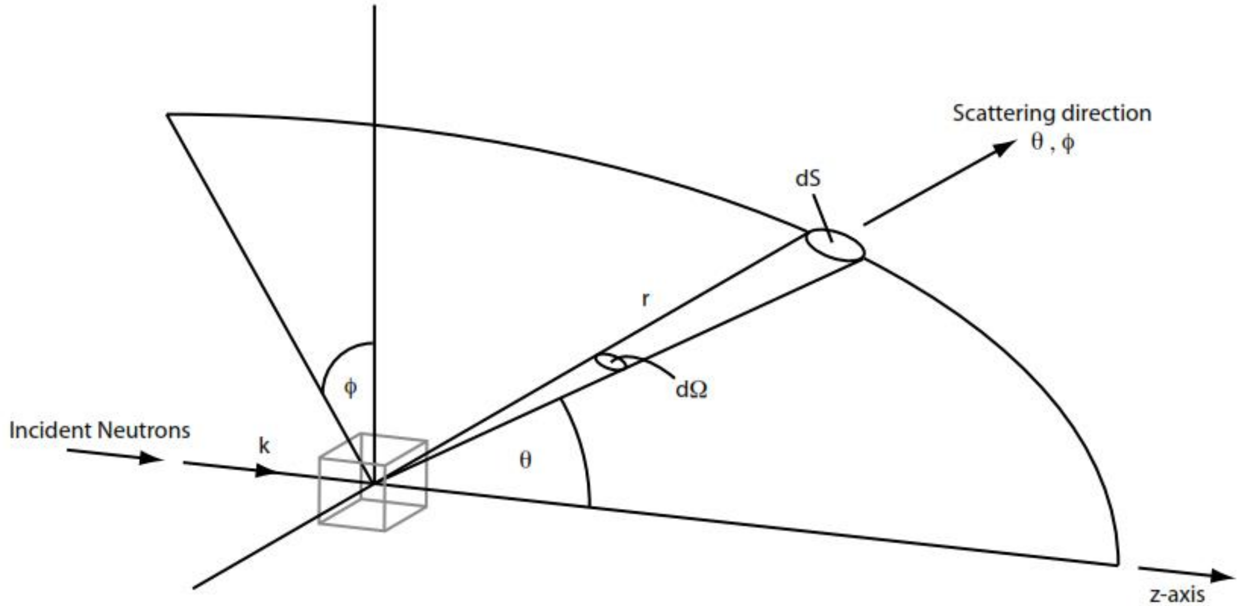
Analysis of Absolute Scattering Intensity Under Uncertainty

Hao Shen
Advisors: Michael Mackay and Yun Liu

NCNR Low Q Seminar

3/05/2014

Differential Scattering Cross Section vs. Intensity



$$\frac{d\sigma}{d\Omega}(\theta,\phi) = \frac{\text{number of neutrons scattered per second into } d\Omega \text{ at } \theta,\phi}{\Phi d\Omega} [=] Area$$

Φ: flux of the incident neutrons.

If we transform the angles into $\vec{q}$ and normalize it by the sample volume:

$$\frac{d\sigma}{d\Omega}(\vec{q}) \simeq I(\vec{q})[=]\mathrm{cm}^{-1}$$

Given:

- Correct instrument calibration
- Known neutron beam area and flux
- Known sample thickness

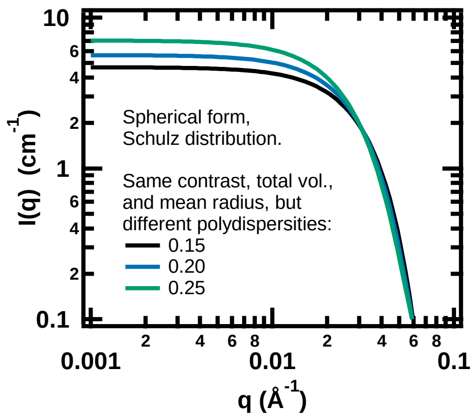
Indices for Absolute Scaling of Intensity

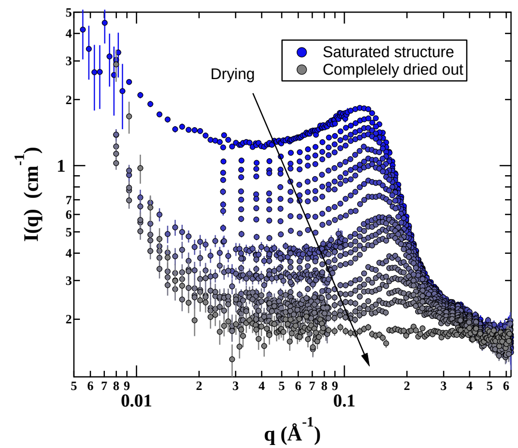
I_0 or I_{peak}

✓ Easy

× Lack of physical meaning

× Highly specific to system

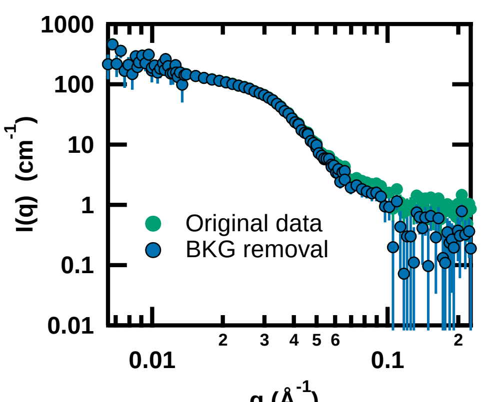


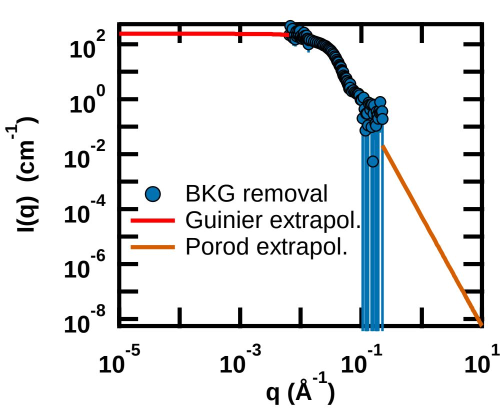


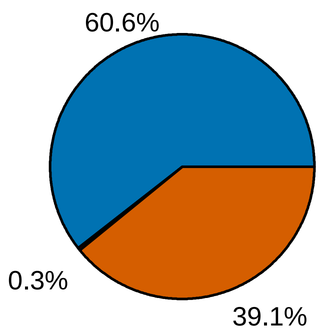
$$Q_{inv} \equiv \int_0^\infty q^2 \frac{d\sigma}{d\Omega} dq$$
$$= 2\pi^2 \Delta\rho^2 \phi(1-\phi)$$

✓ Model independent

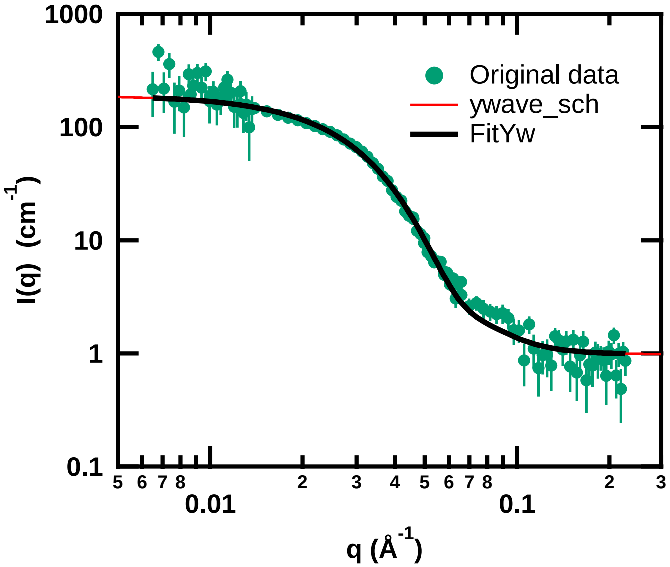
× Precision depends on the available q range







Extract The Scale Factor From A Fit Function



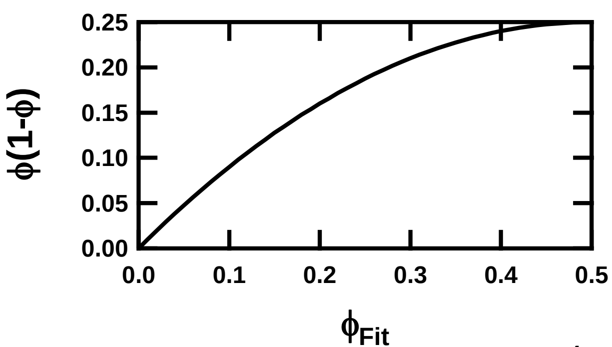
Spherical form with Schulz distribution:

Parameter	Value
Volume Fraction (scale)	0.204276
mean radius (A)	57.9304
polydisp (sig/avg)	0.236649
SLD sphere (A-2)	3.6e-06
SLD solvent (A-2)	1.10836e-06
bkg (cm-1 sr-1)	0.98013

- Three parameters, but only one independent variable for scaling: $\Delta\rho^2_{fit}\phi_{fit}$
- For concentrated system, the actual scaling variable is $\Delta\rho^2\phi(1-\phi)$
  $\rightarrow \phi$ need to be corrected
- Regardless, the following quantity will be constant:

$$\Delta\rho^2_{fit}\phi_{fit} = \Delta\rho^2\phi(1-\phi) \equiv \text{Scale Factor (SF)}[=]\text{Å}^{-4}$$

- SF is the scaling of measured data, so theoretically it is also model independent



A Slight Revision of SANS Data Fitting Procedure

Find a model and fit the data

↓

Extract from model:
$SF = \Delta\rho^2_{fit}\phi_{fit}$

↓

Assign the value of SF:
$(\rho_1 - \rho_2)^2\phi(1-\phi) = SF$

↓

Consider the values and physical constrains of ρ_1,ρ_2 and ϕ

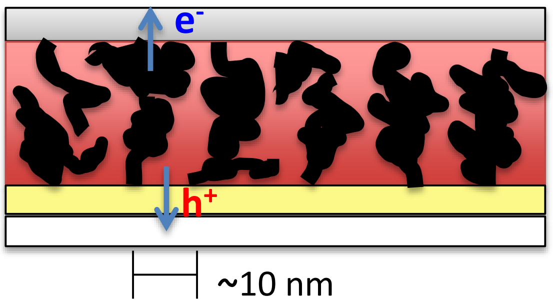
↓

Solve or estimate each value

This method is especially important when:

1. The system is concentrated
2. One or more of the SLDs cannot be independently measured

A Complicated Example: Polymer-Based Solar Cells



Aluminum

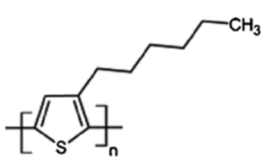
"Bulk-Heterojunction"

PEDOT:PSS

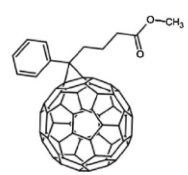
Conducting Glass

- Excitons in polymer have short diffusion length ~10 nm
- Thus, morphology in the bulk-heterojunction dictates the device performance

P3HT (poly(3-hexylthiophene))



PCBM ([6,6]-phenyl-C61-butyric acid methyl ester)



1. The system is concentrated: A typical active layer consists of 50% or more PCBM.
2. One can assume the phase-separated PCBM in the mixture has the same SLD as its pure form.
3. Still, unknown amount of fullerene is suspended within amorphous P3HT, and the SLD is unknown.

Coakley et al., *Chem. Mater.* ***2004, 16 (23), 4533.***

Two models to describe the PCBM phase

Polydisperse spheres with Schulz distribution:

$$I(q) = \rho_0^2 v^2 \frac{9(sin(qR) - qRcos(qR))^2}{(qR)^6}$$ Single sphere

$$f(R) = (z+1)^{z+1}(\frac{R}{R_{avg}})^z \frac{\exp[-(z+1)\frac{R}{R_{avg}}]}{\Gamma(z+1)R_{avg}}$$ Schulz distribution

$$I_0 = \phi(1-\phi)(\Delta\rho)^2 \frac{4\pi}{3} R_{avg}^3 \frac{(z+6)(z+5)(z+4)}{(z+1)^3}$$

Teubner-Strey Model:

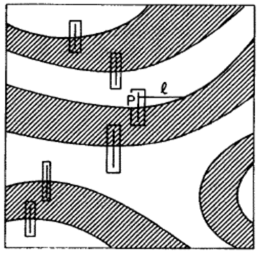
$$I(q) = \frac{\phi(1-\phi)(\Delta\rho)^2(\frac{8\pi}{\xi})c_2}{a_2 + c_1 q^2 + c_2 q^4} + Bkg$$

$$d = 2\pi \left[\frac{1}{2}\left(\frac{a_2}{c_2}\right)^{\frac{1}{2}} - \frac{c_1}{4c_2}\right]^{-\frac{1}{2}}$$

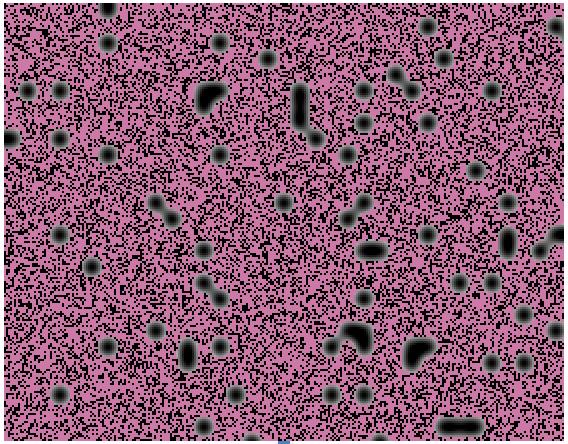
Repeat distance: average center to center distance

$$\xi = \left[\frac{1}{2}\left(\frac{a_2}{c_2}\right)^{\frac{1}{2}} + \frac{c_1}{4c_2}\right]^{-\frac{1}{2}}$$

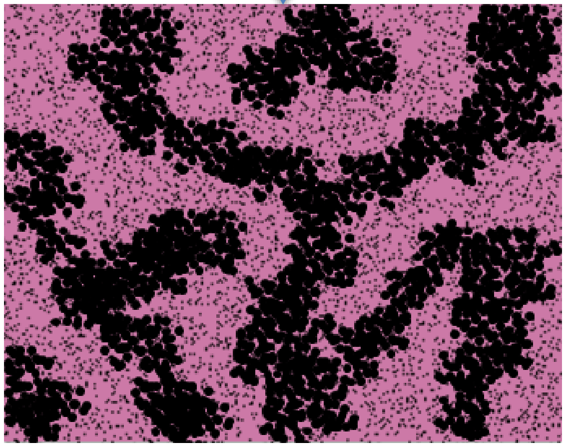
Correlation length: dispersion of *d*



Phase Separation Upon Annealing



Annealing



Trapped states due to fast drying of spin coating

$$\rho_{PCBM} = 3.6 \times 10^{-6}\ \text{Å}^{-2}$$

$$\rho_{P3HT} = 7 \times 10^{-7}\ \text{Å}^{-2}$$

$$\rho_{matrix} = \phi_2{}'\rho_{PCBM} + (1-\phi_2{}')\rho_{P3HT}$$

$$SF = (\rho_{PCBM} - \rho_{Matrix})^2\phi(1-\phi)$$

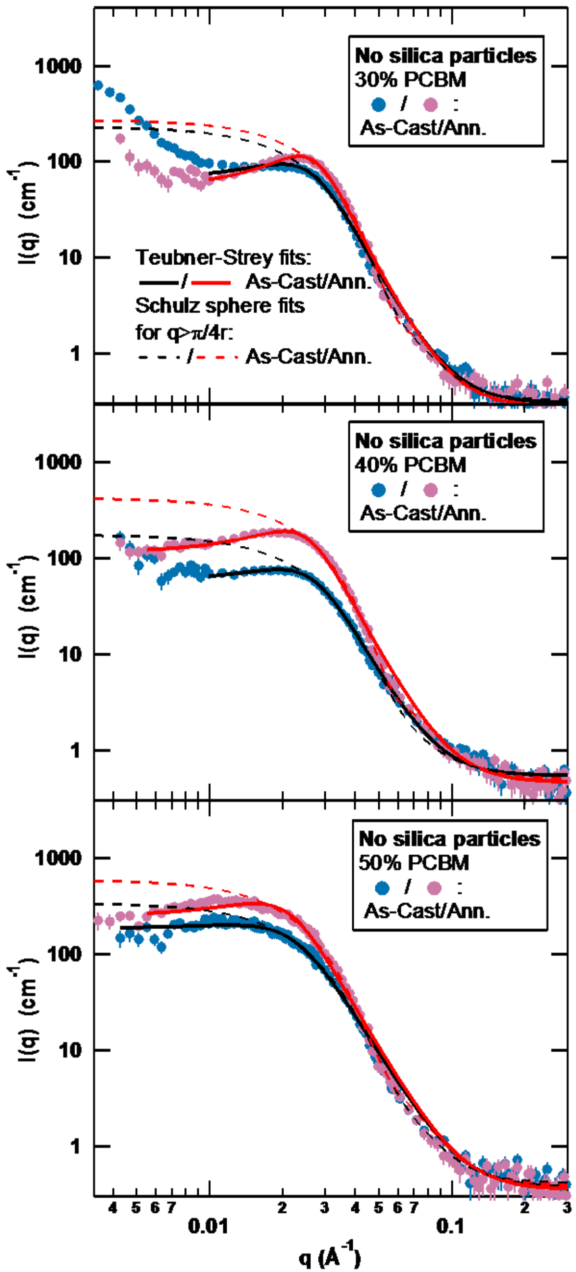
same

Toward complete phase separation

Overall effect: SF ↑

However, both ϕ and ρ_{matrix} are unknown.

Effect of Annealing on SF

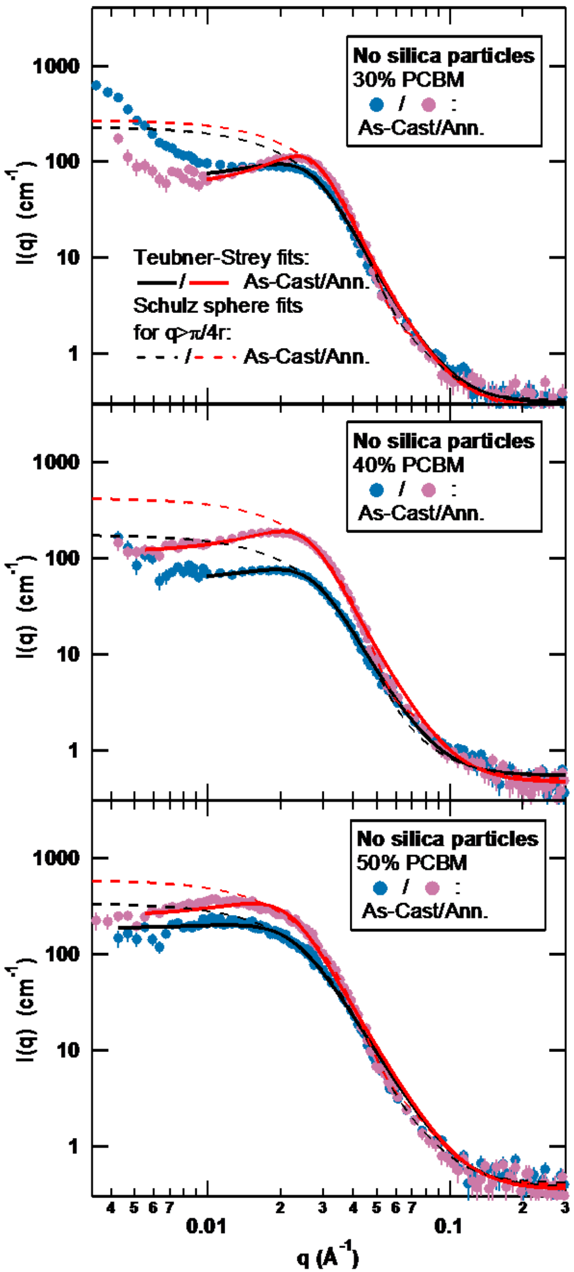


PCBM Wt%	As-Cast SF Spheres	As-Cast SF T-S	Annealed SF Spheres	Annealed SF T-S
30%	1.09	1.04	1.37	1.21
40%	0.925	0.907	1.91	1.81
50%	1.42	1.51	2.03	2.05

SF Unit: 10^{12} Å^{-4}

- Relative constant SF extracted from two different models
- Significant increase in SF after annealing
- Need additional physical constraint:
  Total mass balance of PCBM, to solve ϕ and ρ_{matrix}

Solving ϕ_1 and ϕ'_2 (ρ_{matrix}) from SF



Total Mass Balance of PCBM:

$$\phi_{PCBM,bulk} = \phi_1 + \phi_2 \text{ (wrt. vol. of sample)}$$

Phase-separated (ϕ_1) Trapped in matrix (ϕ_2)

$$\phi_2{}' = \frac{\phi_2}{1-\phi_1} \text{ (wrt. vol. of matrix)}$$

$$= \frac{\phi_{PCBM,bulk} - \phi_1}{1-\phi_1} \qquad (1)$$

$$\rho_{matrix} = \phi_2{}'\rho_{PCBM} + (1-\phi_2{}')\rho_{P3HT}$$

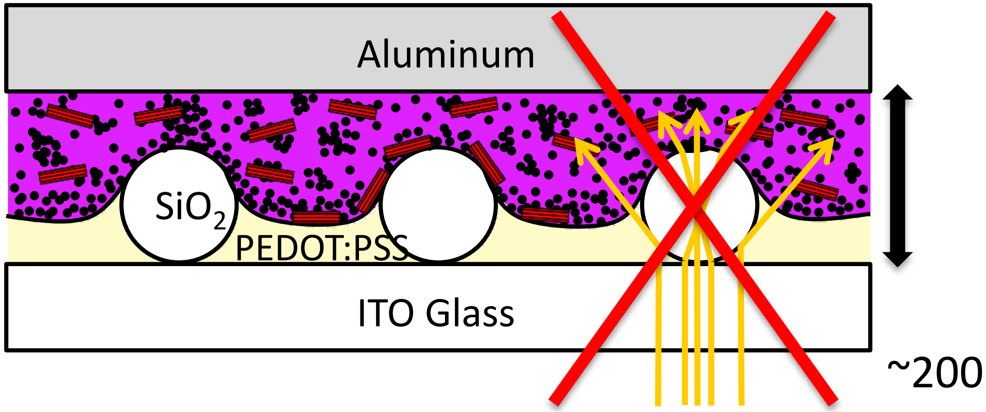
$$\Delta\rho = (1-\phi_2{}')(\rho_{PCBM} - \rho_{P3HT})$$

$$SF = (1-\phi_2{}')^2(\rho_{PCBM} - \rho_{P3HT})^2\phi_1(1-\phi_1) \qquad (2)$$

Solve (1) and (2) simultaneously

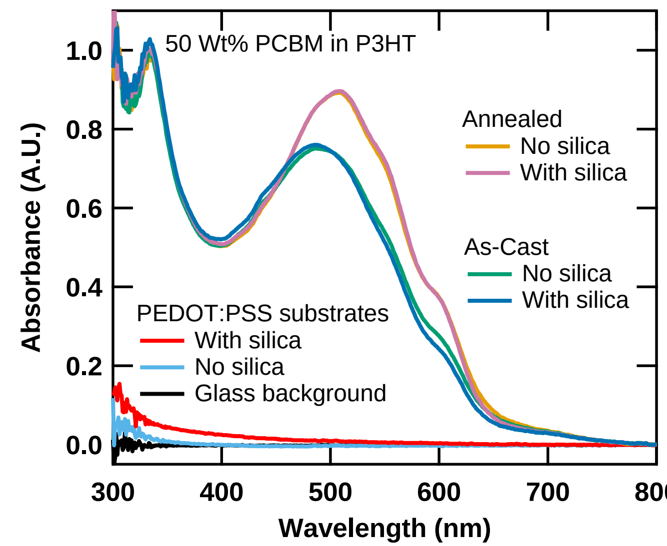
	As-Cast			Annealed		
PCBM Wt%	SF Spheres	ϕ_1	ϕ'_2	SF Spheres	ϕ_1	ϕ'_2
30%	1.09	0.20	0.096	1.37	0.24	0.050
40%	0.925	0.22	0.20	1.91	0.36	0.012
50%	1.42	0.37	0.15	2.03	0.46	0.014

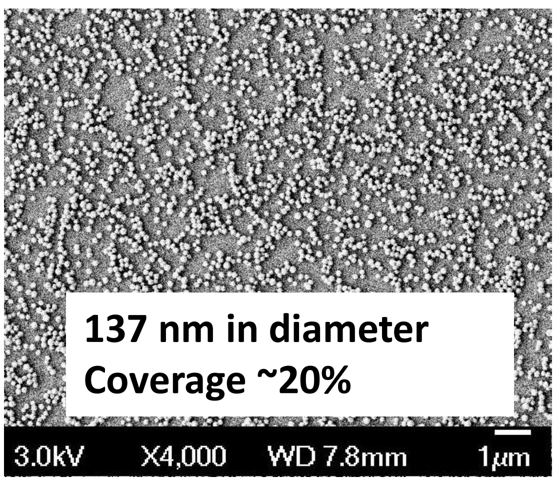
Controlling the phase separation of PCBM using silica



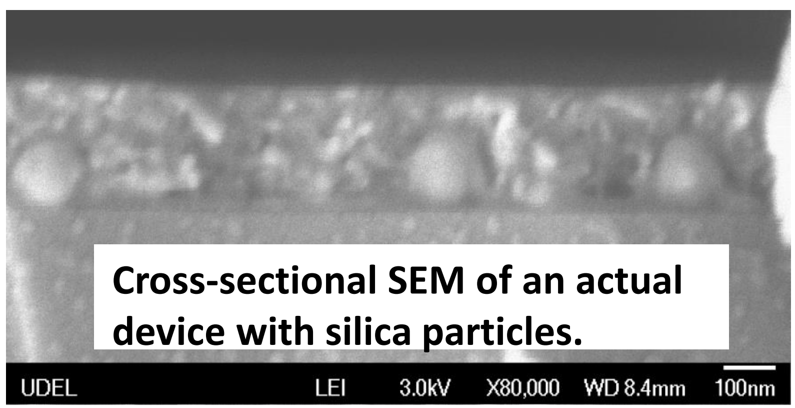
Vertical assembling of PCBM

Change of orientation of P3HT crystals





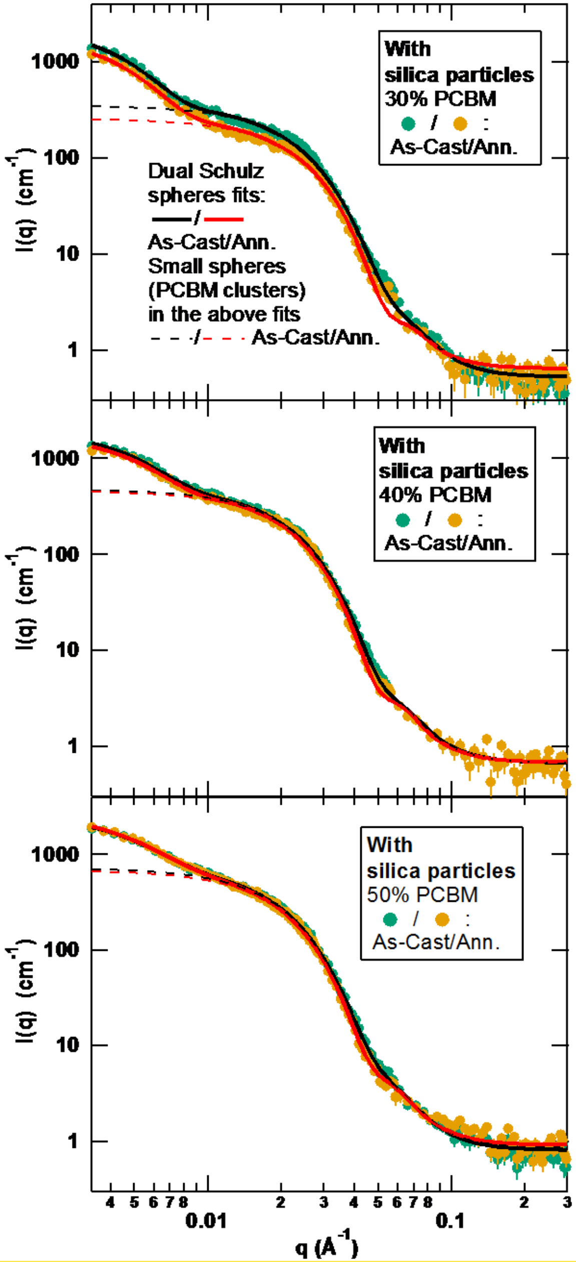
137 nm in diameter
Coverage ~20%



Cross-sectional SEM of an actual device with silica particles.

Goal:

- Eliminate optical (surface plasmon) and electrical effect of nanoparticles
- Focus only on the effect of morphology



What if SF drops after annealing?

PCBM Wt%	As-Cast SF Spheres	As-Cast SF T-S	Annealed SF Spheres	Annealed SF T-S
30%	1.31	N/A	0.98	N/A
40%	1.46	N/A	1.33	N/A
50%	1.74	N/A	1.59	N/A

SF Unit: 10^{12} Å^{-4}

Dropping of SF after annealing could mean either thing:

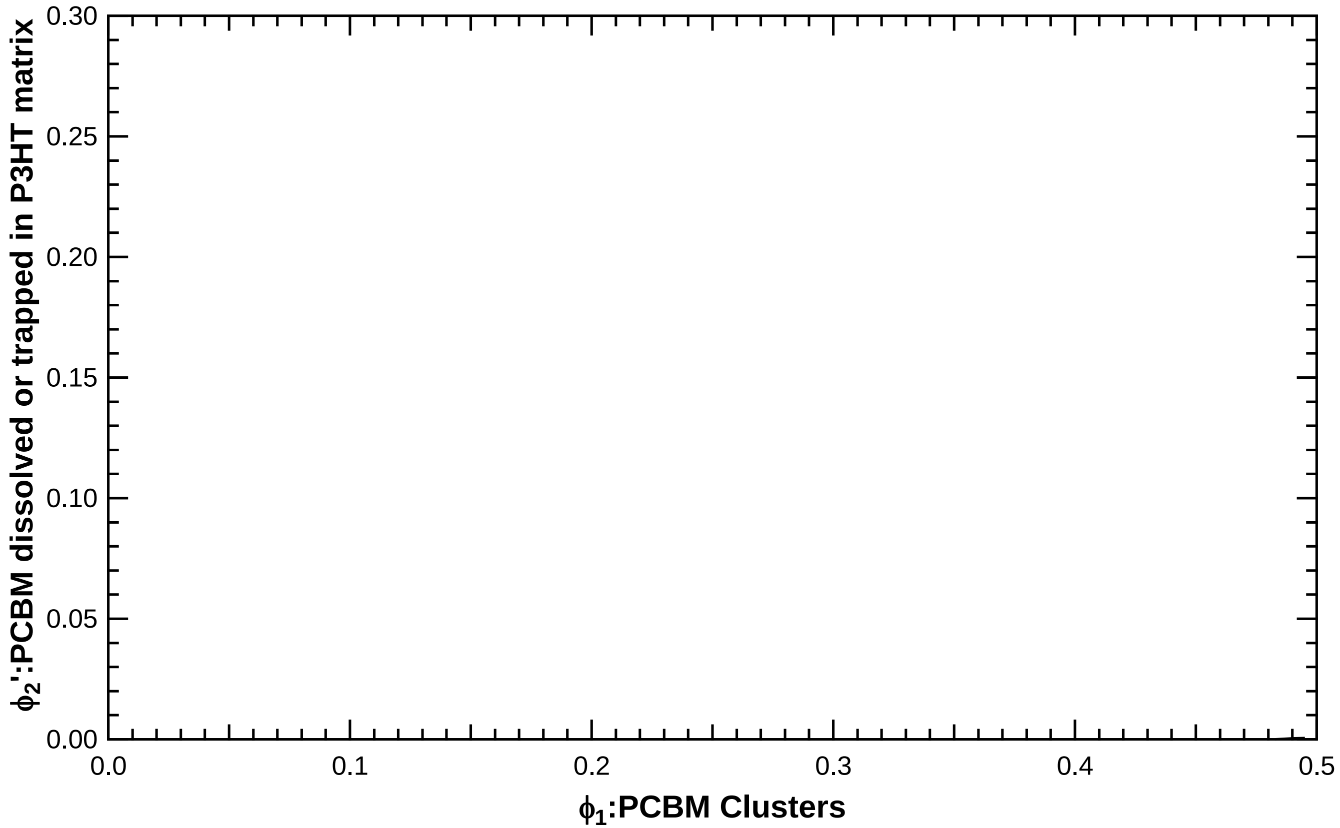
1. Given mass balance, PCBM is re-dissolve back to matrix → unlikely

$$SF = (1-\phi_2')^2(\rho_{PCBM}-\rho_{P3HT})^2\phi_1(1-\phi_1)$$

2. The apparent mass balance does not hold, because PCBM is forming large structure with silica, falling outside the size range of SANS

$$SF = (1-\phi_2')^2(\rho_{PCBM}-\rho_{P3HT})^2\phi_1(1-\phi_1)$$

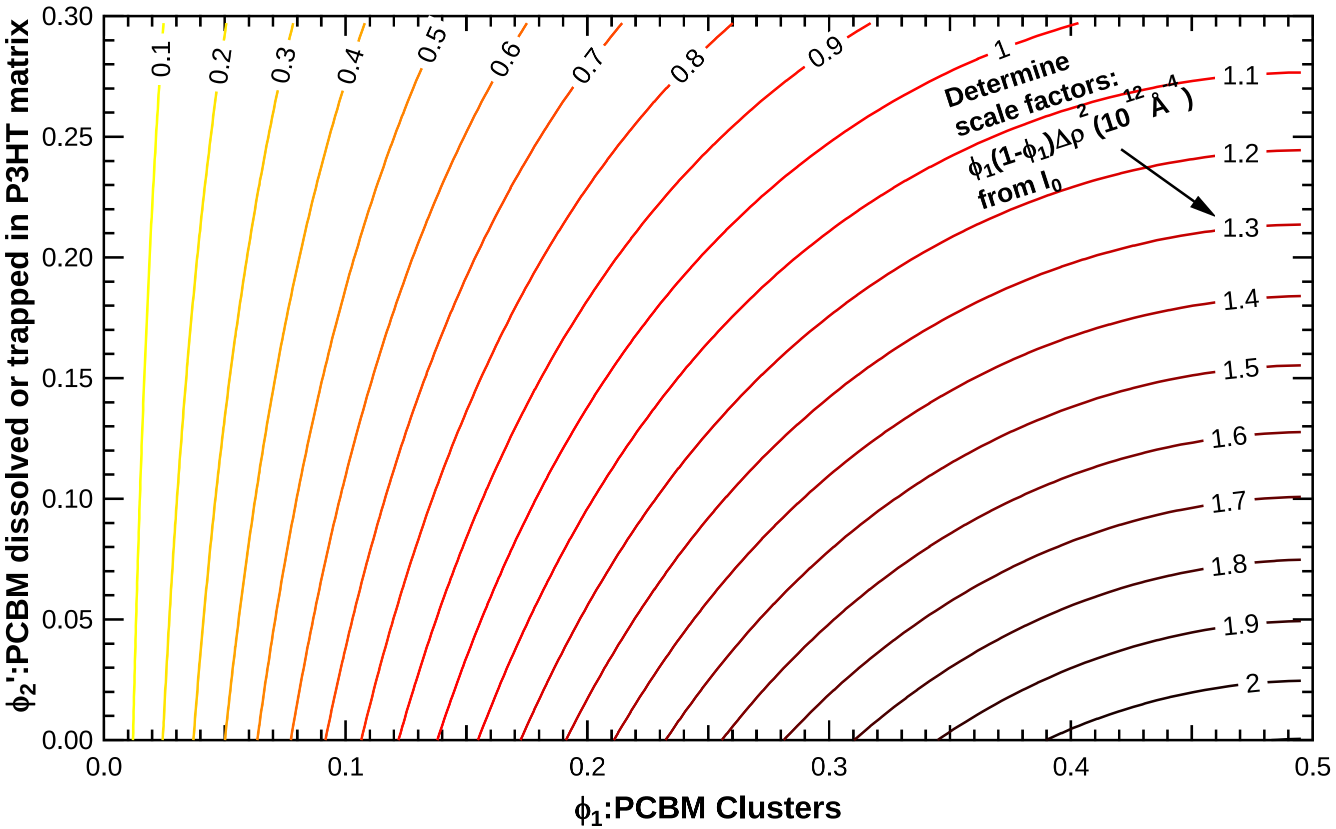
Graphical solutions of ϕ_1 and ϕ'_2



1. Consider the solution space of ϕ_1 and ϕ'_2

Graphical solutions of ϕ_1 and ϕ'_2

$$SF = \phi(1-\phi)(\Delta\rho)^2$$
$$= (1-\phi_2{}')^2(\rho_{PCBM} - \rho_{P3HT})^2\phi_1(1-\phi_1)$$

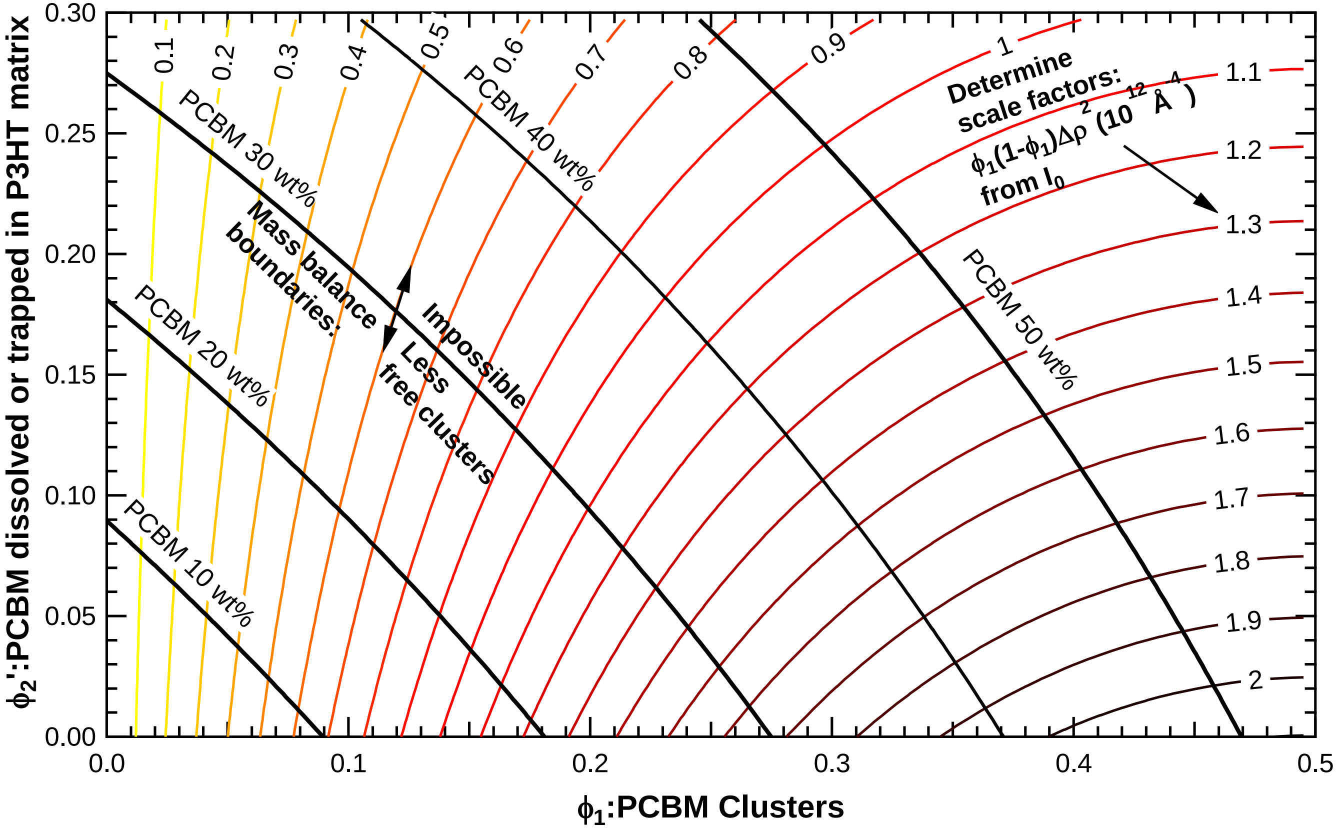


1. Consider the solution space of ϕ_1 and ϕ'_2
2. Calculate all possible SF as a function of ϕ_1 and ϕ'_2

Graphical solutions of ϕ_1 and ϕ'_2

$$SF = \phi(1-\phi)(\Delta\rho)^2$$
$$= (1-\phi_2')^2(\rho_{PCBM}-\rho_{P3HT})^2\phi_1(1-\phi_1)$$

$$\phi_2' = \frac{\phi^* - \phi_1}{1-\phi_1}$$

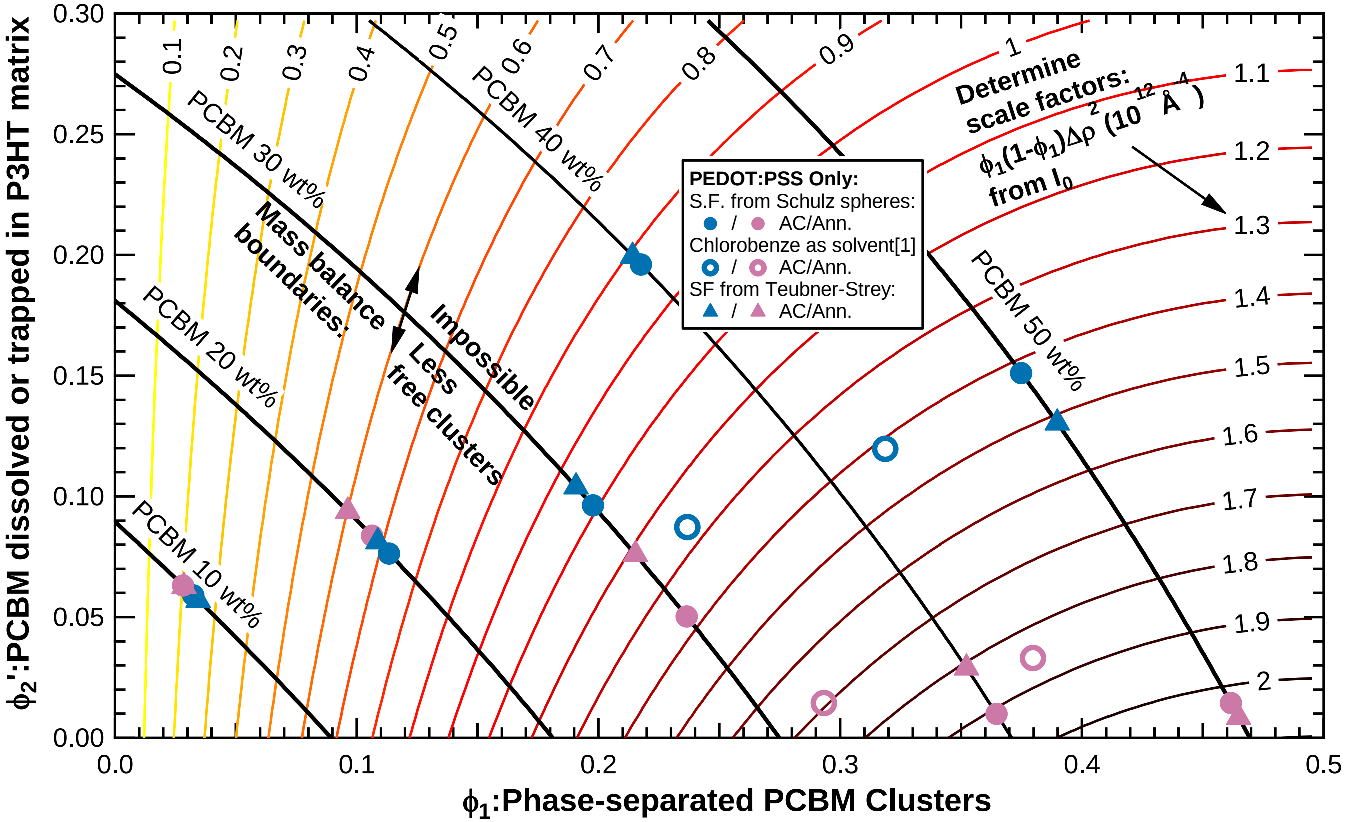


1. Consider the solution space of ϕ_1 and ϕ'_2
2. Calculate all possible SF as a function of ϕ_1 and ϕ'_2
3. Put the mass balance limits for each bulk concentration

Graphical solutions of ϕ_1 and ϕ'_2

$$SF = \phi(1-\phi)(\Delta\rho)^2 = (1-\phi_2')^2(\rho_{PCBM} - \rho_{P3HT})^2\phi_1(1-\phi_1)$$

$$\phi_2' = \frac{\phi^* - \phi_1}{1-\phi_1}$$



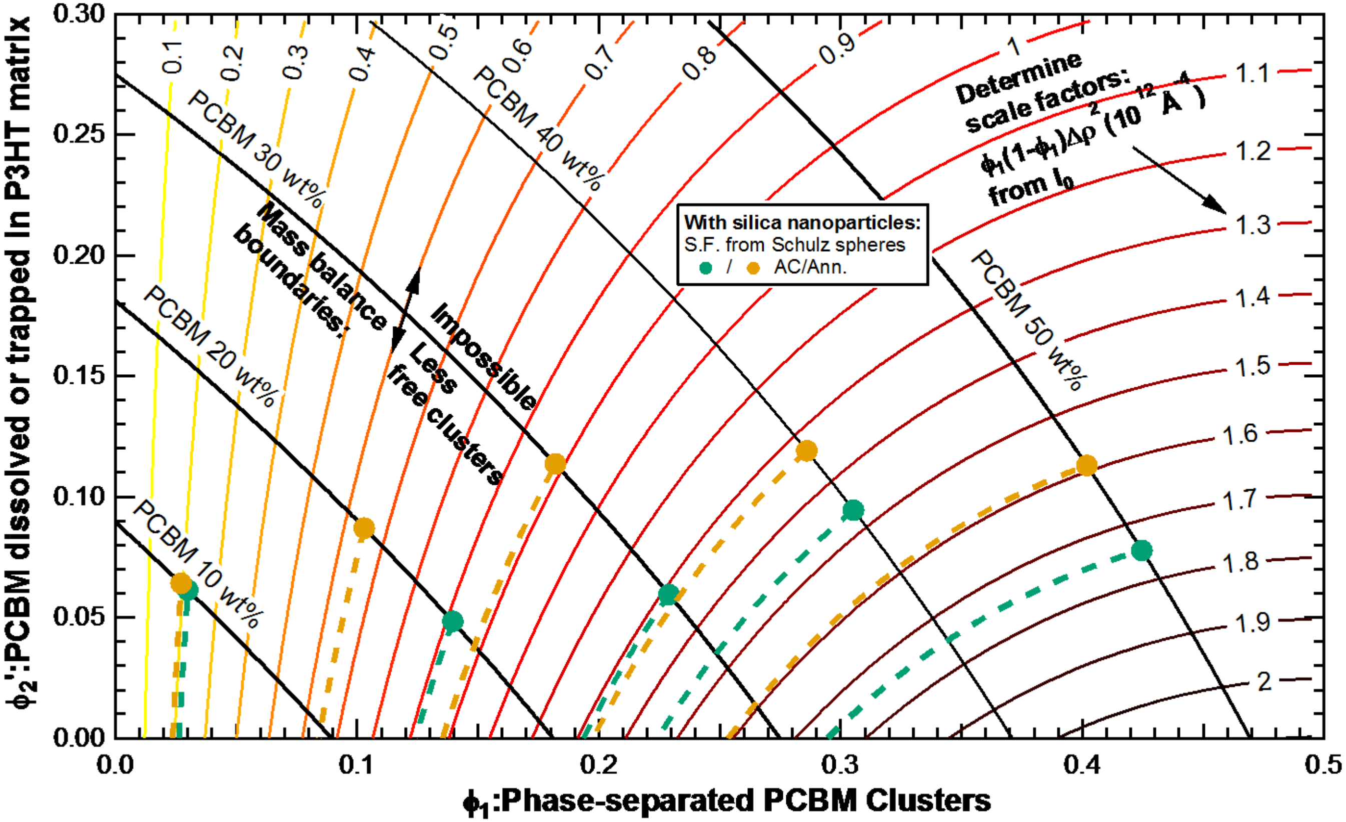
1. Consider the solution space of ϕ_1 and ϕ'_2
2. Calculate all possible SF as a function of ϕ_1 and ϕ'_2
3. Put the mass balance limits for each bulk concentration
4. Put the experimentally determined SF on the graph

- SF is a measurable physical constant, independent of the models.
- At least ~5% of PCBM will be trapped in the matrix

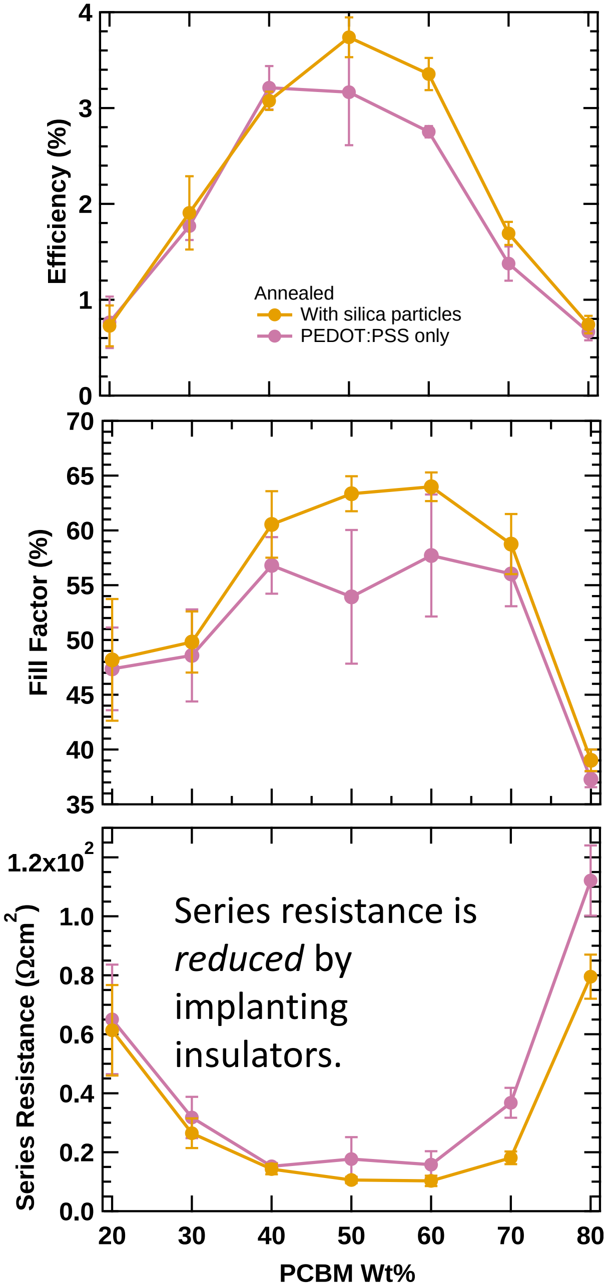
Graphical solutions of ϕ_1 and ϕ'_2

$$SF = \phi(1-\phi)(\Delta\rho)^2 = (1-\phi_2')^2(\rho_{PCBM}-\rho_{P3HT})^2\phi_1(1-\phi_1)$$

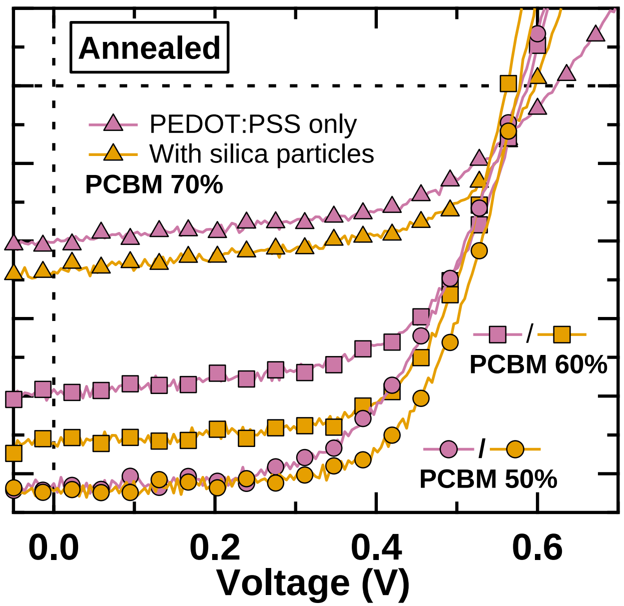
$$\phi_2' = \frac{\phi^* - \phi_1}{1-\phi_1}$$



- Does large-scale phase separation happen?
  No → crossing is the unique solution.
  Yes → any point on the left side of the SF curve can be the solution.
- For 20-30% PCBM, the amount of PCBM at scale of ~10 nm must decreases after annealing in the presence of silica.
- We may conclude the aggregation of PCBM onto silica due to the high surface energy.

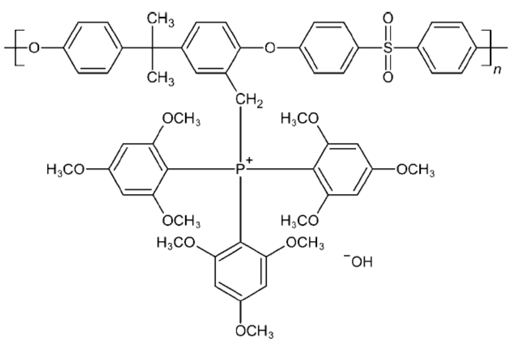


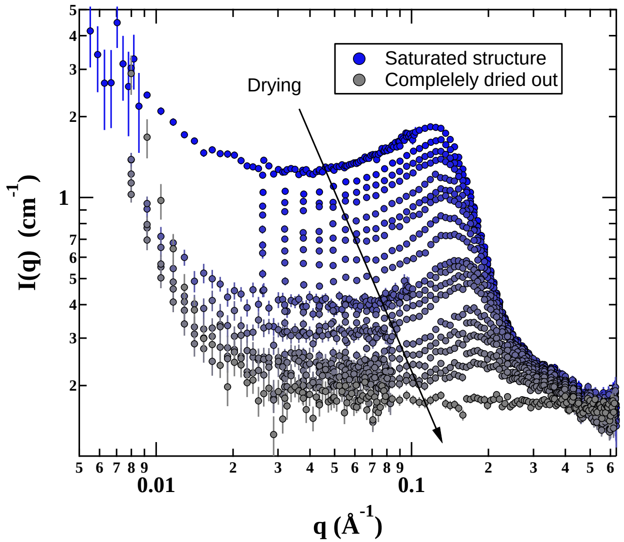
Performance of solar cells

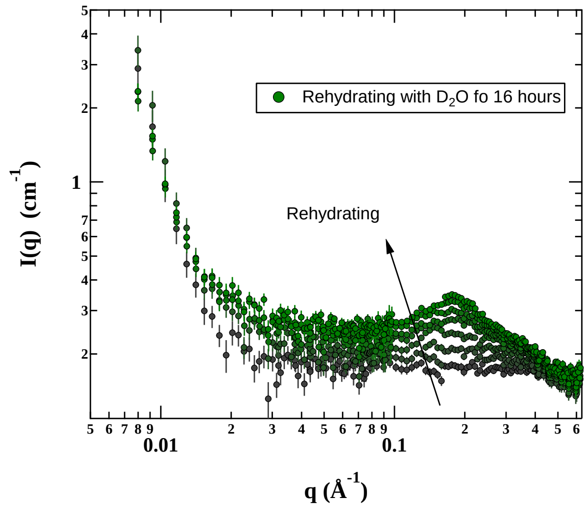


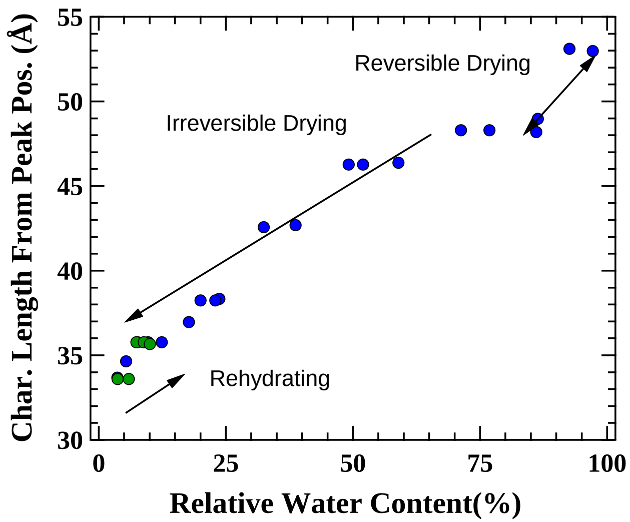
Efficiency, annealed (%)			
PCBM (Wt %)	No silica	With silica	Relative Improvement
50	3.17±0.553	3.74±0.208	20%
60	2.75±0.059	3.35±0.169	30%
70	1.38±0.179	1.69±0.121	20%

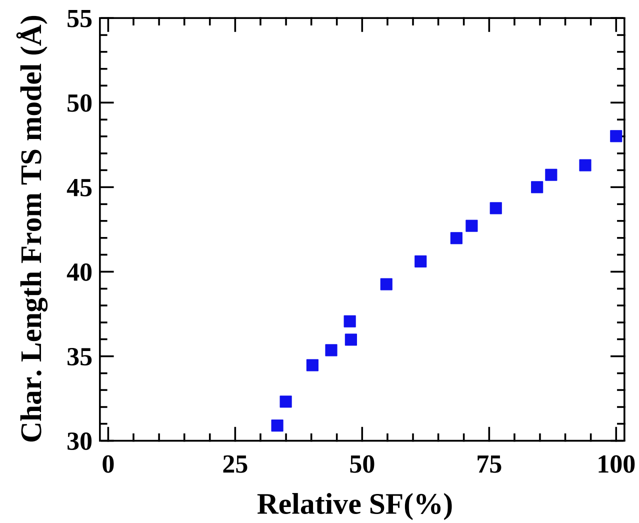
Structure of water in an ion-exchange membrane











Conclusion

Find a model and fit the data

↓

Extract from model: $SF = \Delta\rho^2_{fit}\phi_{fit}$

↓

Assign the value of SF: $(\rho_1 - \rho_2)^2\phi(1-\phi) = SF$

↓

Consider the values and physical constrains of ρ_1,ρ_2 and ϕ

↓

Solve or estimate each value

$$I = SF\ S(q)P(q)$$