mesostructured electrodes

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Trieste, 28th October 2008

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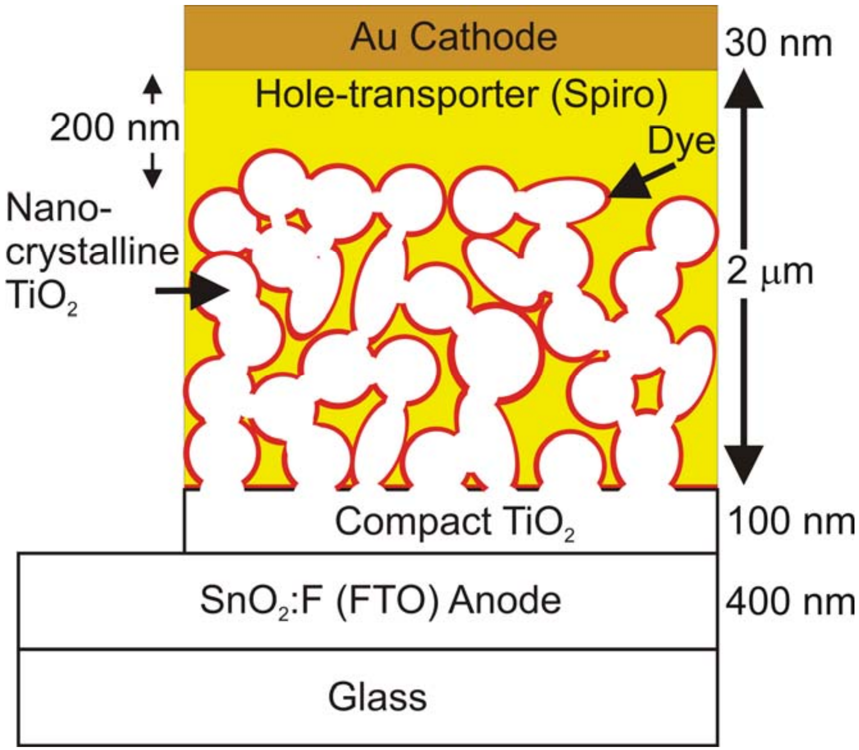
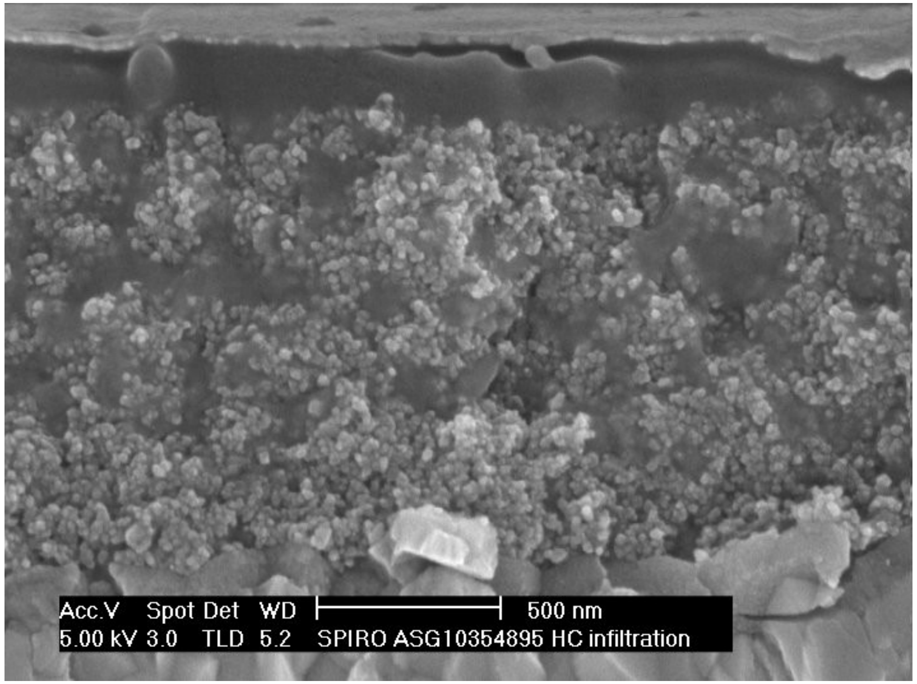
Overview

- Probing the loss mechanisms in solid-state DSCs: current collection and pore filling
- Probing the electron transport in mesoporous TiO_2
- TiO_2 electrodes structured by diblock copolymers templates: probing the structure-function relationship

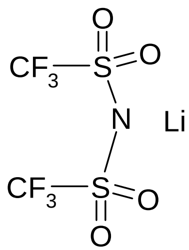
Solid-state dye-sensitized solar cell*

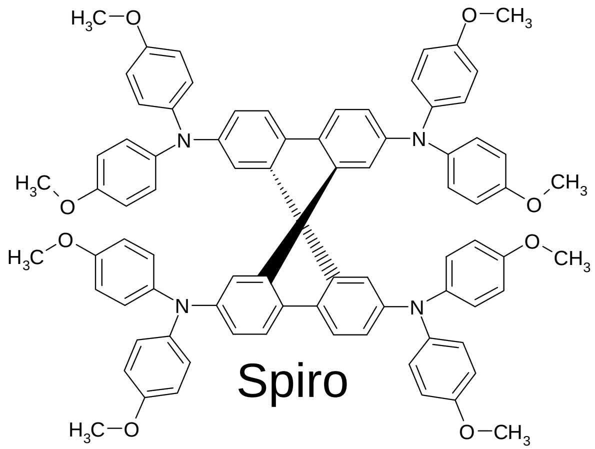




Light absorption in dye, electron transfer to TiO_2,
hole transfer to Spiro-OMeTAD.

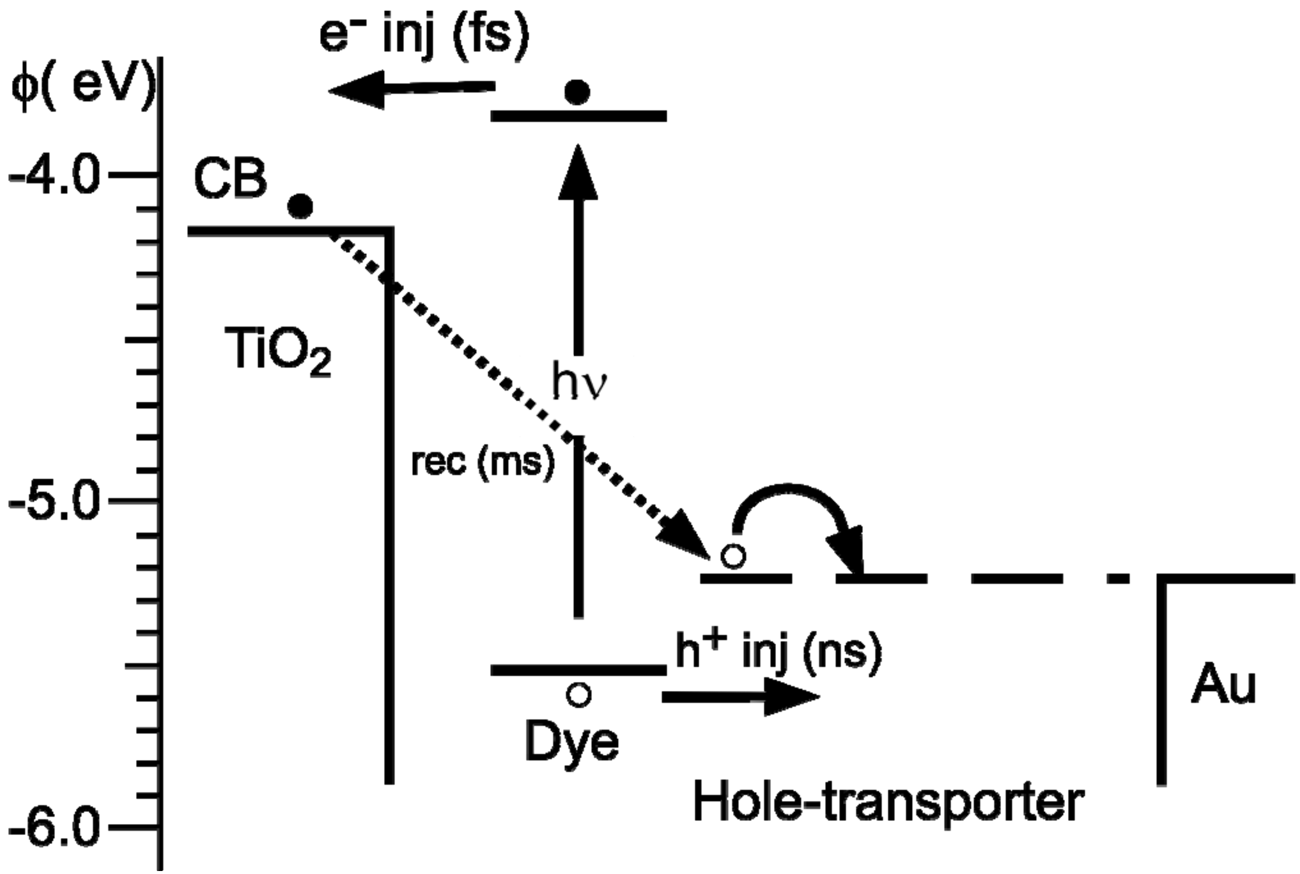
Additives in HTM: tbp and Lithium TFSI



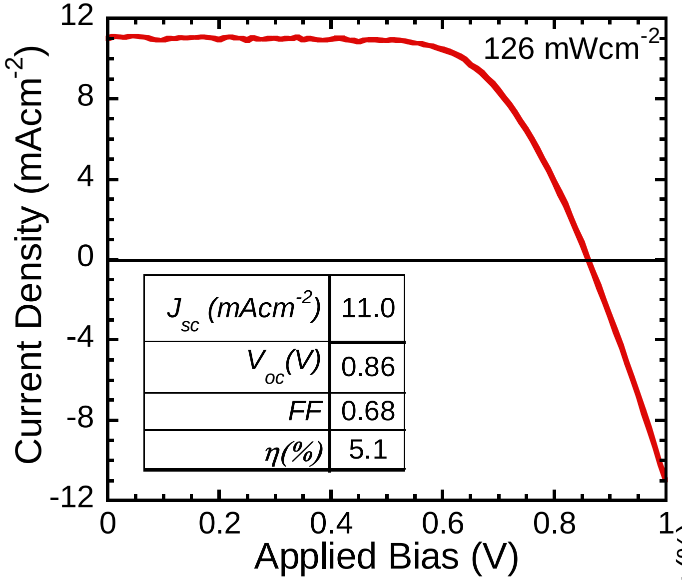


*Bach, U. et al. Nature 395, 583–585 (1998)

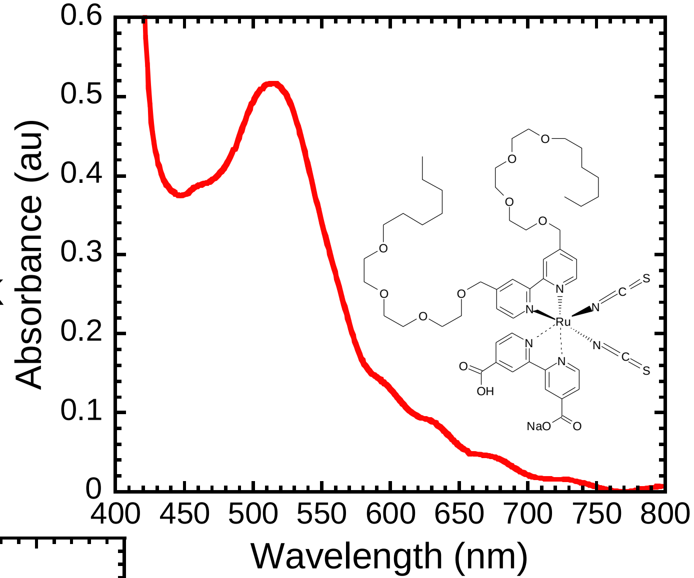
Solid-state DSC operation

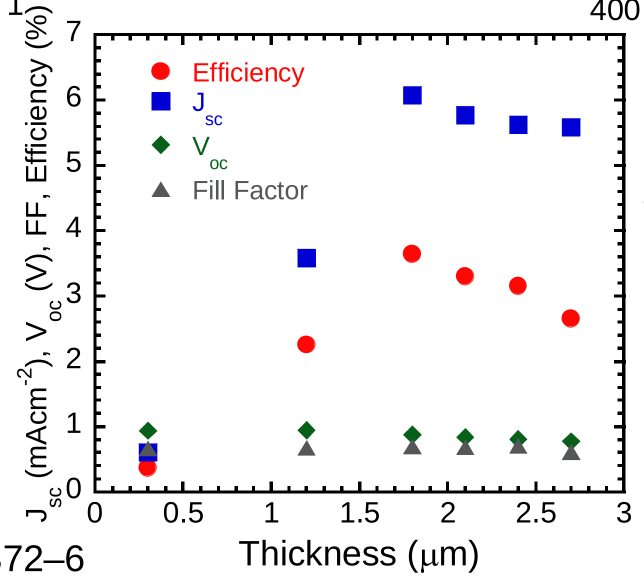


Solar Cell performance



Maximum solar cell performance
when only 2 μm thick





Only 70% light absorbed
At peak wavelength

Generate 6 to 9 mA/cm^{-2}
out of possible 23 mA/cm^{-2}

H. J. Snaith et al. Nano. Lett. 2007 7 3372–6
H. J. Snaith et al. Adv. Matter. 2007 19 3187–200

Possible losses

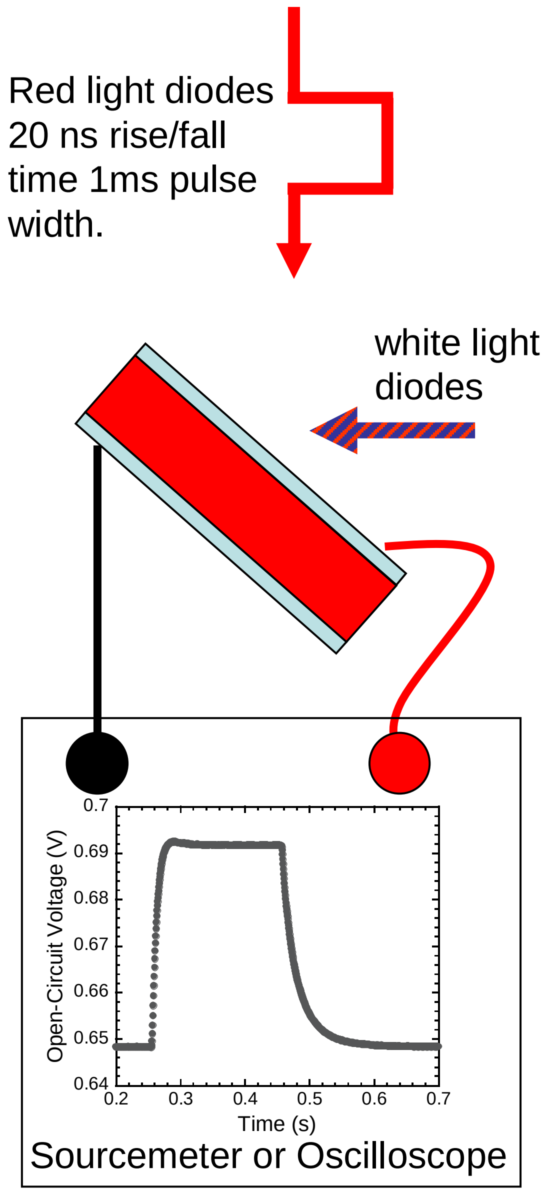
Electronic-

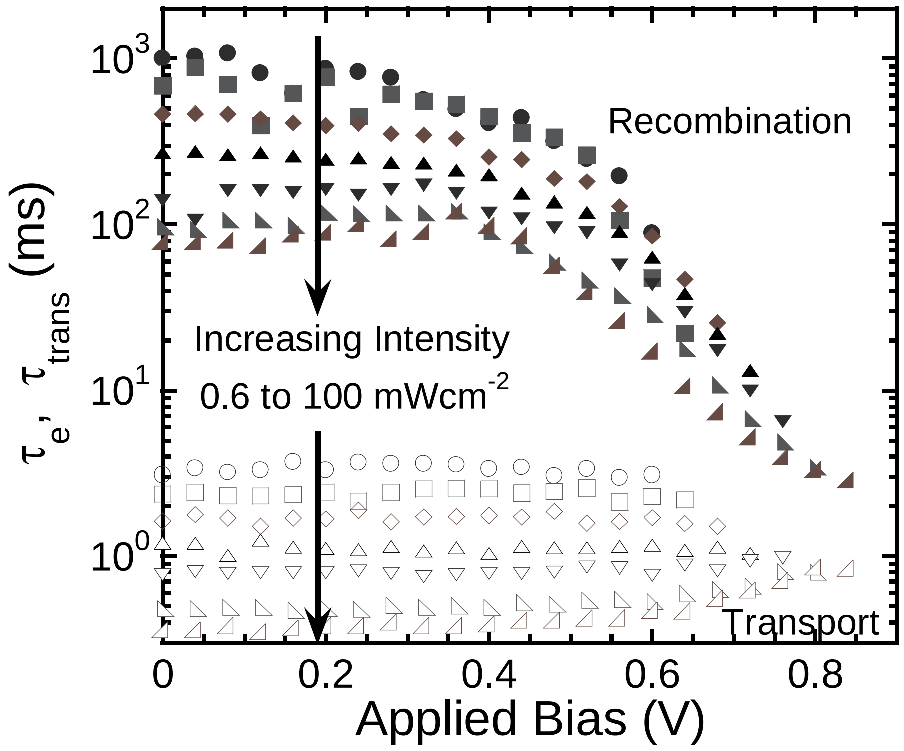
- Recombination (bi-molecular)
- Poor charge generation
  - Electron injection
  - Hole-transfer
  - Electron hole separation

Physical-

- Ineffective pore infiltration with spiro-OMeTAD

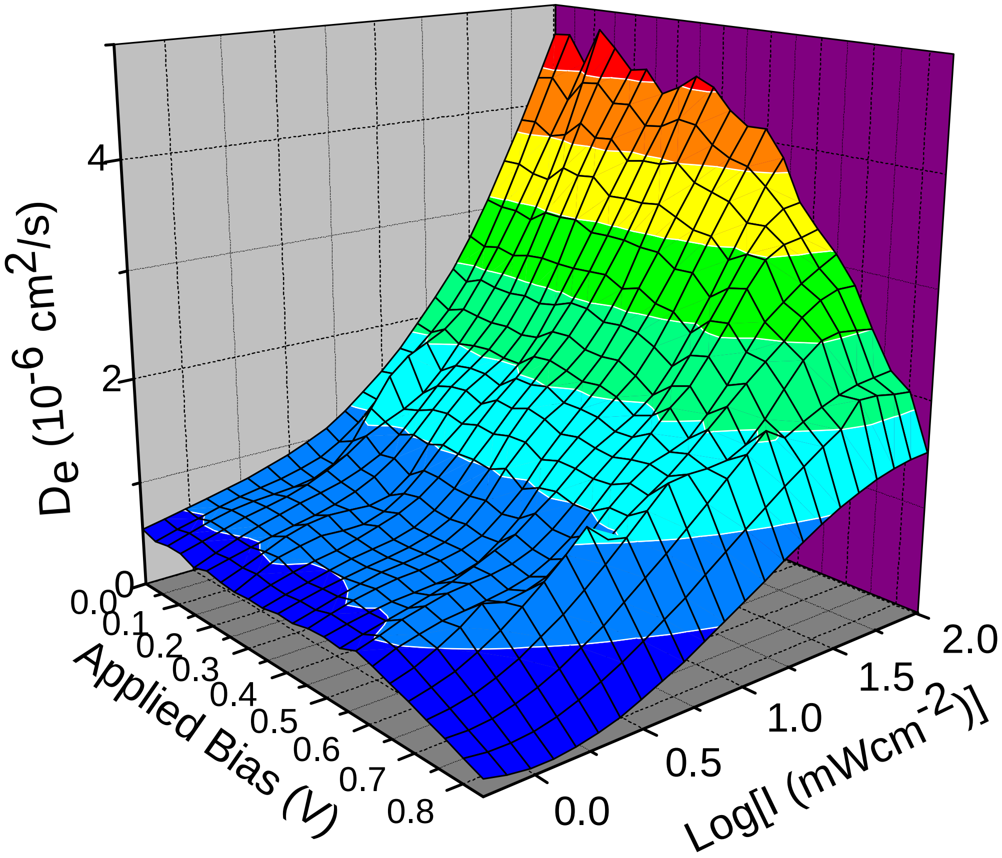
Transport and recombination



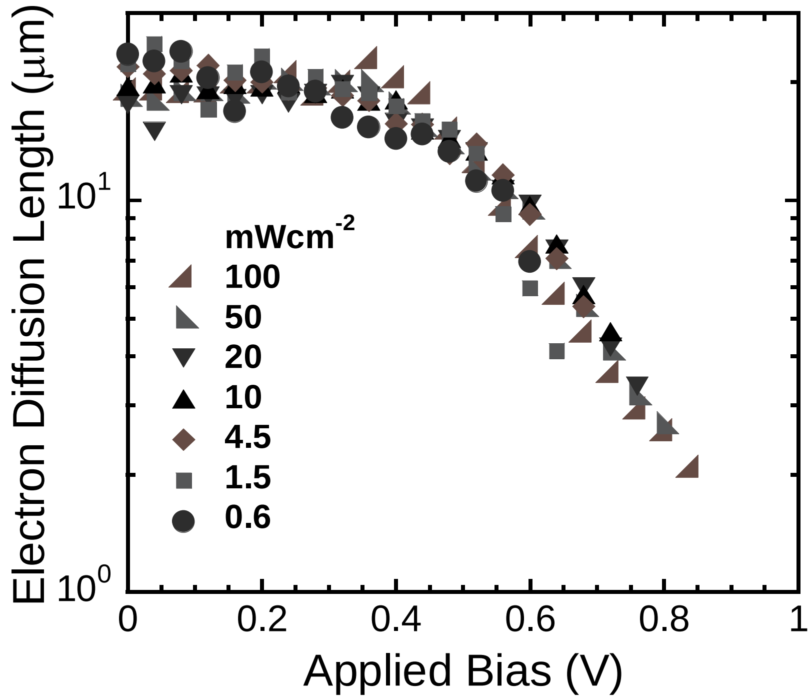


Transport and recombination

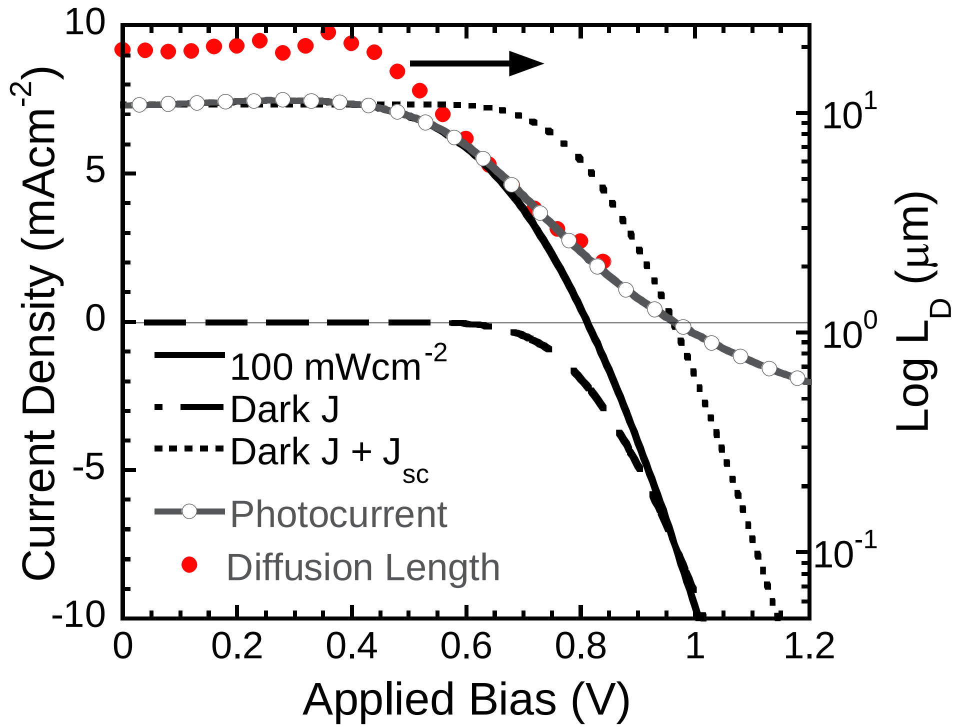
$D_e \sim d^2 / 2.35\,\tau_{trans}$



$L_D \approx \sqrt{D_e \tau_e}$

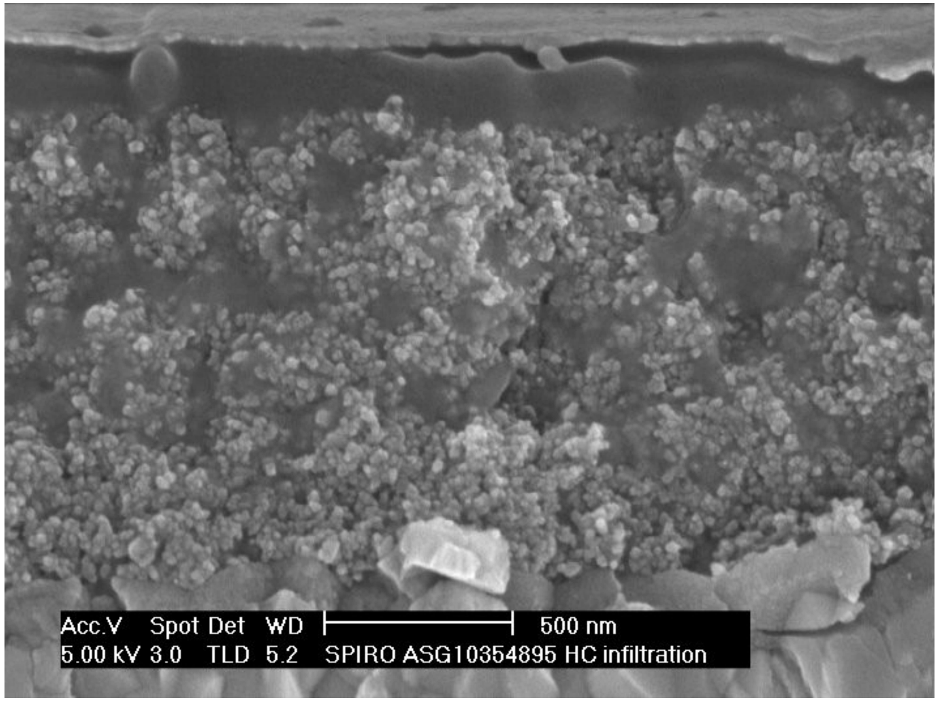


Collection Limiting Photocurrent

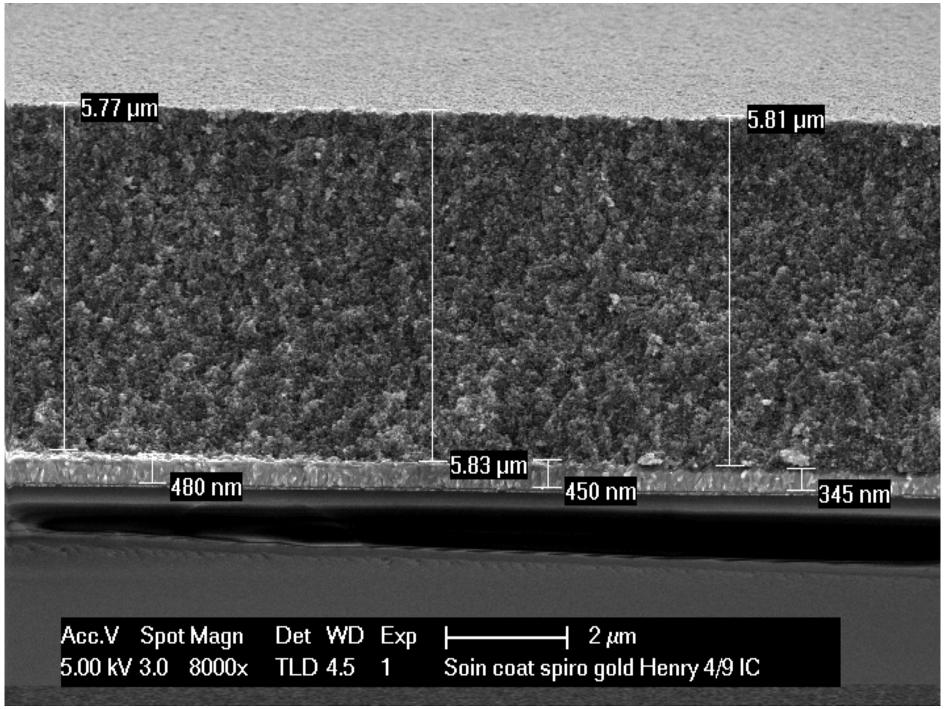


- •Loose PC from ~ 0.5V
- •Coincides well with drop in L_d
- •No influence near J_{sc}
- • η goes from 4 to 5% if all short-circuit PC collected up to 1V

SEM images: pore-filling

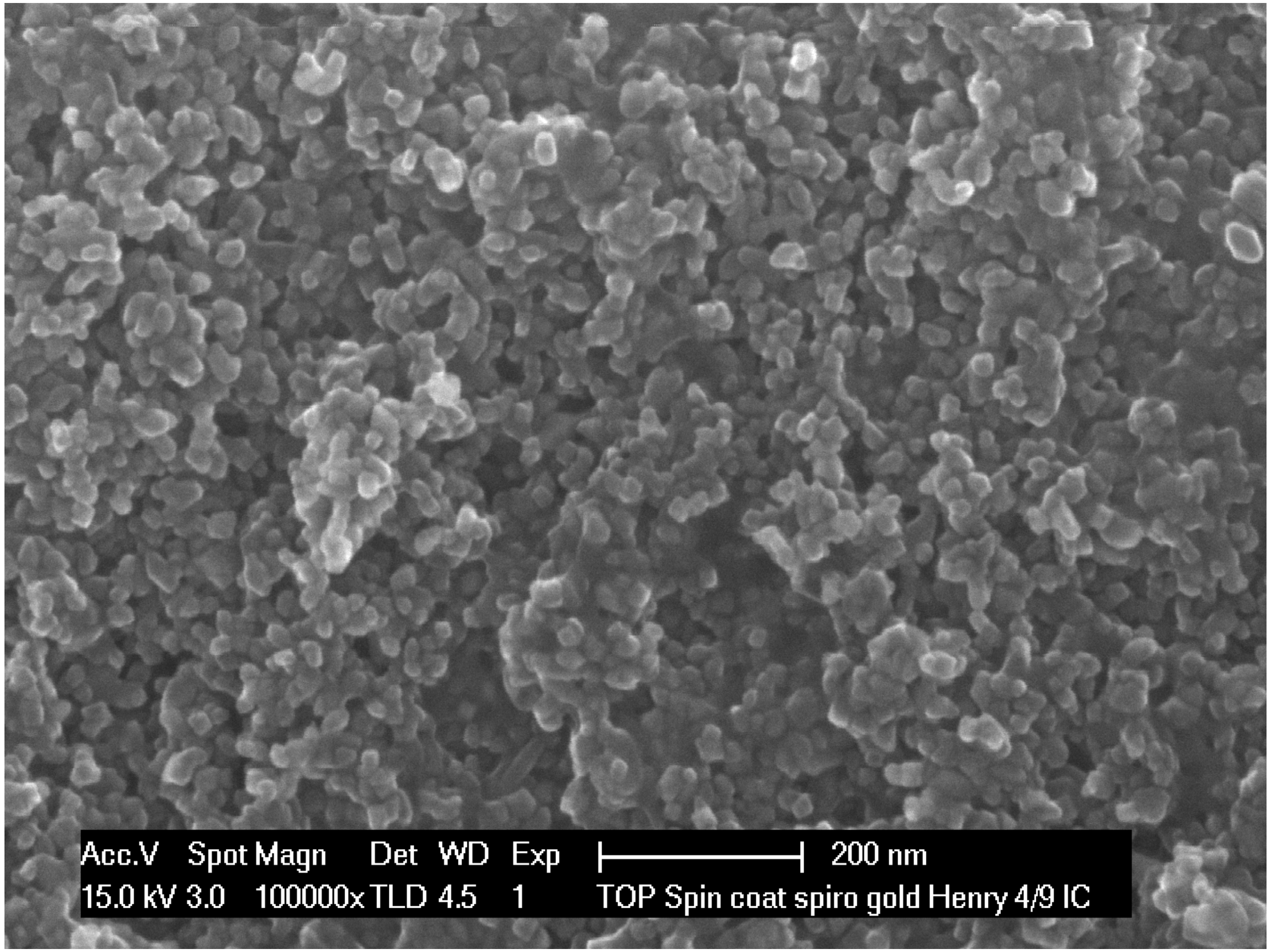


2 μm thick film

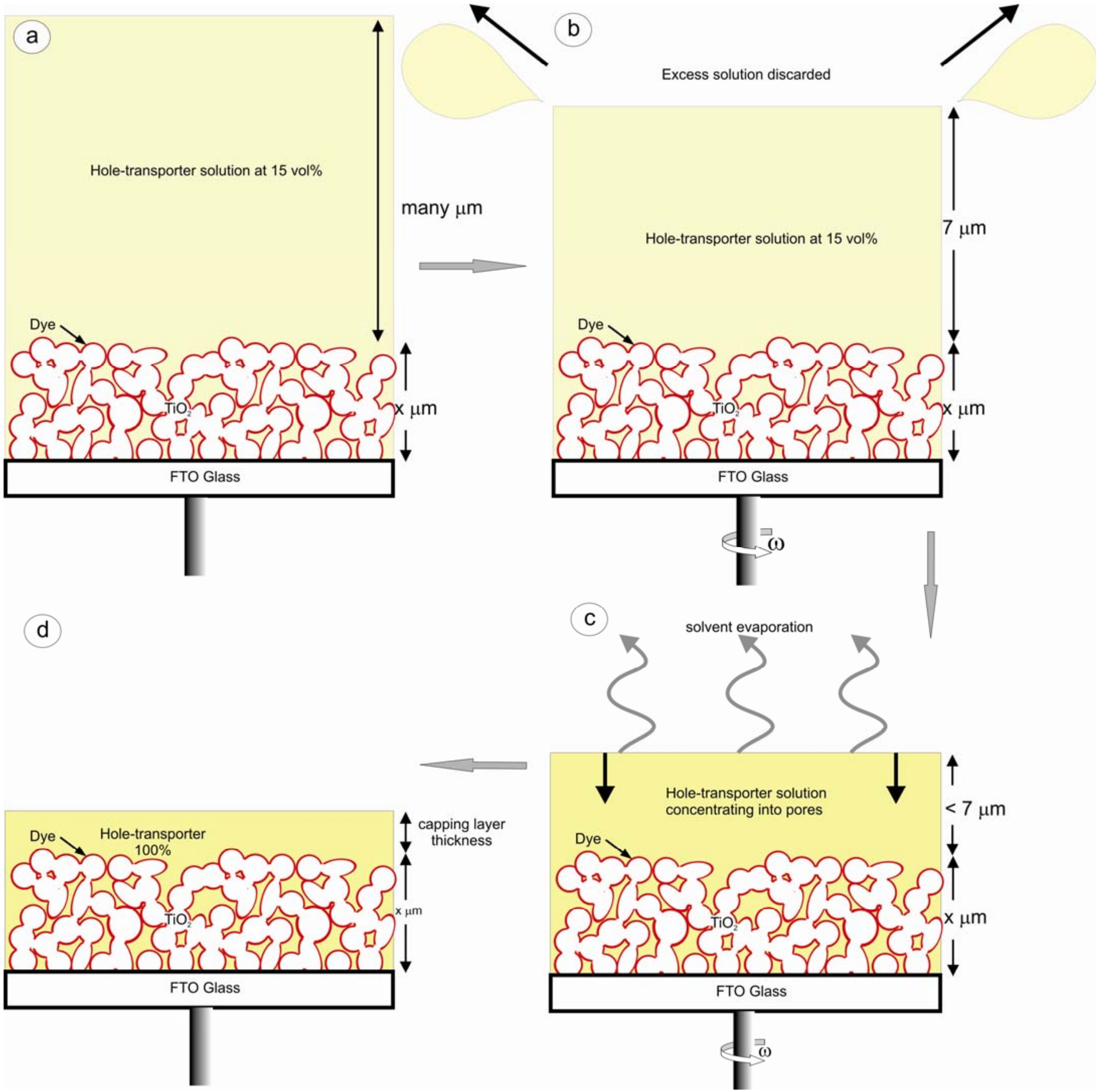


6 μm thick film

SEM images: pore-filling



Spin-coating process



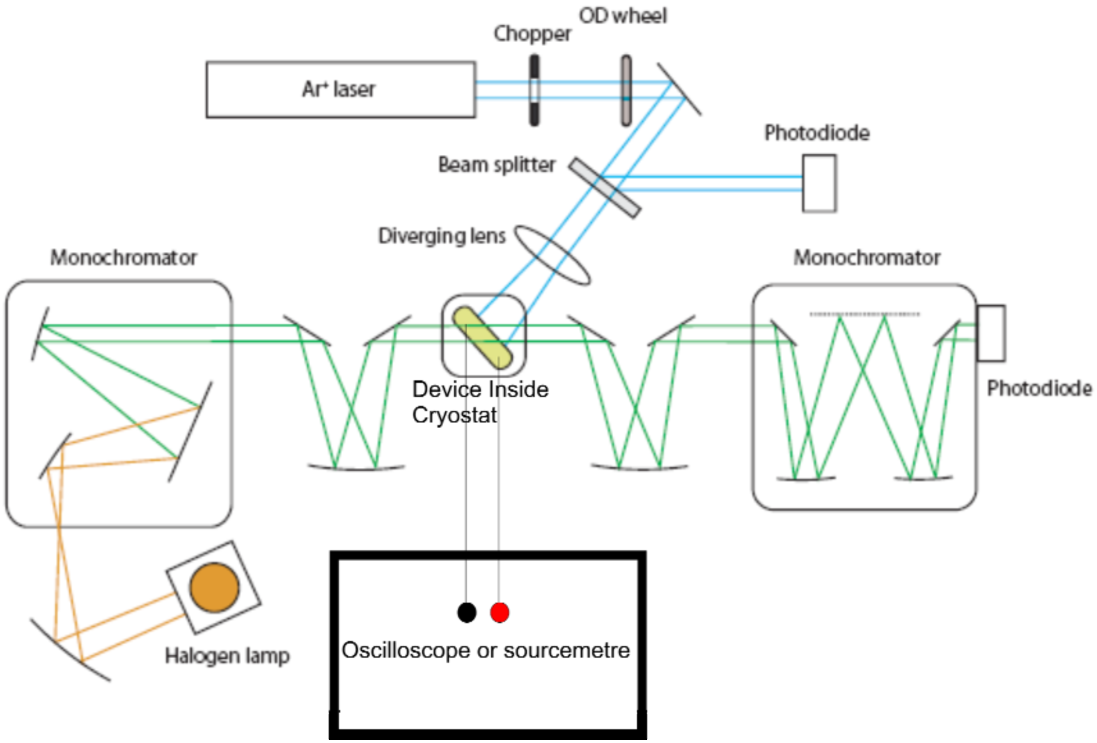
Quantifying pore filling

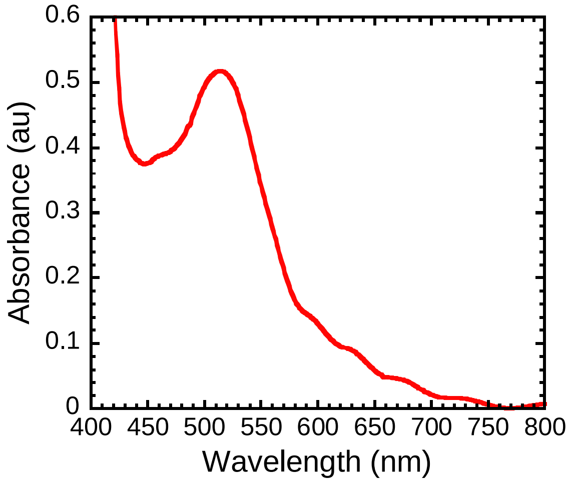
- t_{spiro} = Sol. Conc.× (wet over layer thickness + (porosity × TiO_2 thickness)) – capping layer thickness

- Pore filling fraction = t_{spiro}/(porosity × TiO_2 thickness).

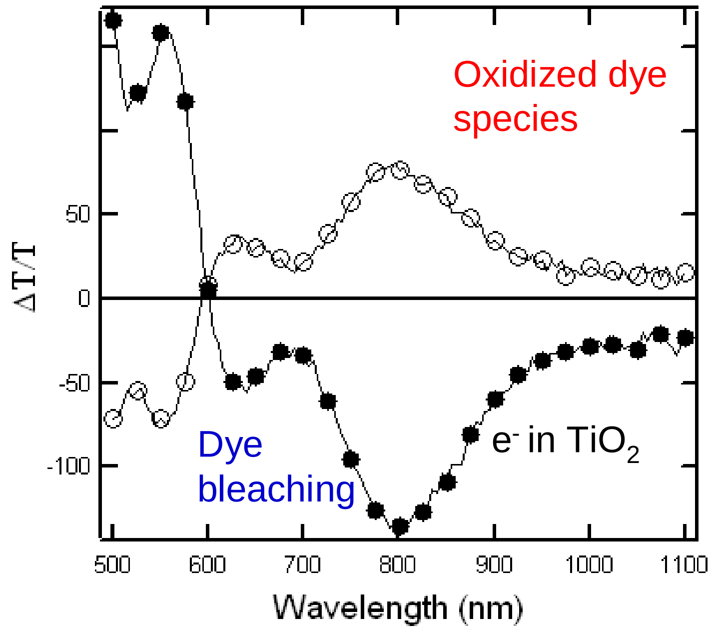
→ 0.85 for thin films of 1.8 μm
→ 0.4 for 6 μm thick films

Photoinduced absorption

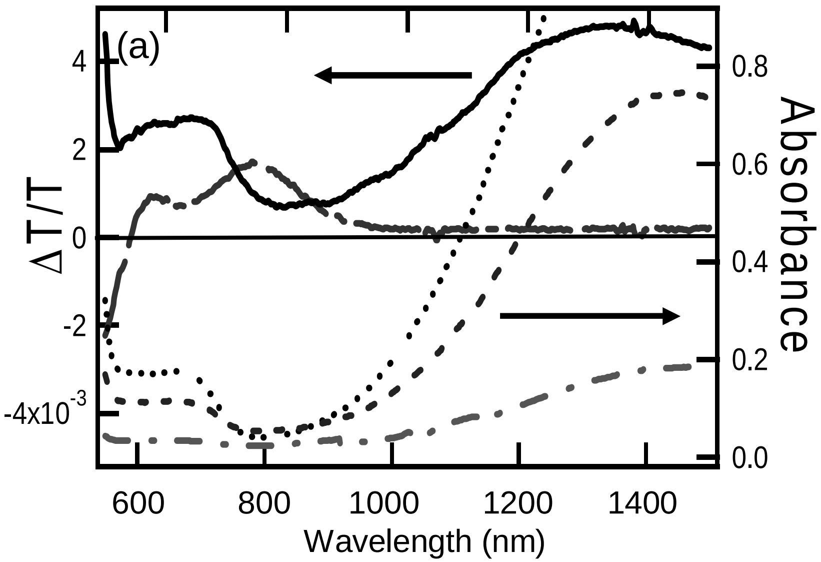


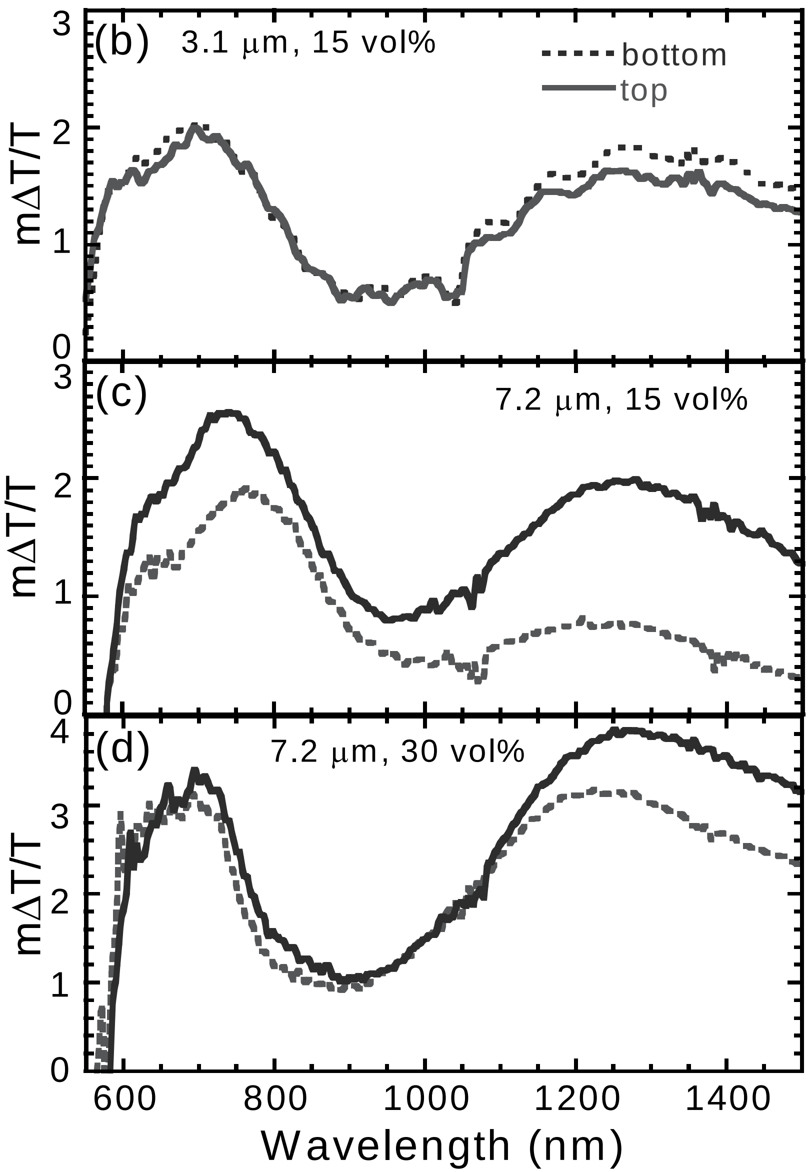


Typical PIA signal

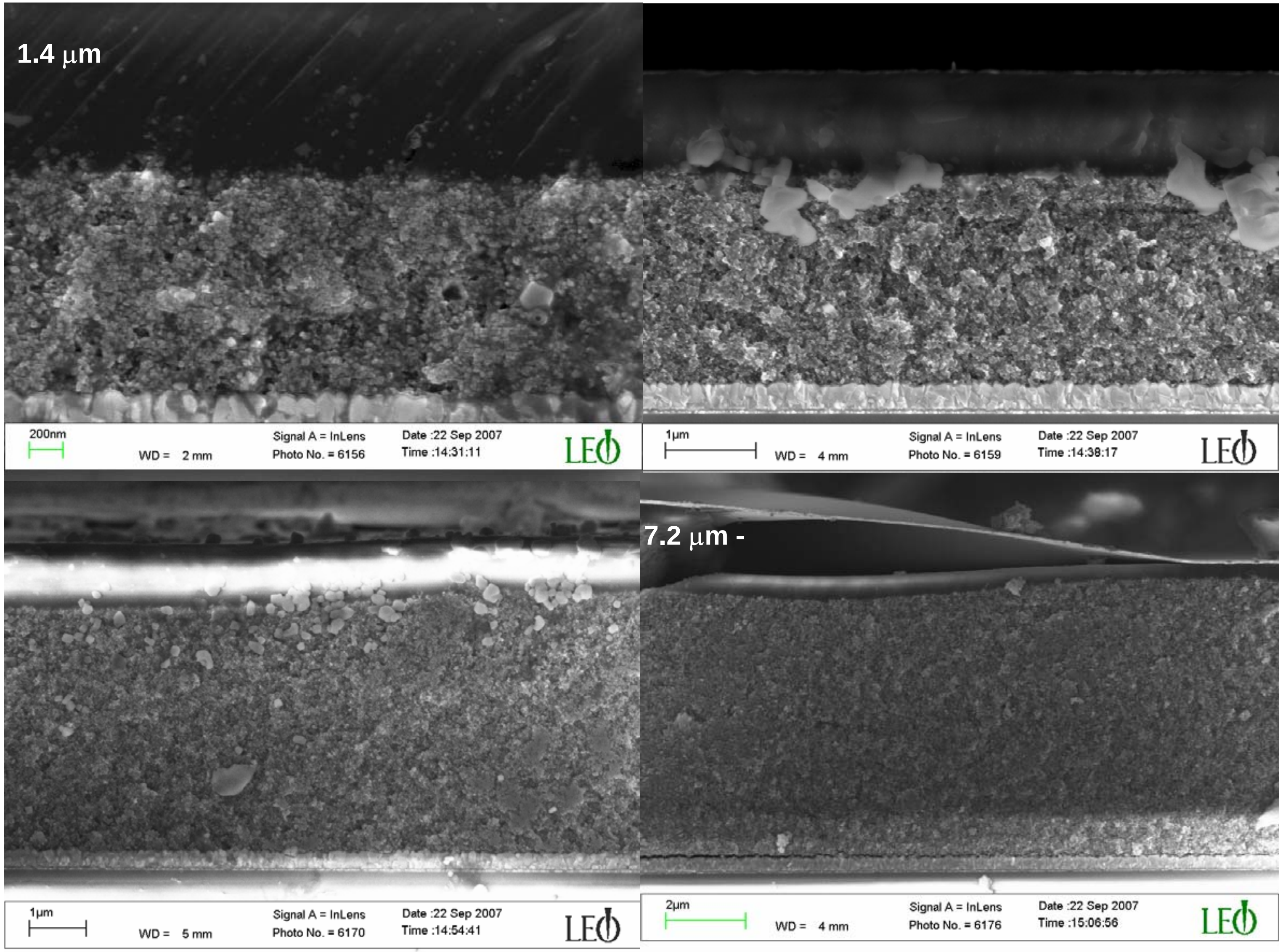


PIA on Devices

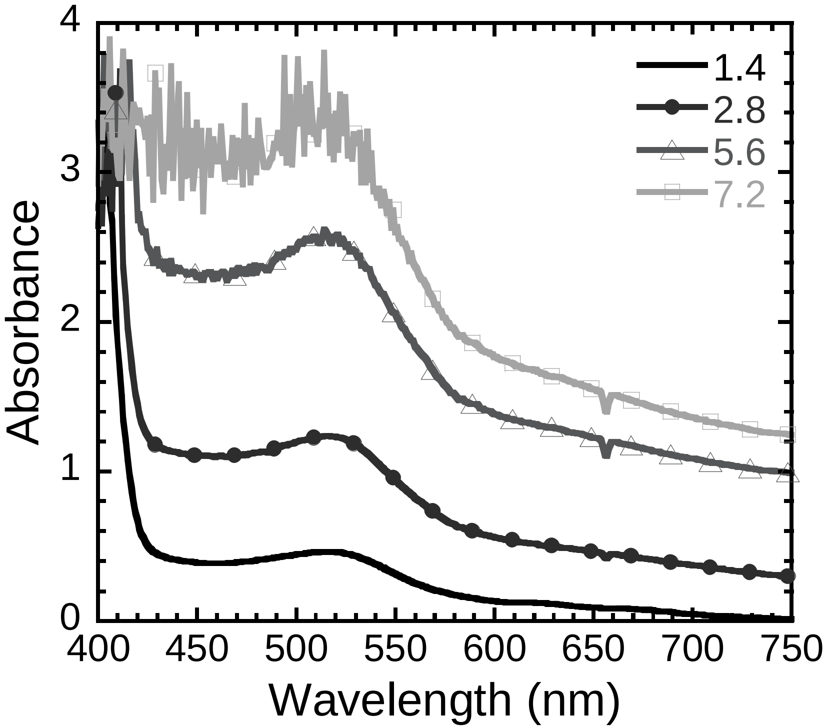


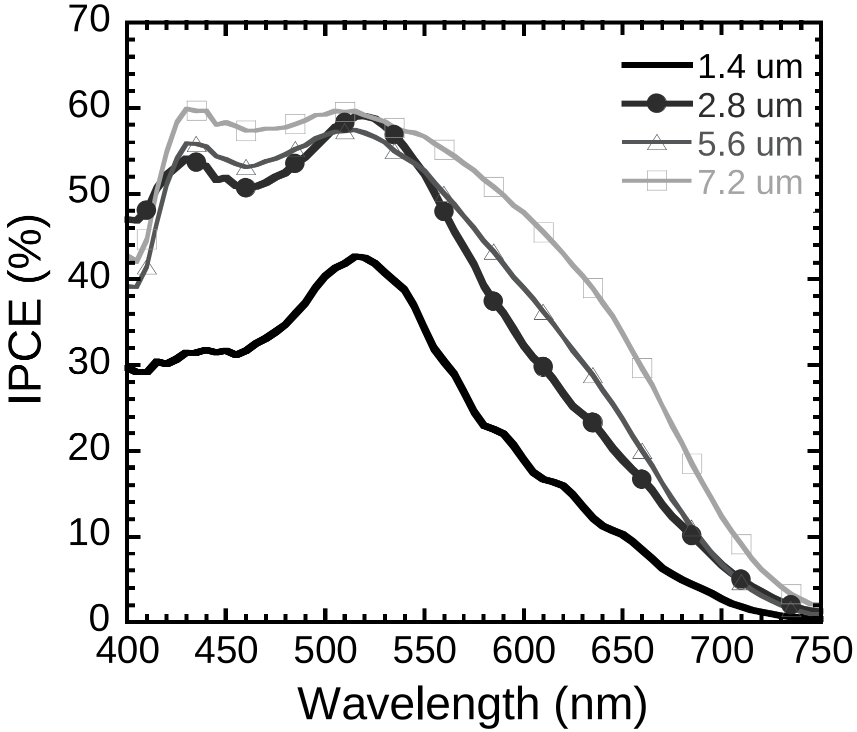


Pore filling with 30 wt%



Charge collection through thick films





IQE ~ 70 to 75%

Where has the other 25 to 30% gone?

Electron injection?

Hole-transfer?

Charge separation?

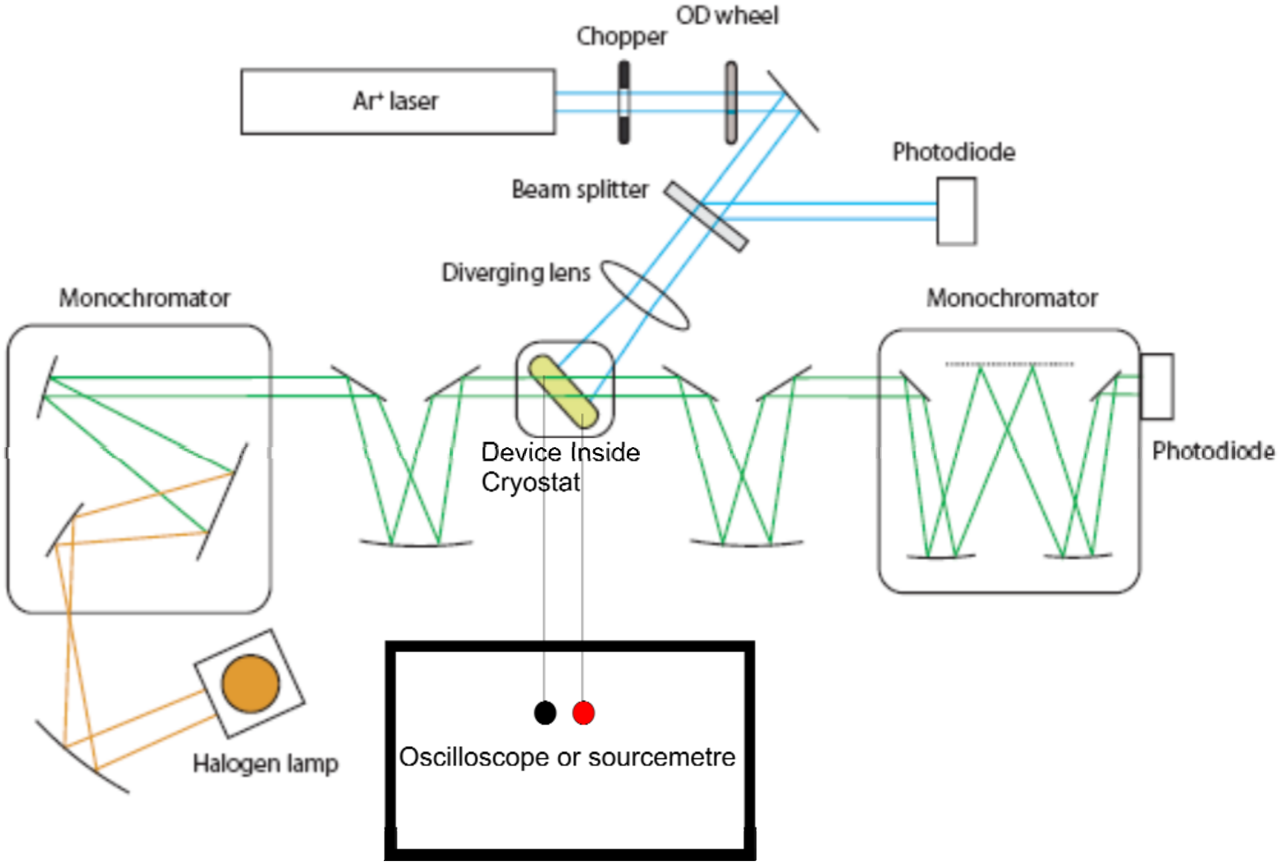
Light absorption in oxidized spiro-MeOTAD?

H. J. Snaith et al. Nanotechnology **19** (2008) 424003

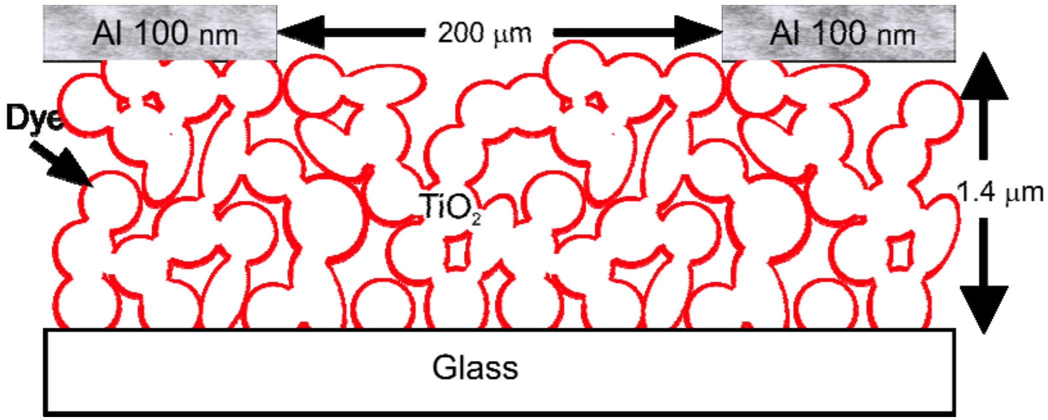
II

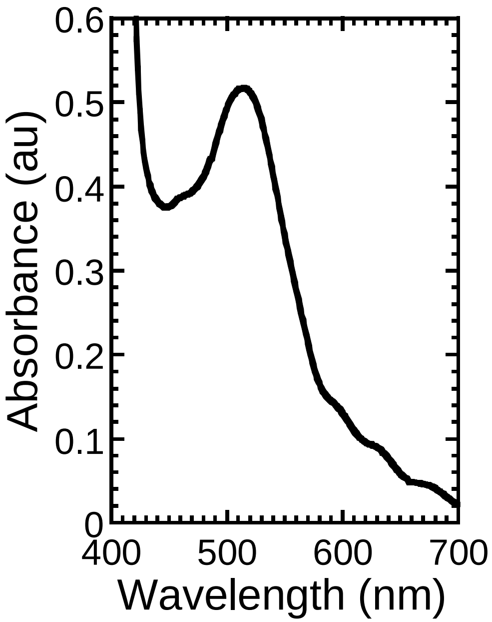
Probing the electron transport in mesoporous TiO_2

“Photo-induced charge-conductivity modulation spectroscopy“



Device structure





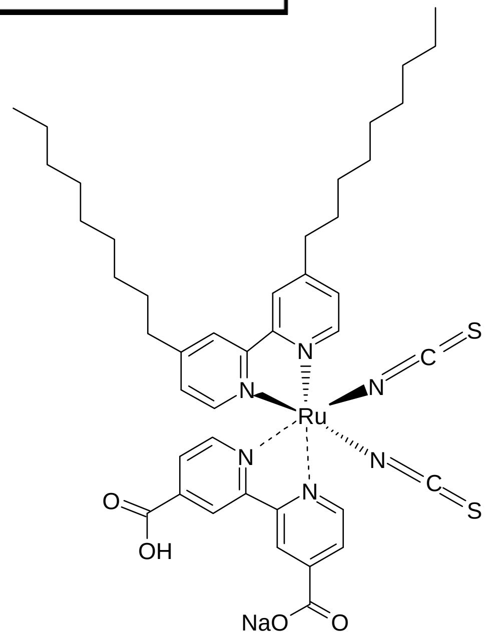
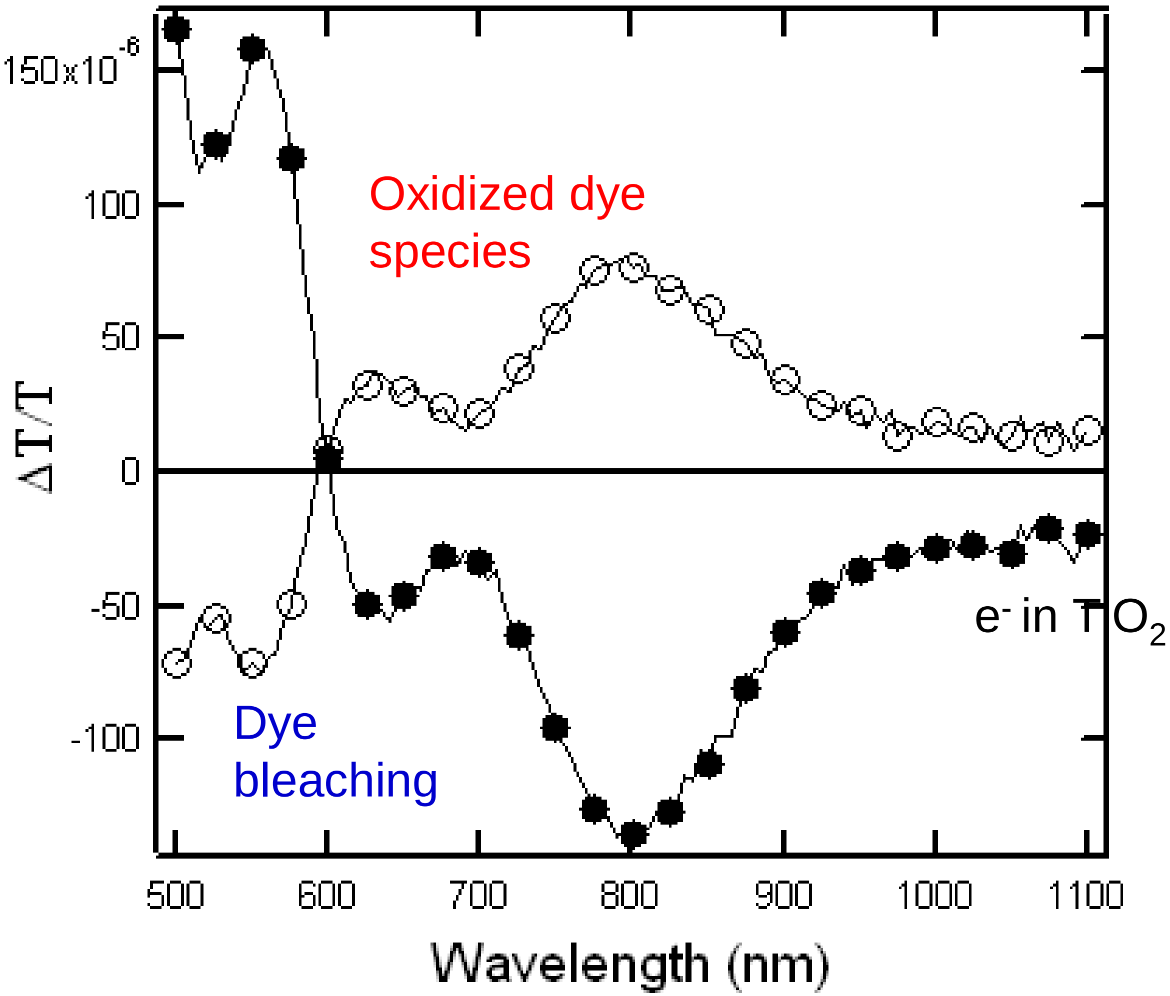
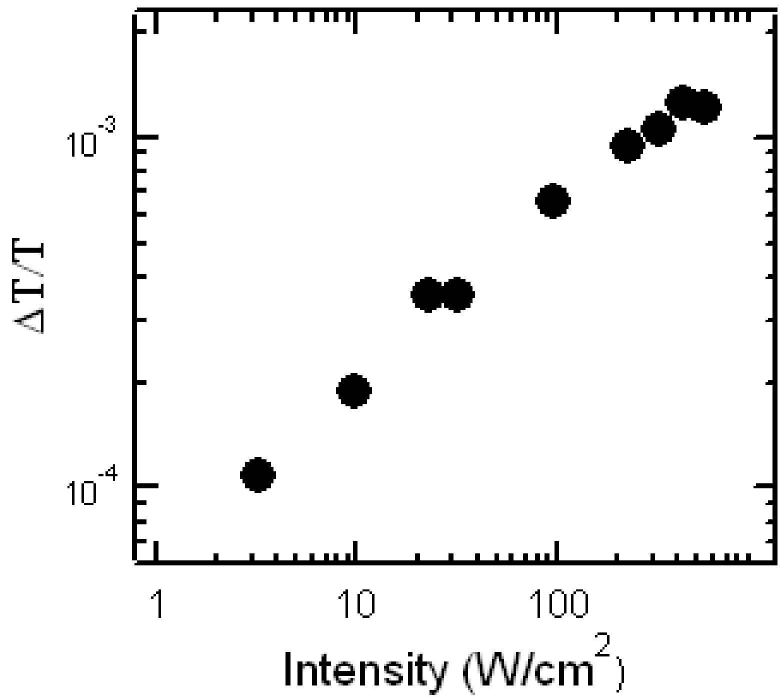
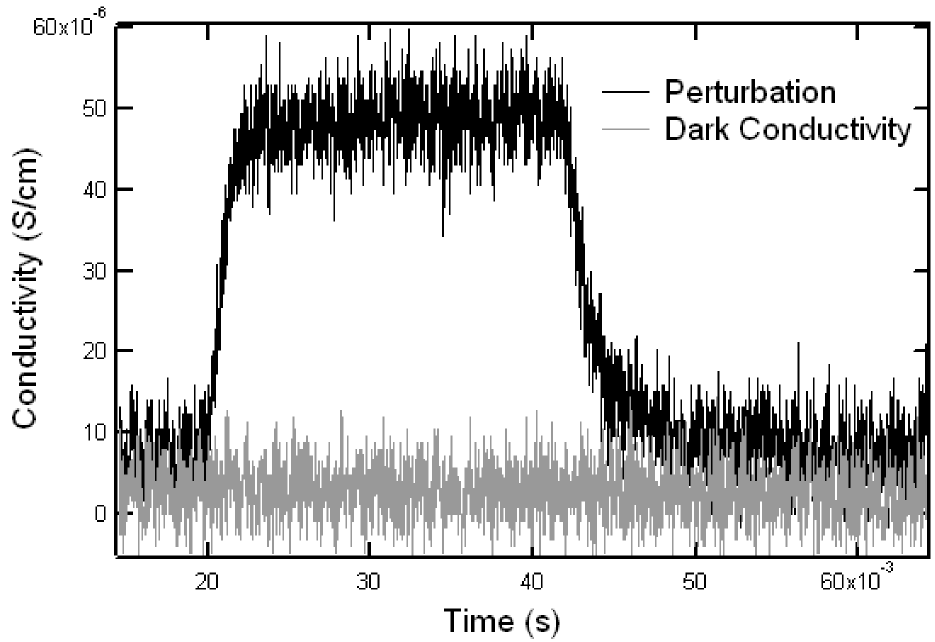


Photo-induced absorption signal



PIA signal and conductivity response





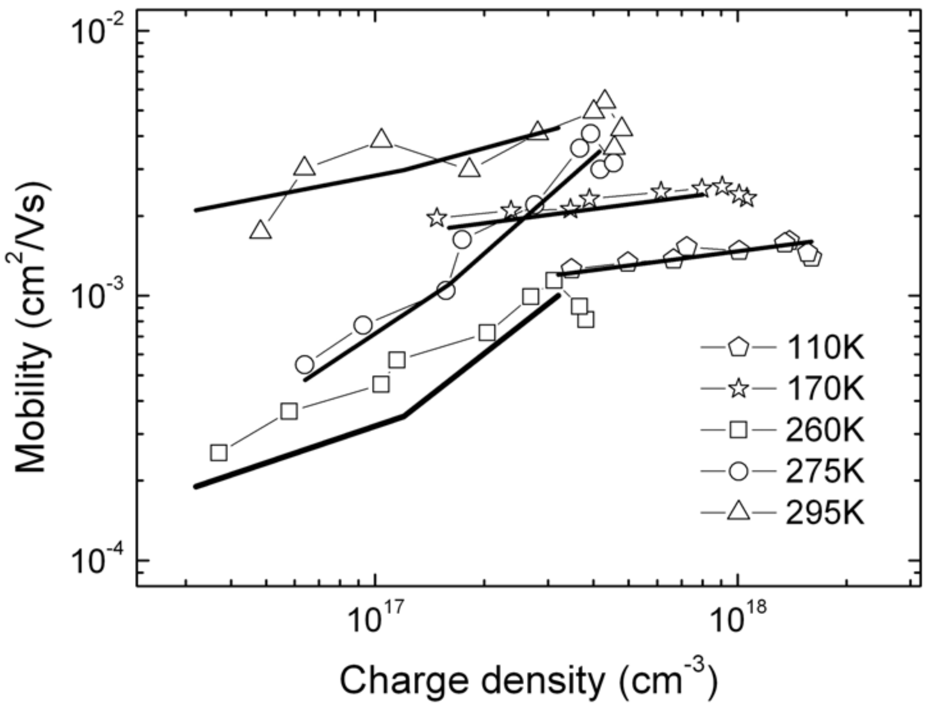
$$\Delta OD = -Log\left[1 + \frac{\Delta T}{T}\right]$$

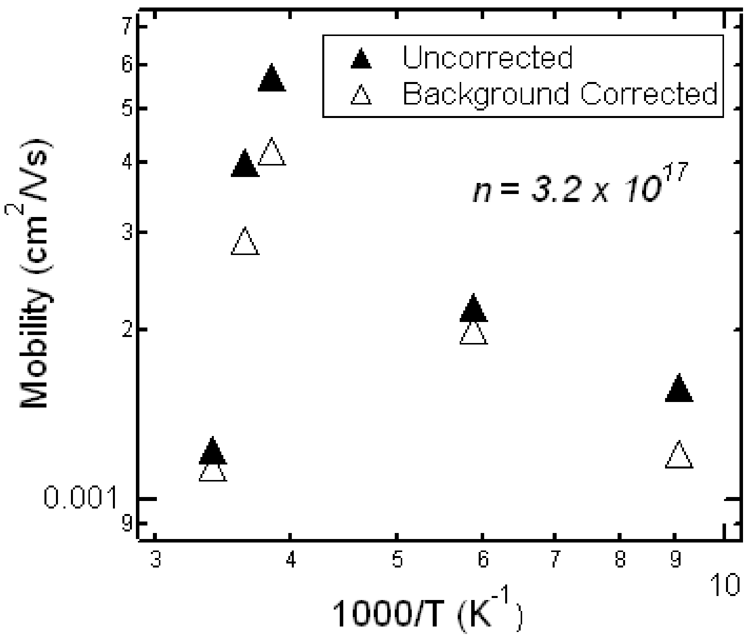
$$\Delta\sigma = \frac{IL}{Vwt} = \frac{\Delta V_{OS} L}{rVwt}$$

$$n_{dye}(cm^{-3}) = \frac{N_a A}{1000\varepsilon \times d}$$

$$\sigma = \mu \times n \times e$$

Mobility data





Funny temperature dependence

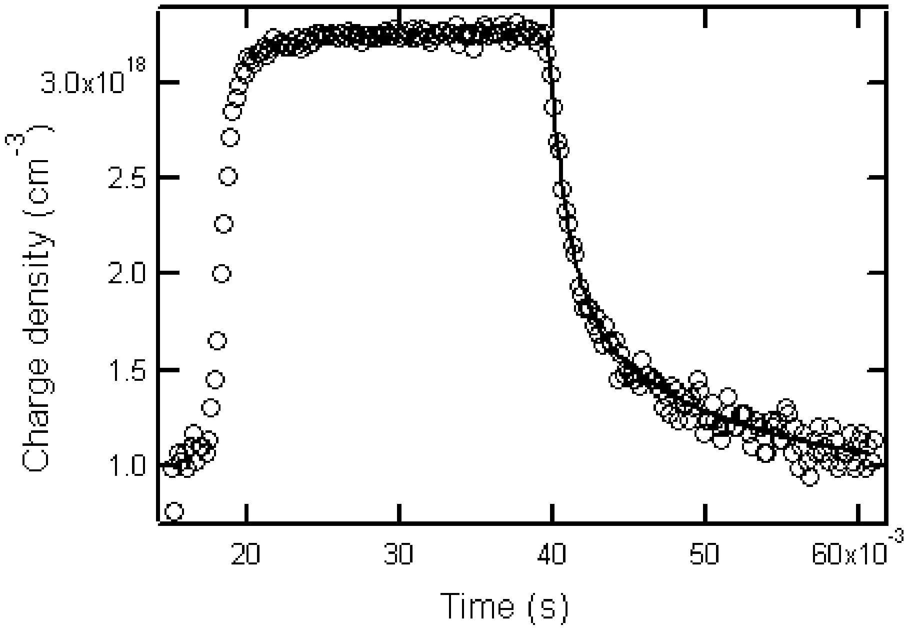
little charge density dependence at low temperature

Extracting charge recombination

$$\sigma = \mu \times n \times e$$

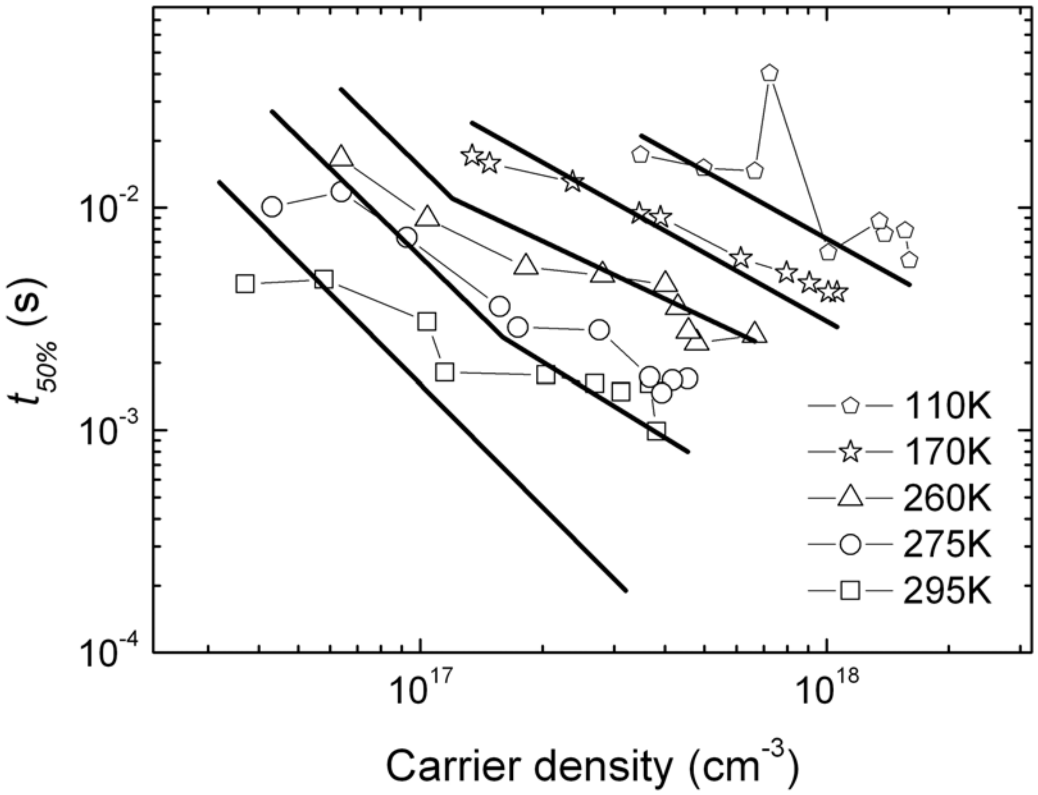
If mobility was constant we could just take the conductivity $t_{50\%}$ to = n $t_{50\%}$
However, it is not…….

We know σ(t) and we know σ(n) therefore extract n(t) →



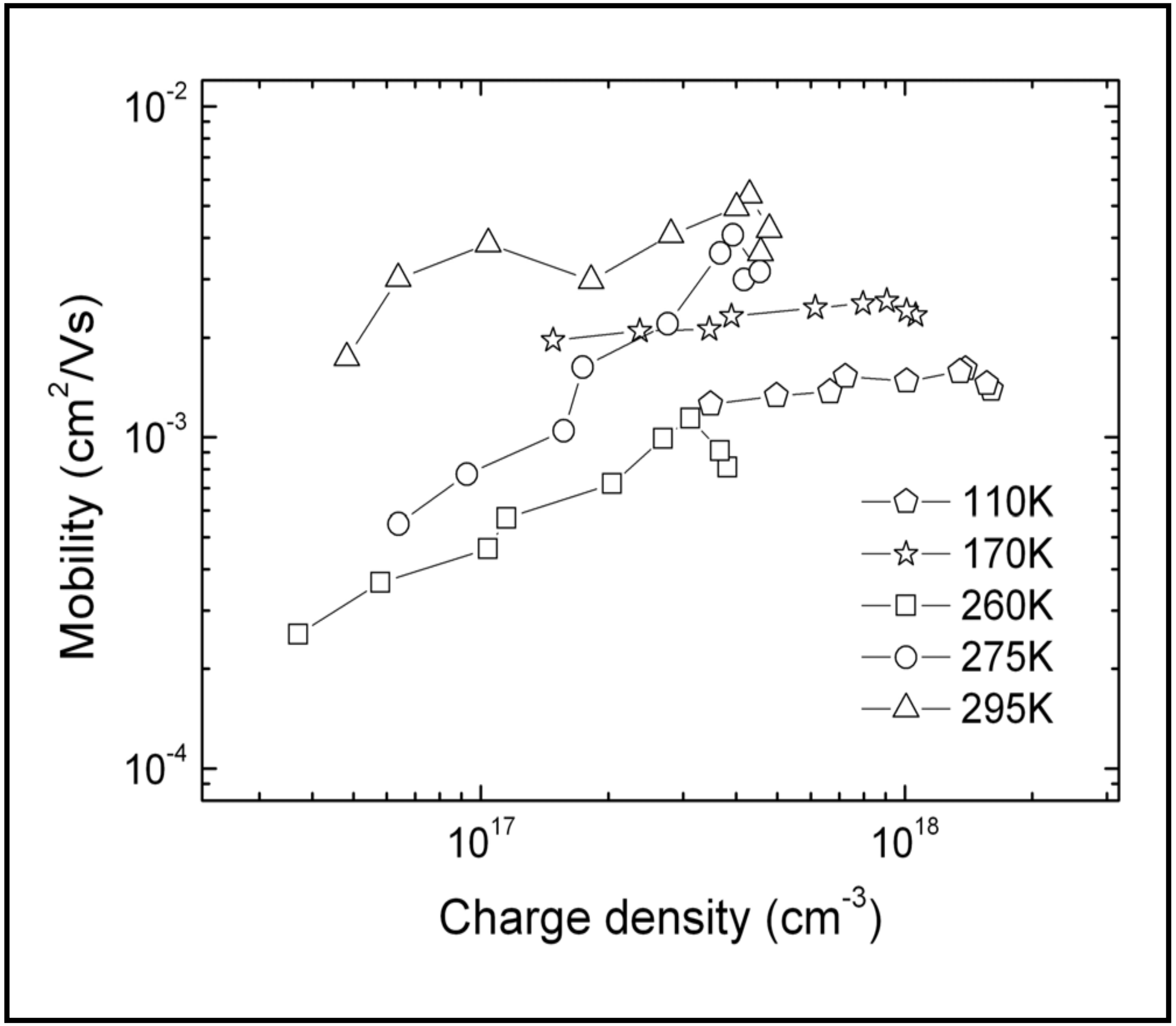
$$n(t) = K \exp(-(\frac{t}{\tau})^{\alpha})$$

Recombination results



$t_{50\%}$ monotonically:
reduces with increasing temperature
reduces with increasing charge density

The transport data



General trends

- Charge density dependence of mobility (indicative of trap filling effects)
- Charge density dependence falls with reducing temperature
- Mobility rises with falling temperature to begin with (up to 260K), and thereafter falls

What could be going on?

- Mobility increasing as temperature falls implies the DoS may be becoming shallower
- The charge density dependence is also a function of the DoS, and this changes with temperature as well

Try fitting to the data while allowing the DoS to vary with temperature

(as it turns out other transport [1] and non-transport based [2] studies also make this assumption)

[1] Anta *et al.*, *J Phys. Chem. C.*, **111** (37), pp. 13997-14000 (2007).
[2] Abayev *et al.*, *J. Solid State Electrochem.*, **11**, pp. 647-653 (2007).

Why might the DoS change with temperature?

- Lots of things that cause traps
  - e.g. crystal structure, degree of protonation, chemical impurities…

  or affect their depth
  - e.g. dielectric constant…

  that change with temperature
- A few people are confident they know what may cause a change in the DoS [2], but we're not amongst them

[2] Abayev *et al.*, *J. Solid State Electrochem.*, **11**, pp. 647-653 (2007).

Developing a model I

- Here we calculate the de-trapping time based upon the trap energy

$$t_{i \to j} = -\ln(r) t_0 \exp(E_i / kT)$$

- The de-trapped carrier then moves with a velocity that has an isotropic (diffusive) and anisotropic (drift) part that is proportional to the field. Transition probability is then…

$$p(i \to j) = \frac{1}{6} + C\overline{u_{i \to j}} \bullet \overline{F}$$

- This approach is actually quite similar to the original MT model [3]

[3] Scher and Montrol, *Phys Rev. B*, **12** (6), pp. 2455-2477 (1975).

Developing a model II

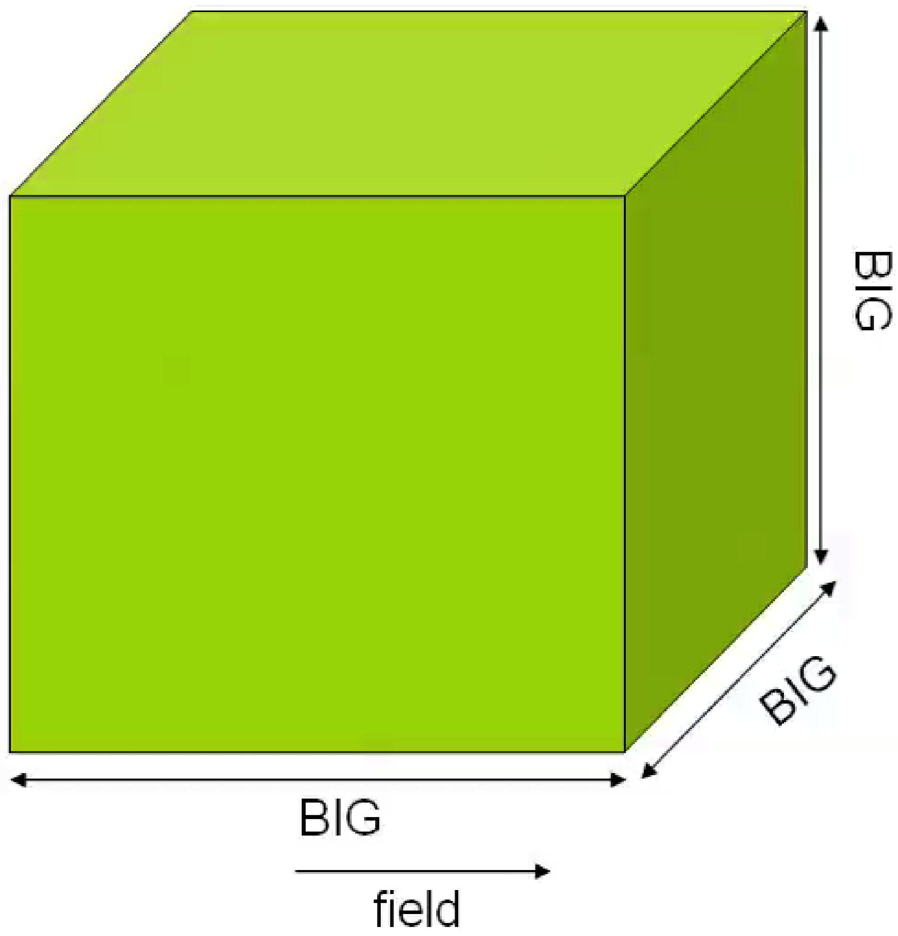
- We take a simulation volume
- Divide it into individual traps spaced by 2nm
- Fill the volume up with an appropriate number of carriers for the charge density to work out the mobility
- Carriers then execute a biased random walk as determined by the equations shown previously
- Repeated many times for many different conformations of trap energy
- Choose parameters to be the same as used in other models where possible

  $t_0 = 2\times10^{12}\ s^{-1}$

  $F = 1.5\times10^{4}$ V/m

  and to be sensible elsewhere

  $C = 10^{-6}$
- The DoS is allowed to vary

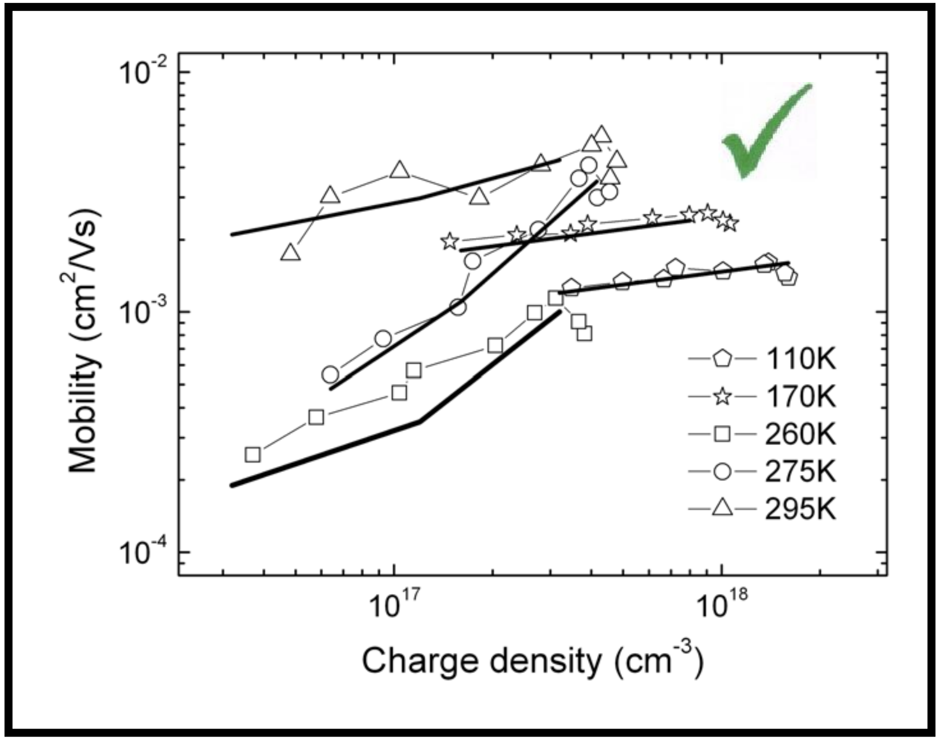


movie

Mobility fits to the data

Remarkably little flexibility to fit to the charge density curves…

- Hopping model didn't work
- Other multiple trapping models didn't work
- Gaussian and exponential DoS could not be used interchangeably

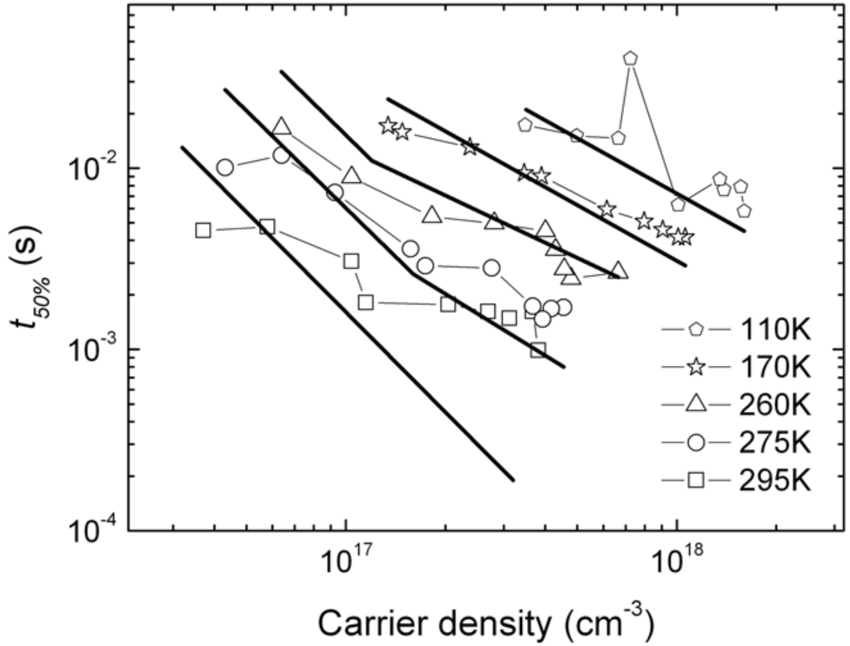


	110	170	260	275	295
Gaussian or exponential	G	G	G	E	E
E_0 (meV)	85	143	30	52	59
σ (meV)	20	20	100	N/A	N/A

General trends as temperature falls

- DoS shallows
- DoS becomes narrower

Recombination fits to the data



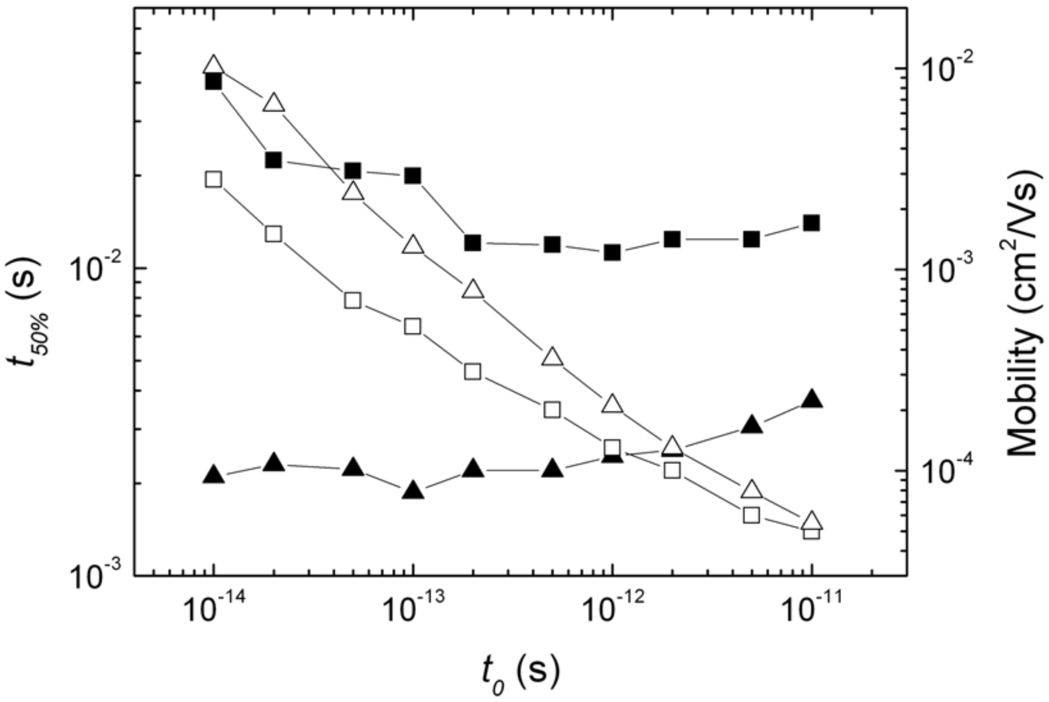
- Use identical DoS as previously
- Only vary k_s
- Good fits with thermally activated k_s

	110K	170K	260K	275K	295K
Gaussian or Exponential	Gaussian	Gaussian	Gaussian	Exponential	Exponential
E_0	85meV	143meV	30meV	52meV	59meV
σ	20meV	20meV	100meV	N/A	N/A
k_s	$6\times10^4 s^{-1}$	$8\times10^4 s^{-1}$	$3\times10^7 s^{-1}$	$4\times10^7 s^{-1}$	$10^{10} s^{-1}$
<*E*>	126meV	170meV	352meV	450meV	500meV

What does this all mean?

- Artificially vary the transport while keeping all other parameters constant

$$t_{i\rightarrow j} = -\ln(r)t_0 \exp(E_i/kT)$$



Charge density dependence arises mainly from bi-molecular nature (rec $\propto$ n×p)

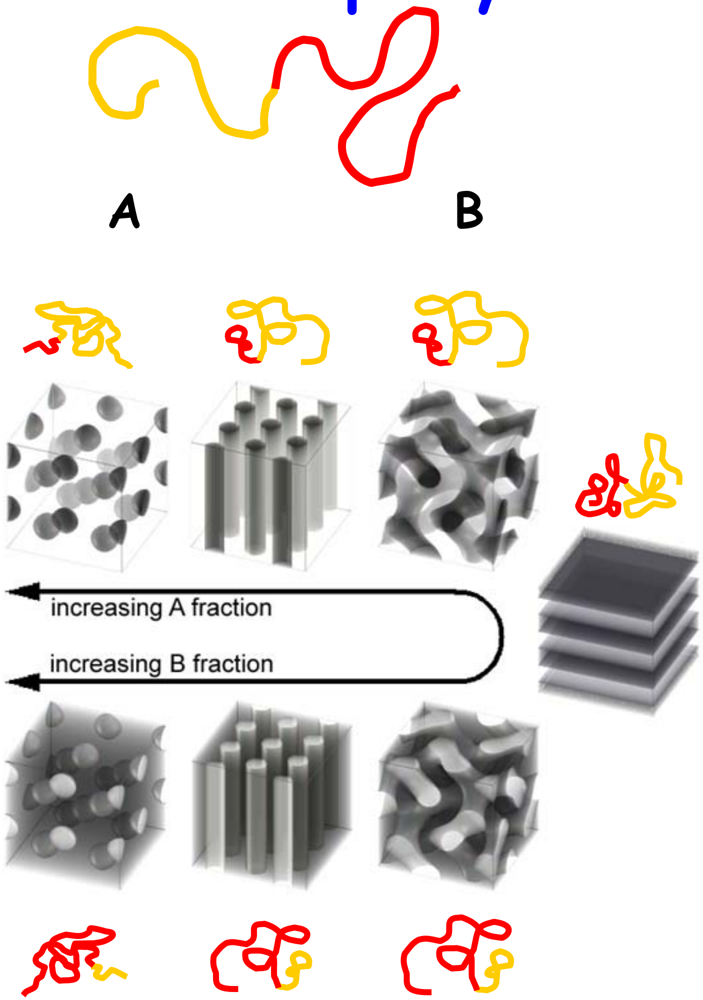
Recombination limited by interfacial recombination process and not transport.

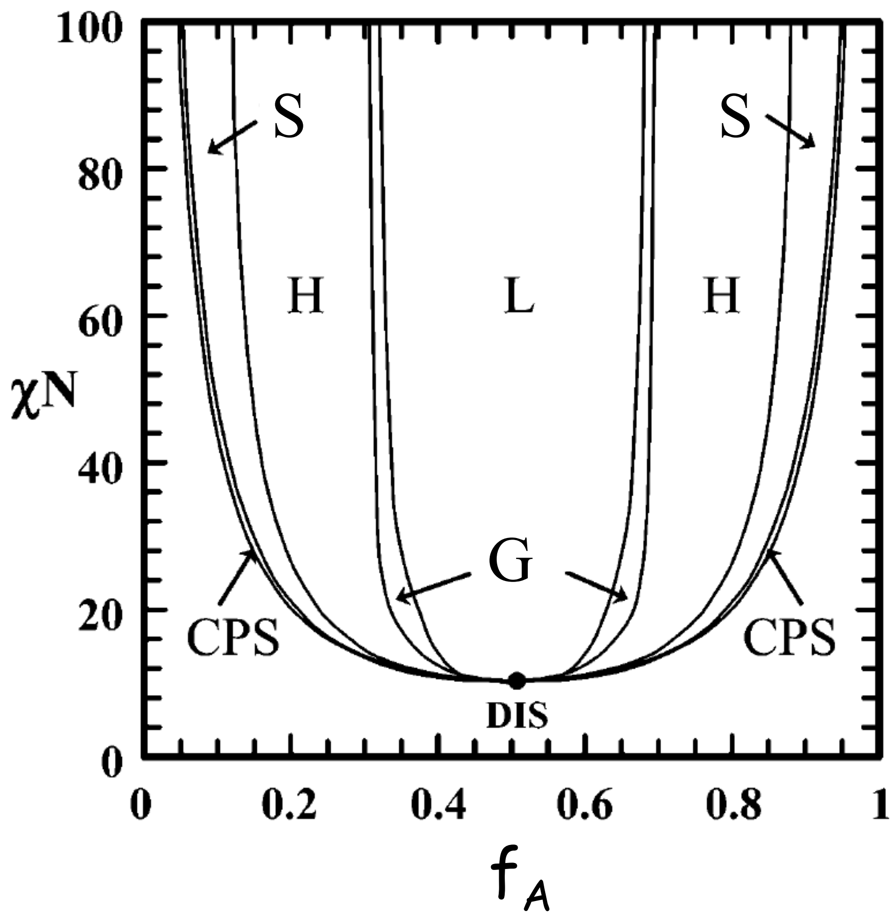
A. Petrozza et al. JACS 2008

III

TiO_2 electrodes structured by diblock copolymer templates:: probing the structure-function relationship

Controlling structure *via* diblock copolymer self-assembly

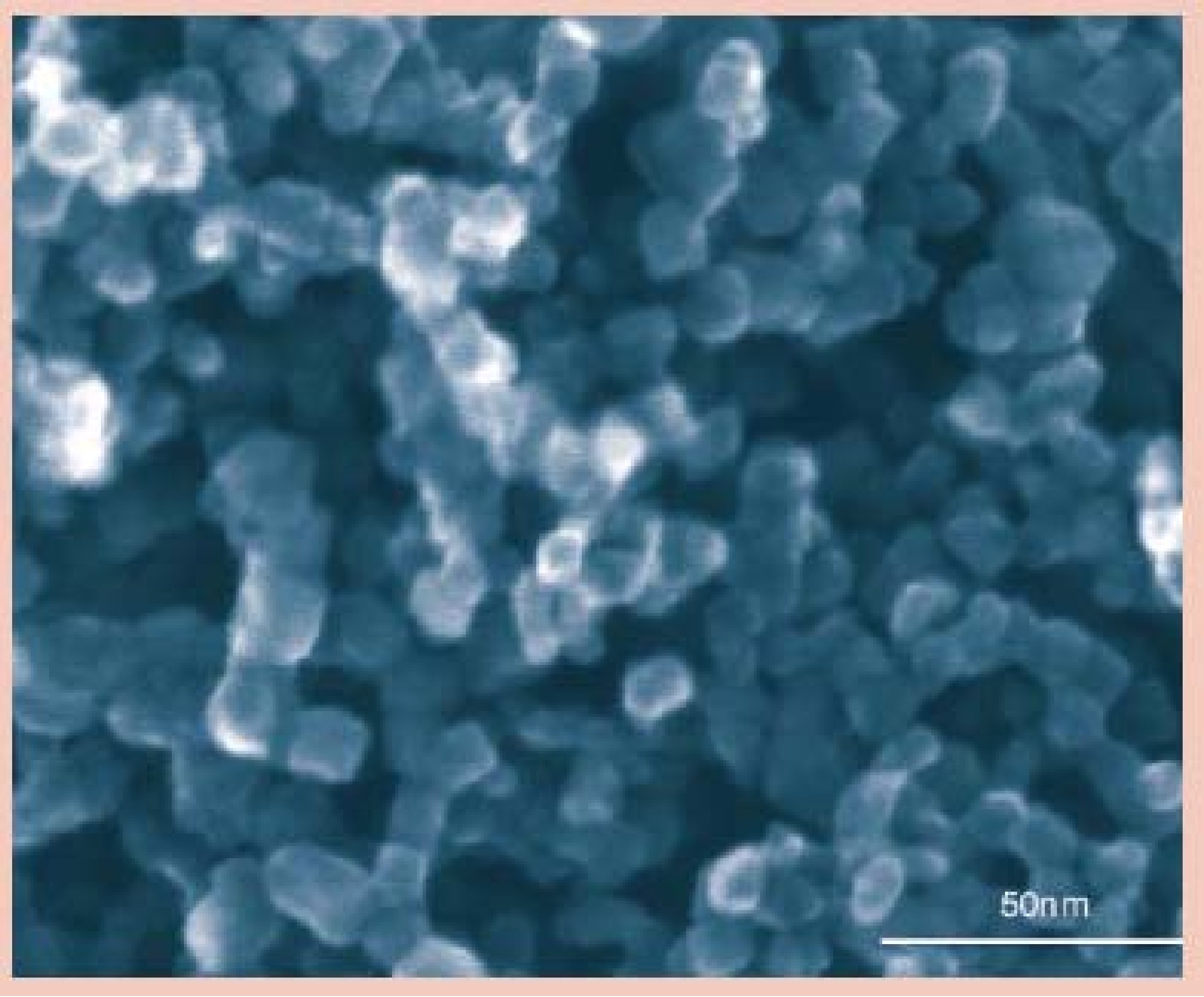




Images : *Mathematical Sciences Research Institute (MSRI) http://www.msri.org*

Theoretical Phase Diagram: Cochran, E. W. et. al. *Macromolecules;* **2006**, *39, 2449-2451*

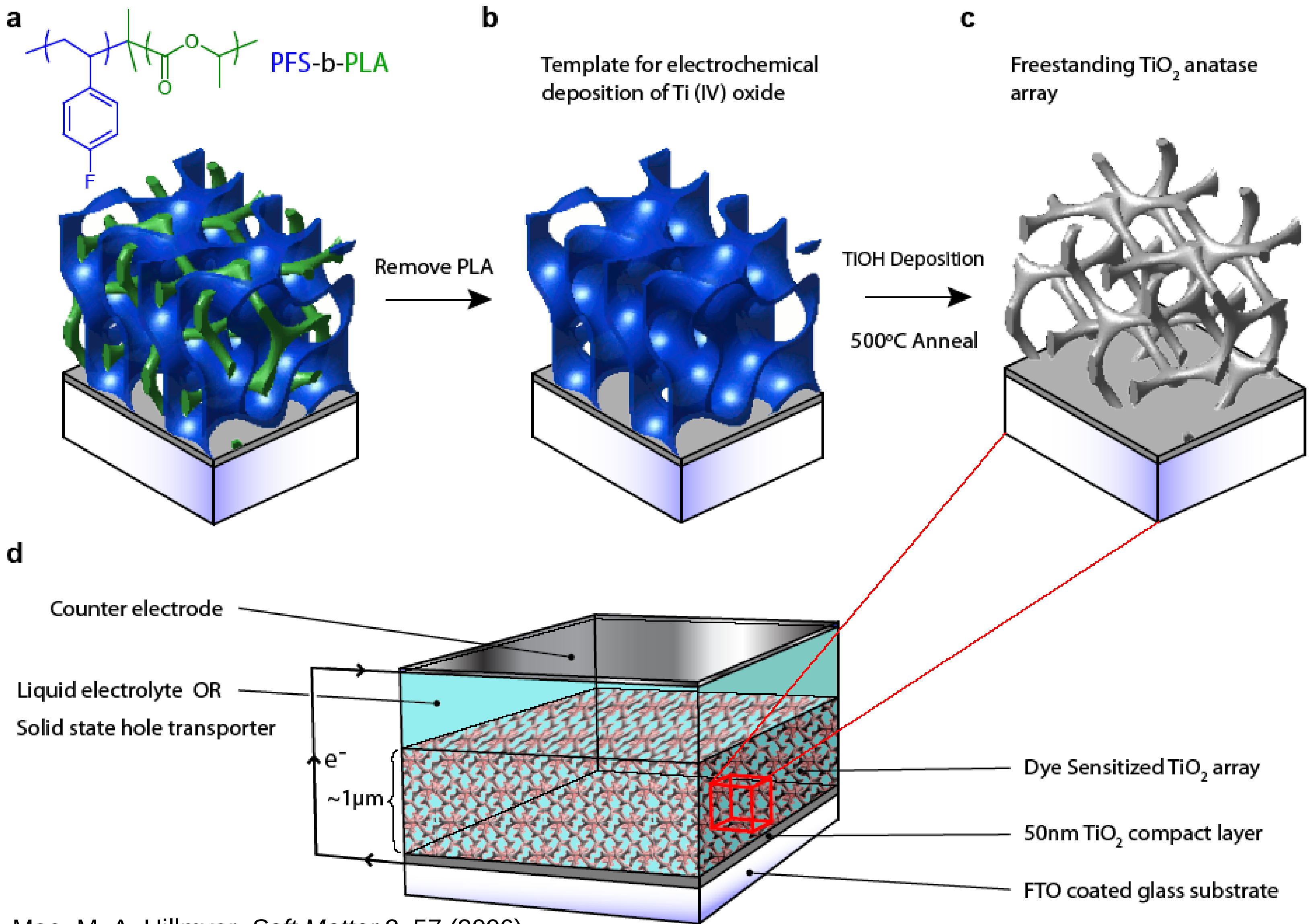
Standard mesoporous titania



Colloidal TiO_2 particles mixed with polymer to make paste

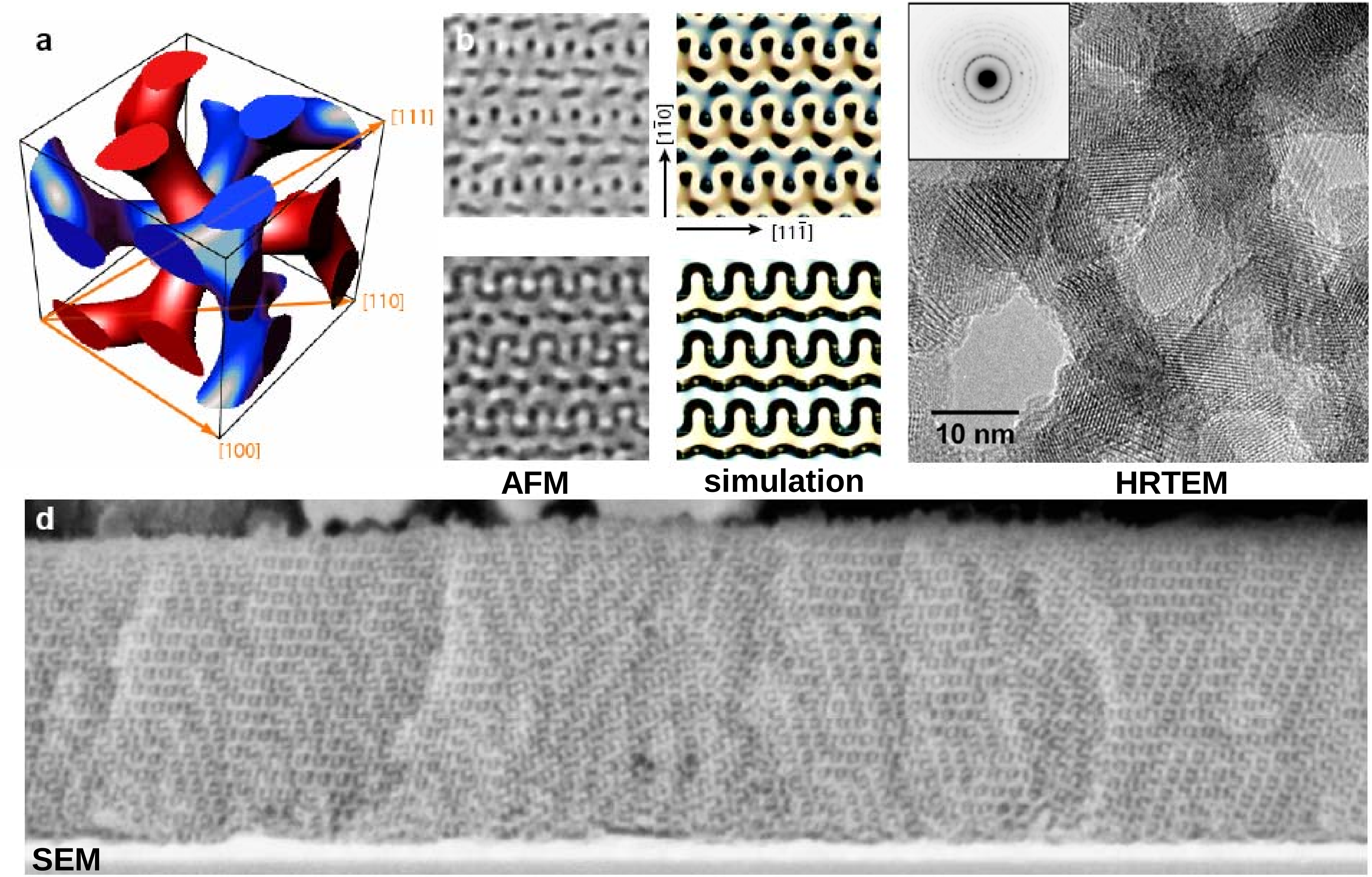
Heated, burnt and sintered at 500degrees

Templating route



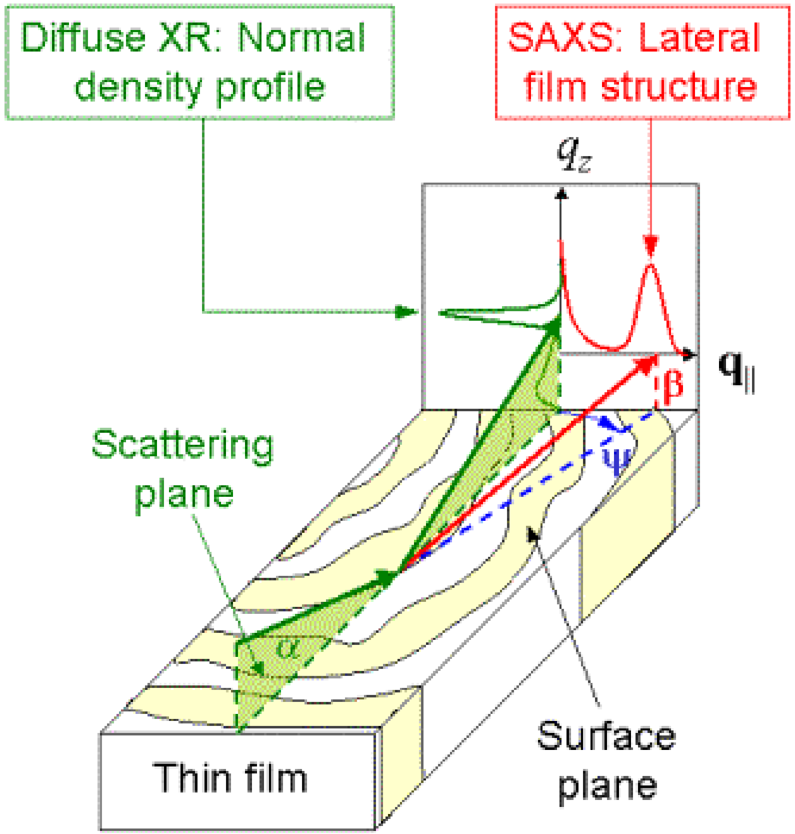
H. Mao, M. A. Hillmyer, *Soft Matter* 2, 57 (2006)
14. G. S. Armatas, M. G. Kanatzidis, *Nature* 441, 1122 (2006).(Germanium)
15. V. N. Urade, T. Wei, M. P. Tate, J. D. Kowalski, H. W. Hillhouse, *Chem. Mater.* 19 (2007).(Platinum)

Replicated Gyroid in TiO_2



Other Gyroid systems: G. S. Armatas, M. G. Kanatzidis, *Nature* 441, 1122 (2006).(Germanium)
V. N. Urade, T. Wei, M. P. Tate, J. D. Kowalski, H. W. Hillhouse, *Chem. Mater.* 19 (2007).(Platinum)

X-ray scattering



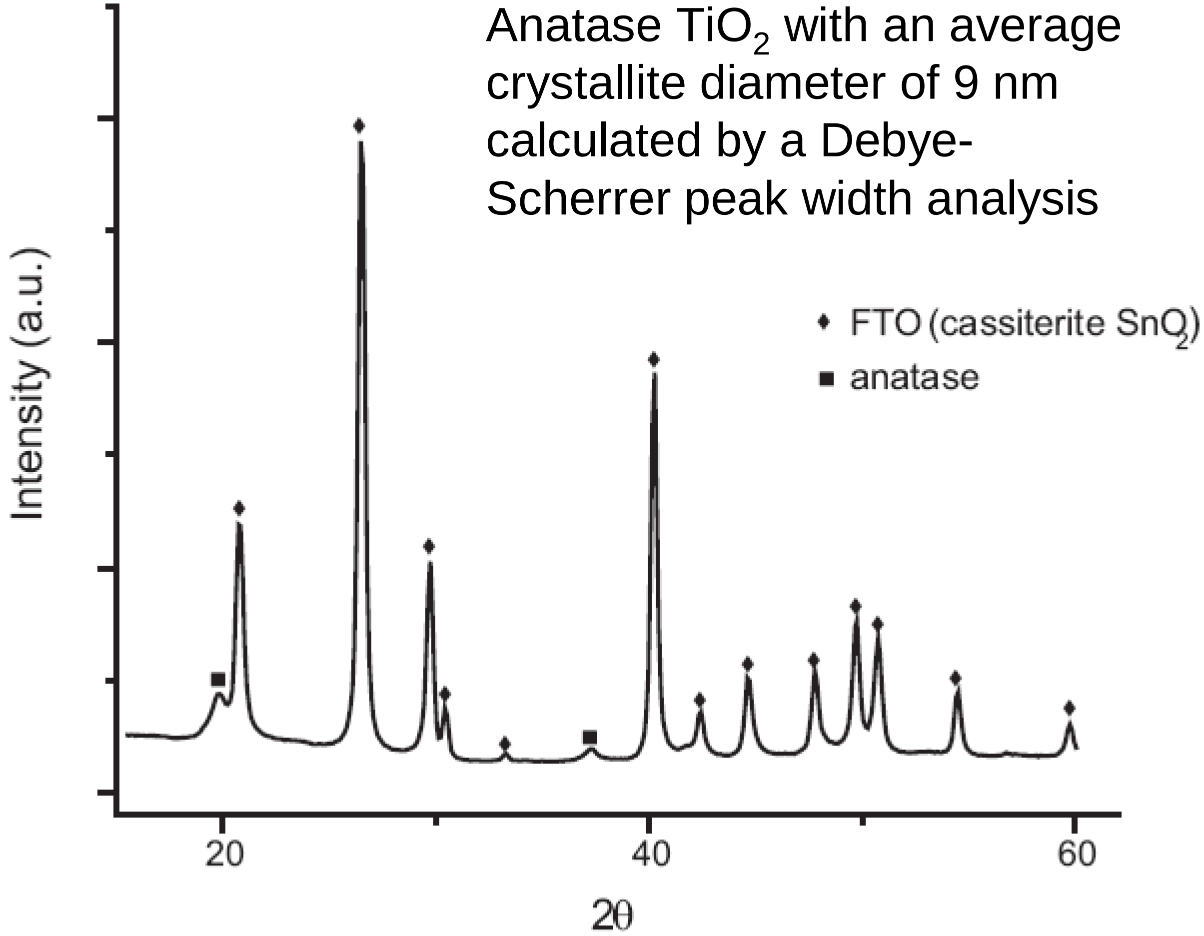
Small angle→ long range film structure

Wide angle→ small feature, crystal structure

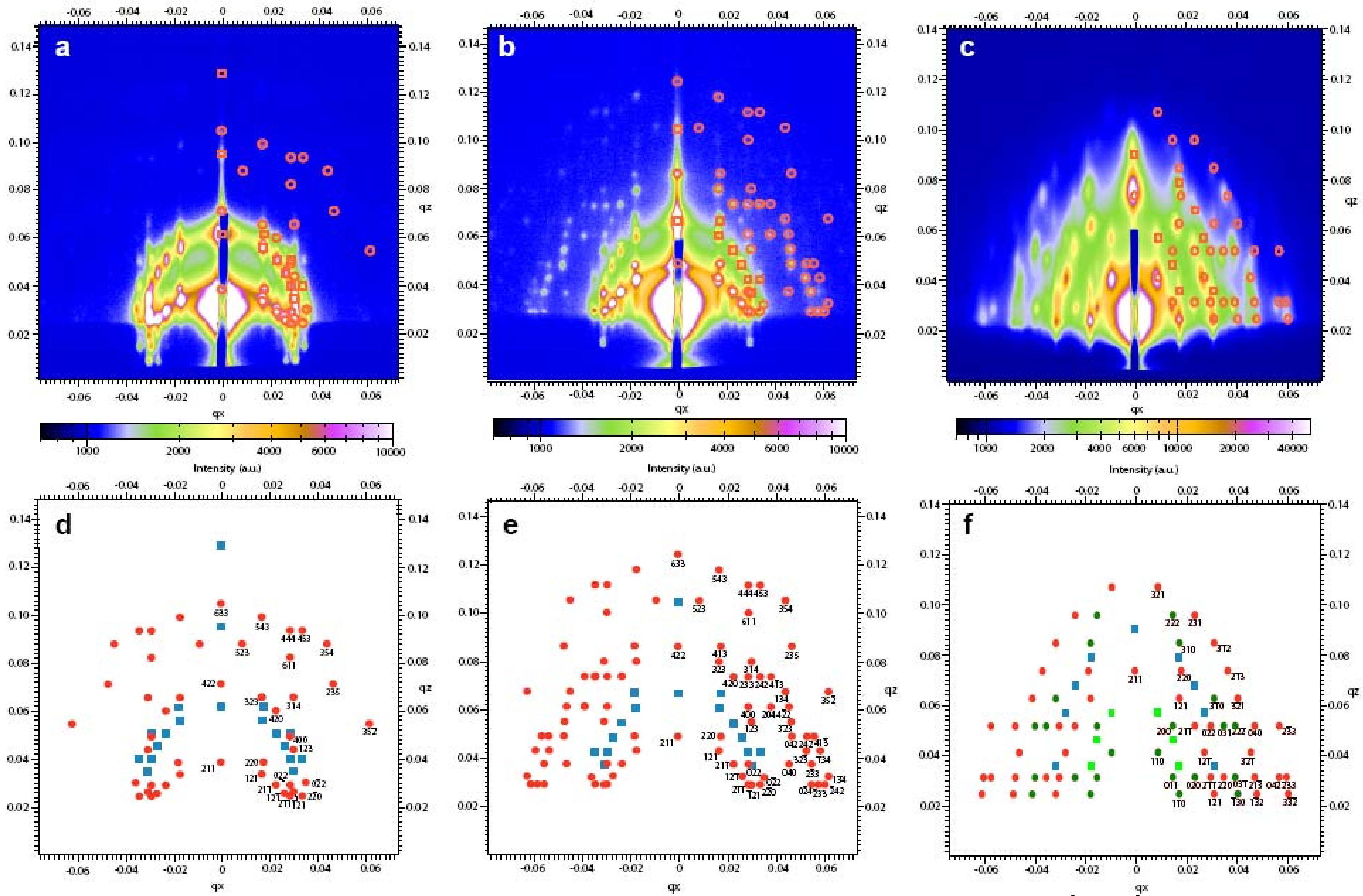
Cornell High Energy Synchrotron Source (CHESS)
Marleen Kamperman, Detlef Smilgies

Grazing incidence wide-angle X-ray scattering (GIWAXS)

Anatase TiO_2 with an average crystallite diameter of 9 nm calculated by a Debye-Scherrer peak width analysis



Characterisation of the gyroid morphology by GISAXS



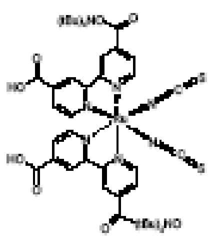
voided PFS template
9% z-compression

Ti(V) hydroxide
21% z-compression

Titania array
53% z-compression

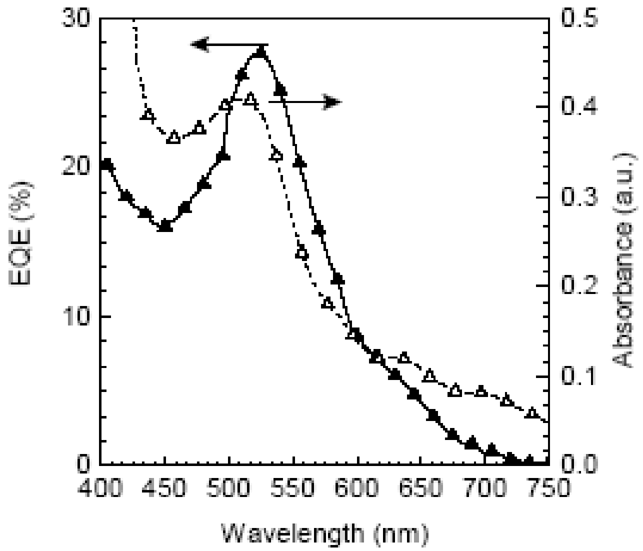
Solar cell performance

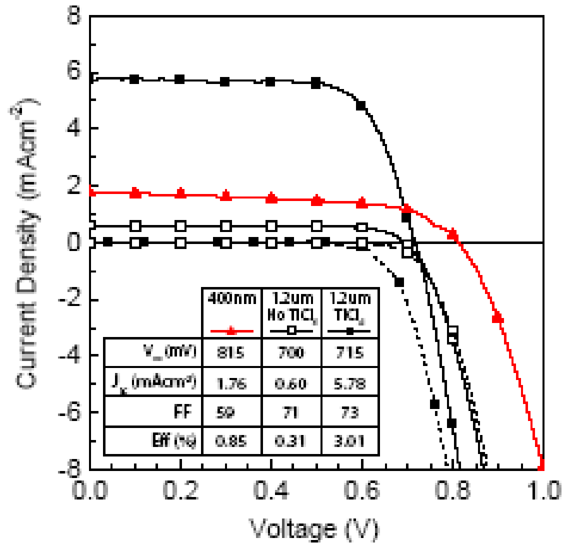
N719



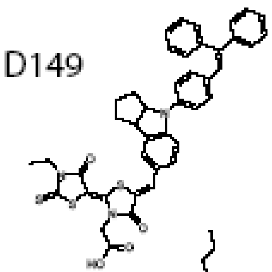
Liquid
1.2 μm

“Robust”
electrolyte



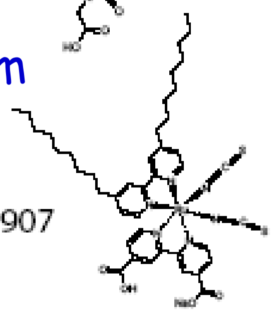


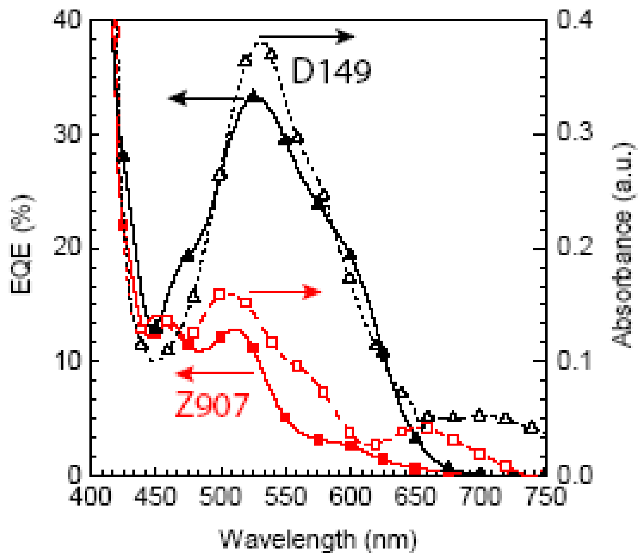
D149

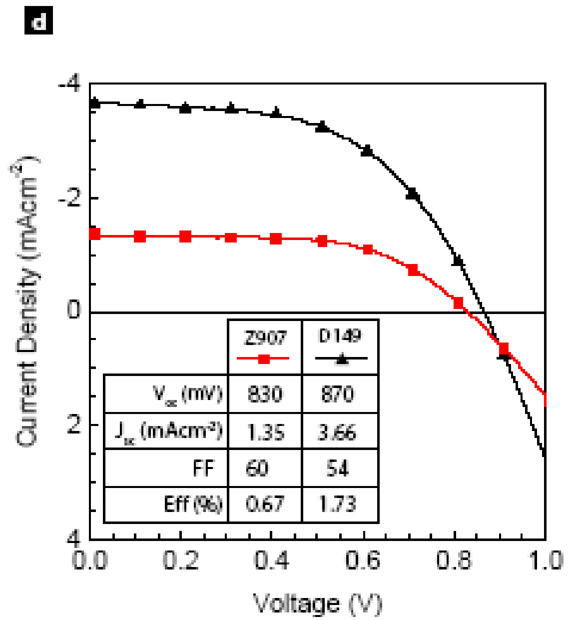


Solid
400 nm

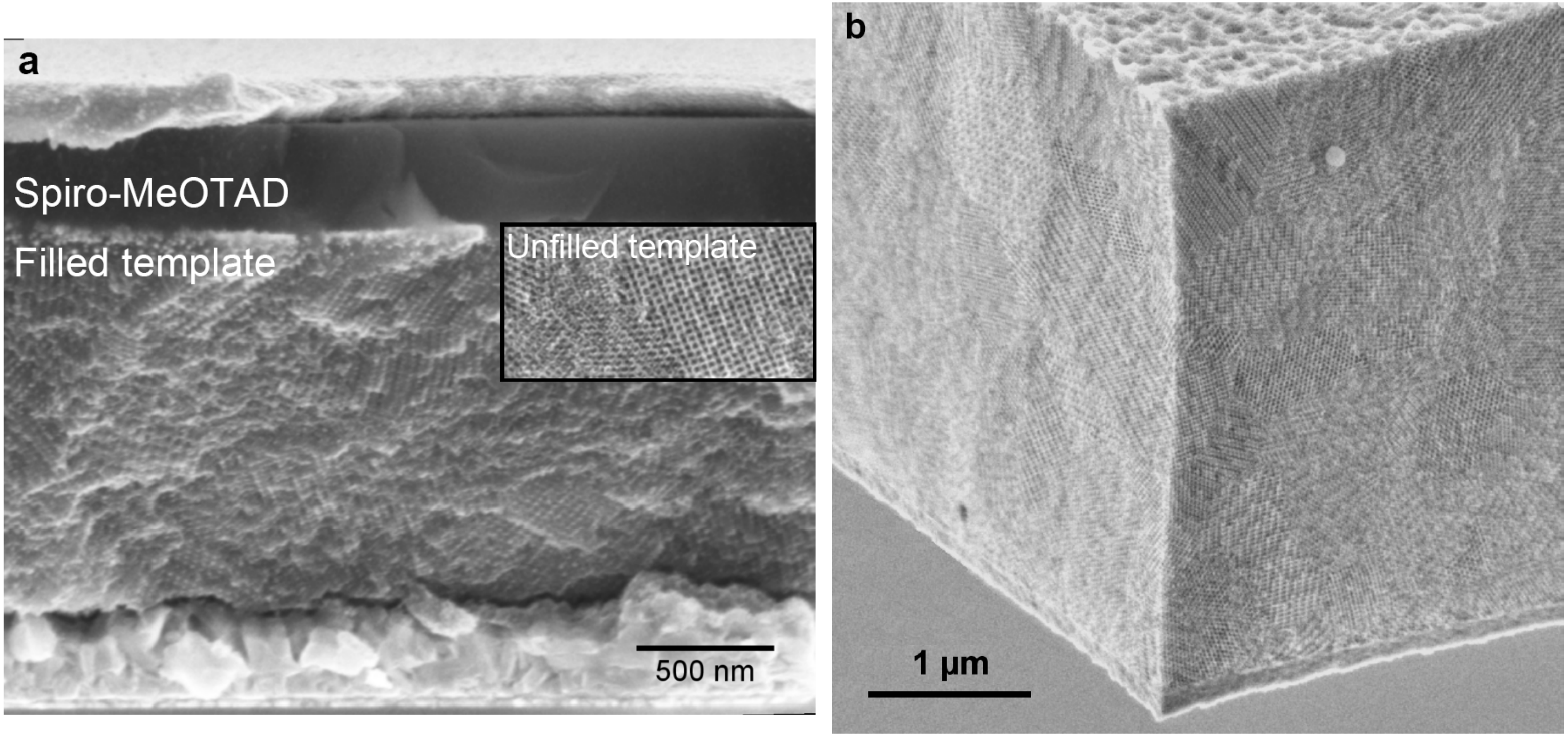
Z907







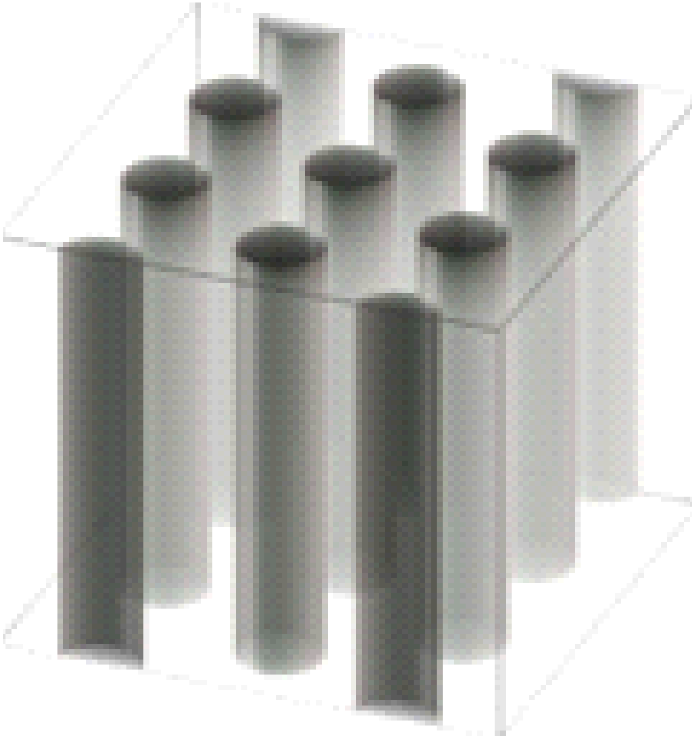
Good pore filling and thick films



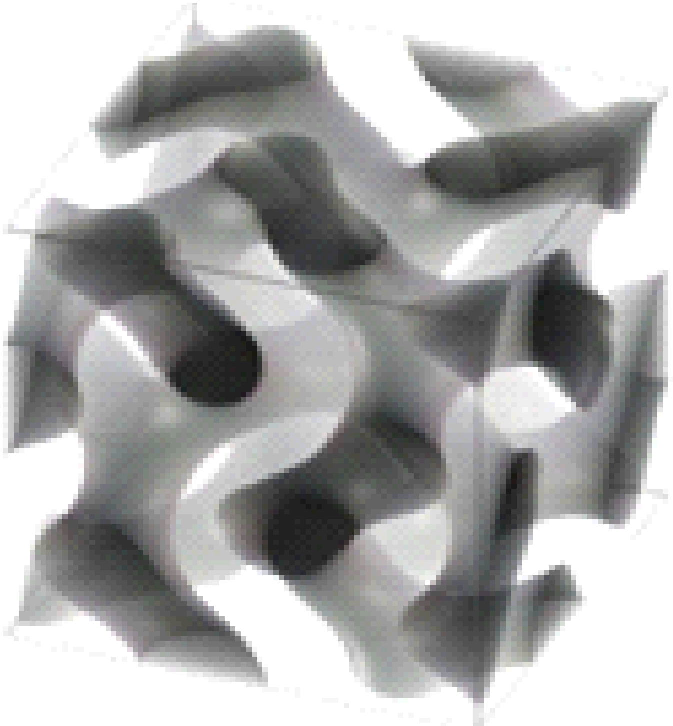
E. J. W. Crossland et al nano. Lett. 2008 in-press

Influence of mesostructure

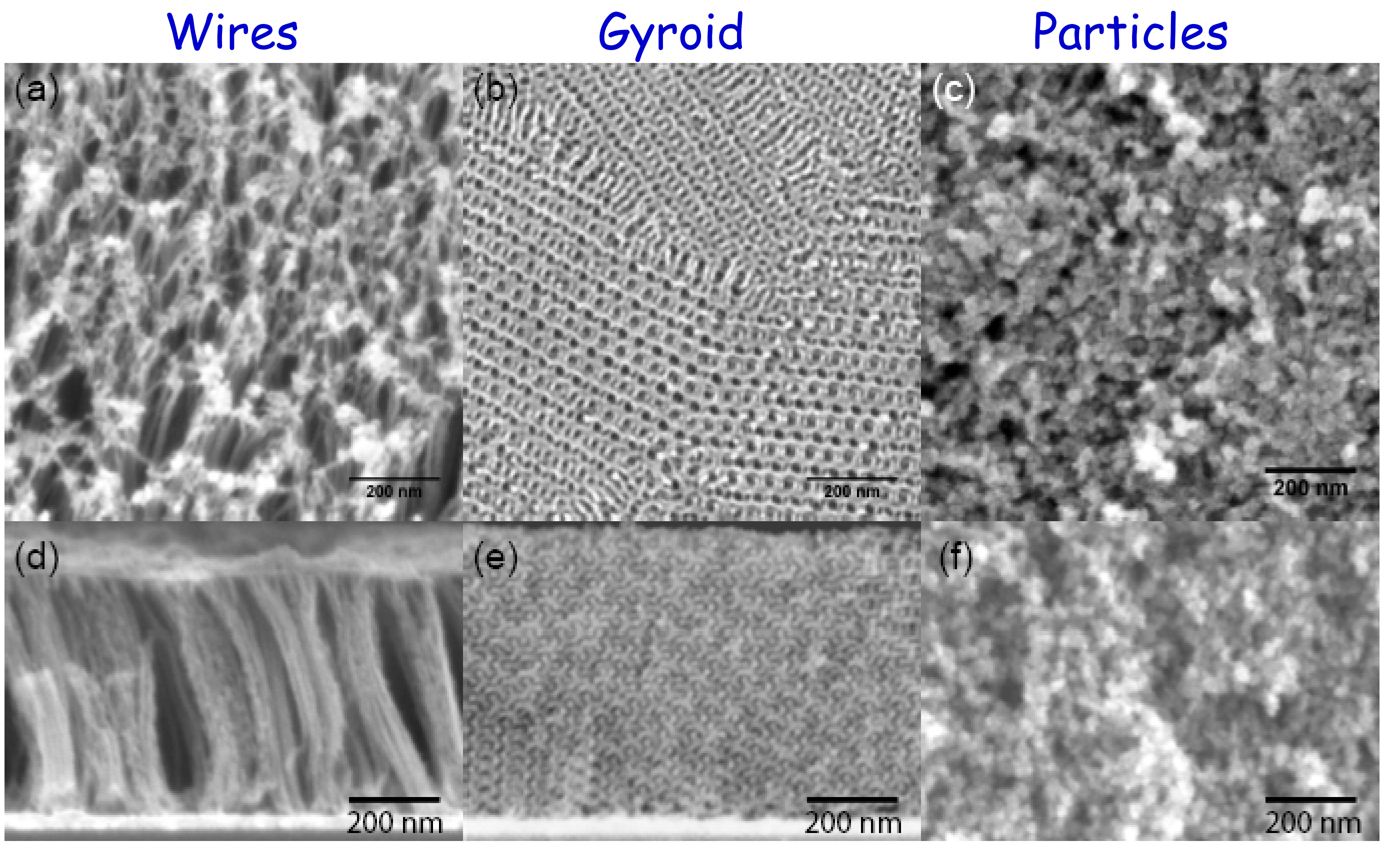
Wires



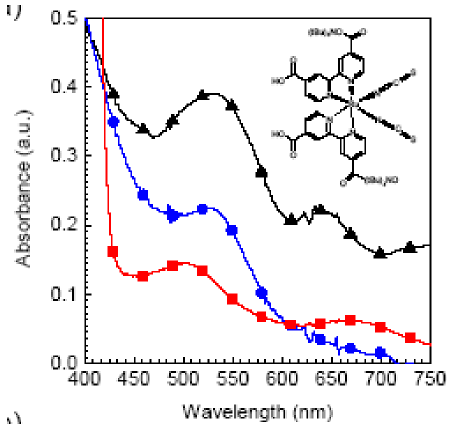
Gyroid



Structure function investigation

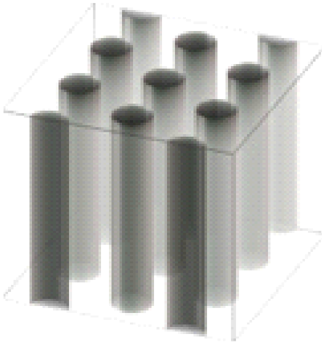


Morphology	RF_{calc}[a]	RF_{meas}[b]	Porosity (%)
Wires	100	60	65
Gyroid	125	130	60
Particles	120	116[21]	60

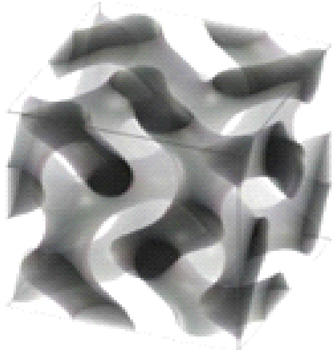


High Resolution TEM

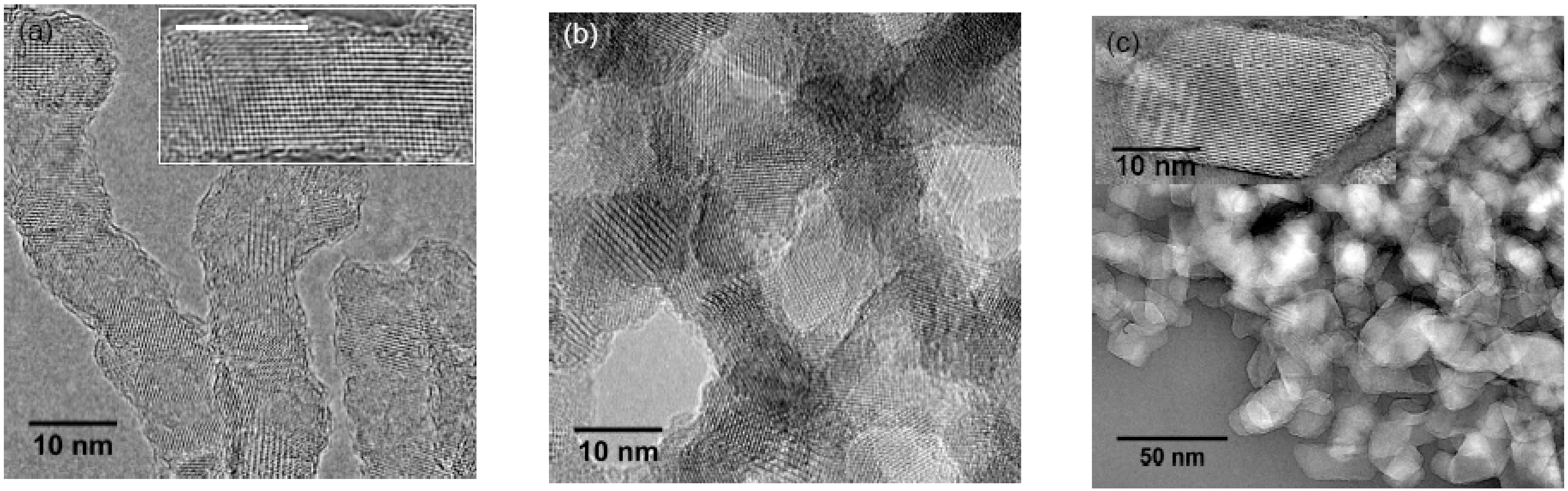
Wires



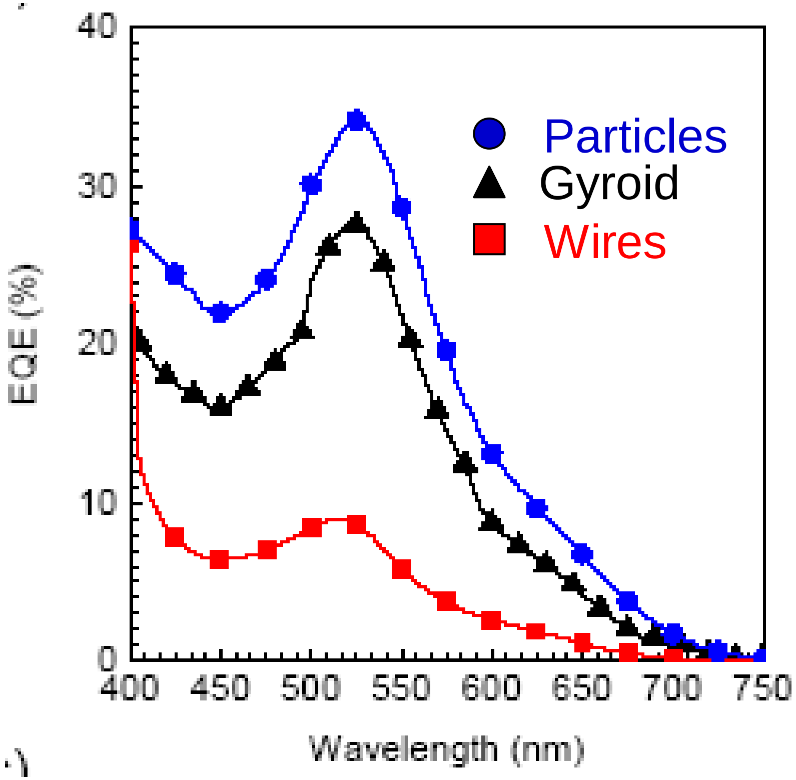
Gyroid

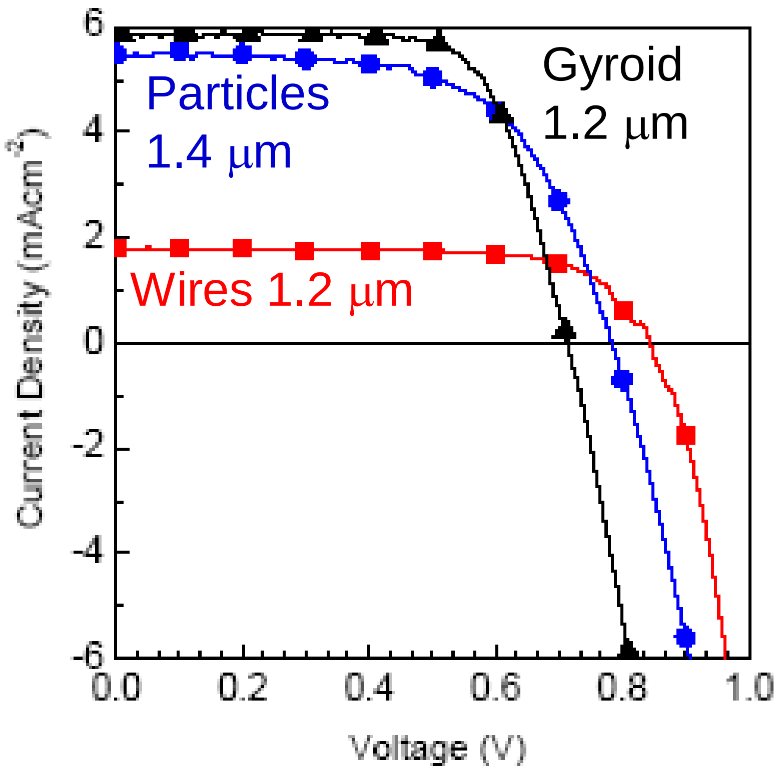


Particles



Solar cell performance (I^-/I_3^-)

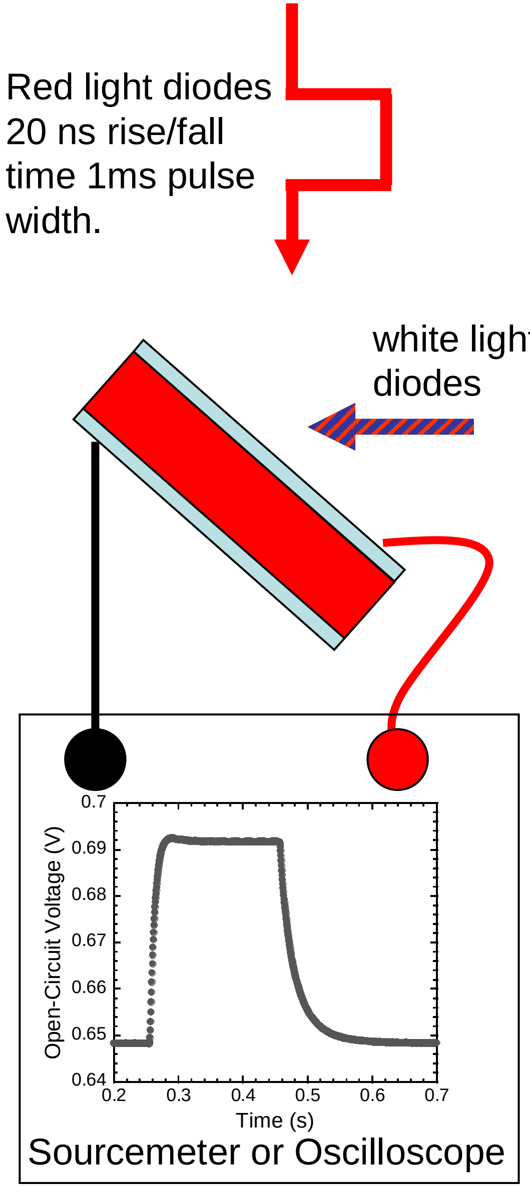


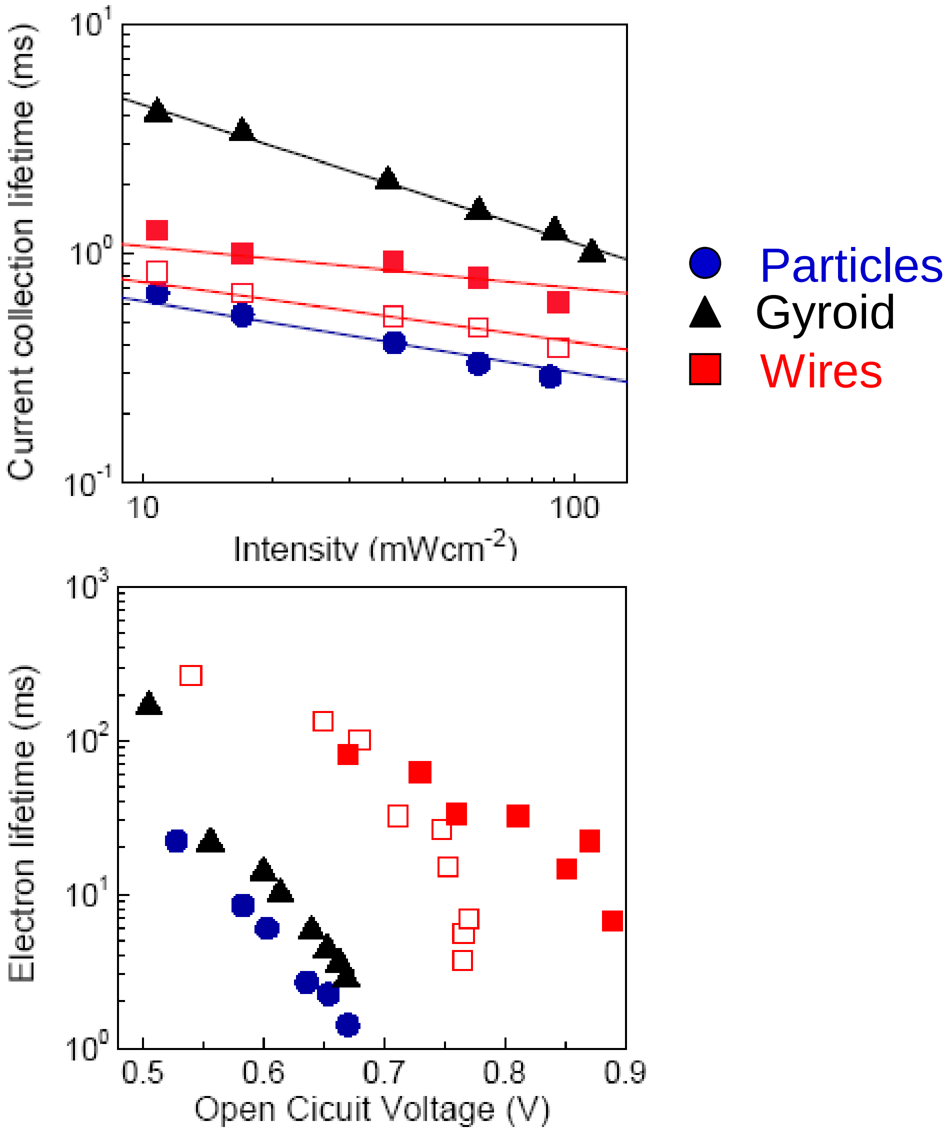


Morphology	J_{SC} (mAcm^{-2})	V_{OC} (mV)	FF (%)	η(%)
Wires	1.79	845	71	1.07
Gyroid	5.83	713	71	2.97
Particles	5.42	785	63	2.67

E. J. W. Crossland et al. Nano. Lett. 2008 (in-pres, on line)

Charge transport and recombination





summary

- Charge diffusion length 20 um in (best) SDSCs
- Recombination limits fill factor and open-circuit voltage
- Pore filling primarily limits short-circuit photocurrent
- Large data set for mobility in TiO_2 only possible to fit to MT model if the DoS is allowed to vary with temperature.

Summary

- First realisation of gyroid structured “semiconducting” material, with application in photovoltaics.
- Initial structure-function study
  - Enhanced transport in wires, however lack of structural integrity c.f. self supporting Gyroid

Acknowledgements

EPFL

- Peter Chen
- Ilkay Cesar
- Seigo Ito
- Robin Humphry-Baker
- Shaik Zakeeruddin
- Pascal Comte
- Michael Grätzel

Cambridge:

- Ed Crossland
- Mihaela Nedelcu
- Annamaria Petrozza
- Chris Groves
- Richard Friend
- Ullrich Steiner

Elsewhere:

- Marleen Kamperman
- Caterina Ducati,
- Detlef Smilgies,
- Gilman Toombes,
- Marc Hillmyer
- Sabine Ludwigs
- Ulrich Weisner