Institute of High Performance Computing

Electronics & Photonics Department

Optoelectronic Simulation of an Organic Bulk Heterojunction Solar Cell with COMSOL

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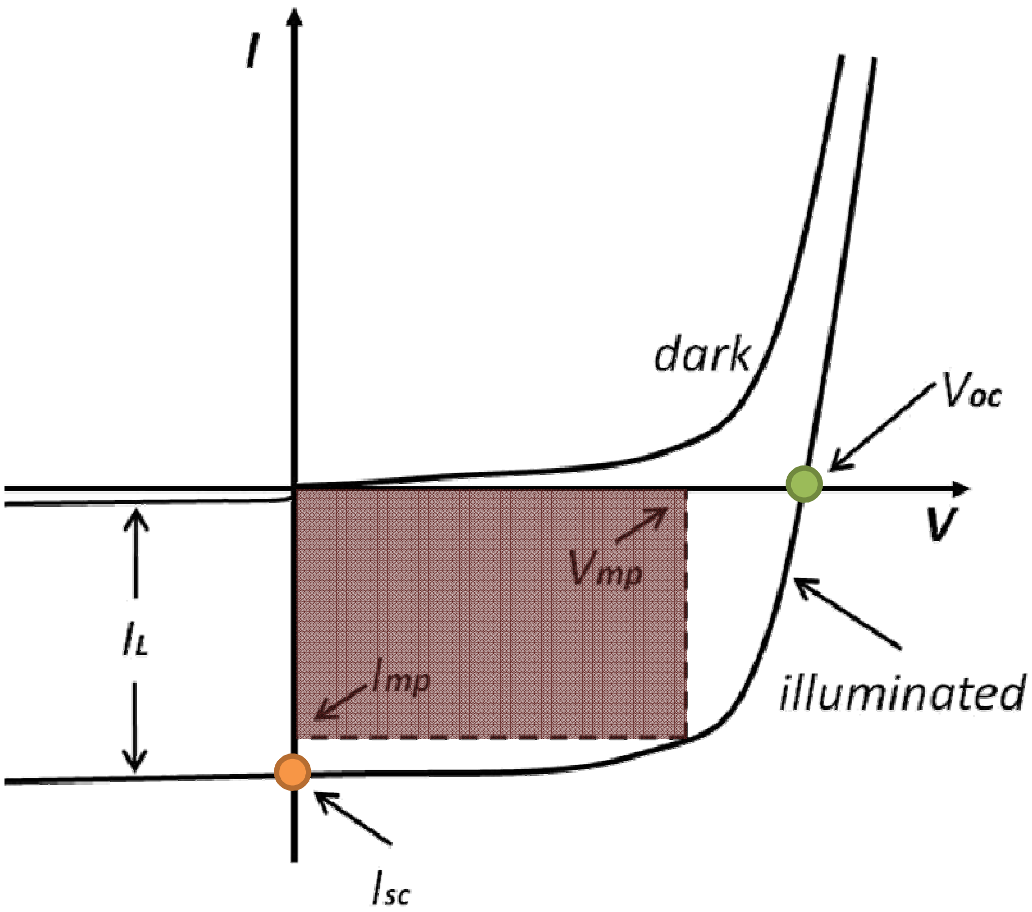
A*STAR IHPC

Outline

- Definitions of Measures of Solar Cells
- Overview of Processes in an Organic BHJ Solar Cell
- Device Model:
  - Optical
  - Polaron Generation & Carrier Recombination
  - Charge Transport
- Validation & Calibration of Simulation Model with Experiment
- Plasmonic OPV device
- Summary
- Acknowledgements

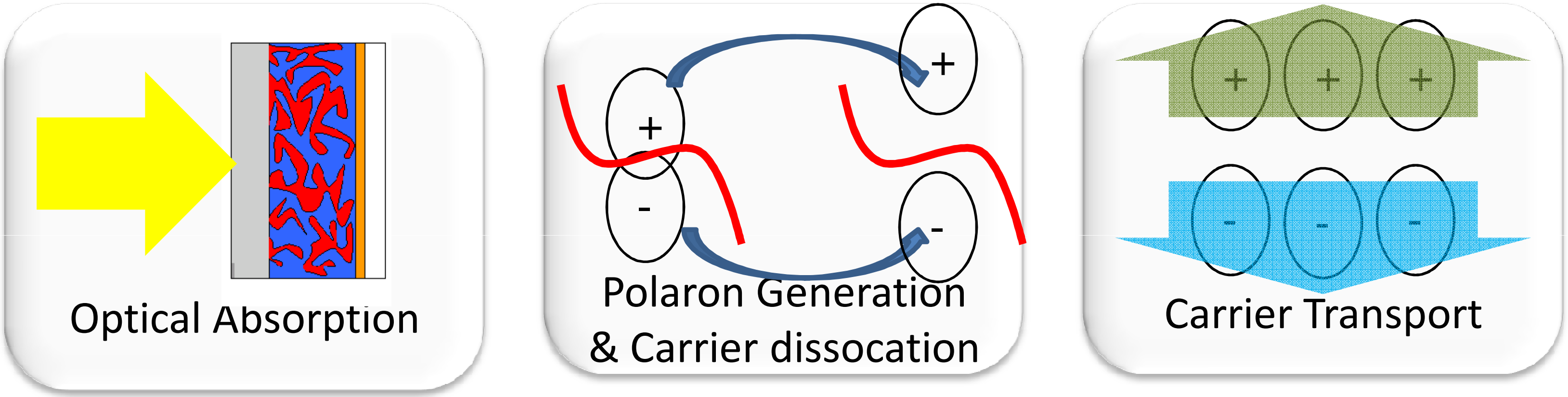
Definitions of Measures of Solar Cells



- I_{sc} = short circuit current
- V_{oc} = open circuit voltage
- I_{mp} = max power point current
- V_{mp} = max power point voltage
- Fill factor, FF = $\frac{I_{mp}V_{mp}}{I_{sc}V_{oc}}$
- Efficiency = $\frac{I_{sc}V_{oc}FF}{P_{in}}$

Review of Physics of Organic Solar Cells

- Basic Processes
  - Optical Illumination & Absorption (in whole structure)
  - Polaron Generation & Carrier Recombination (in P3HT:PCBM only)
  - Carrier Transport (in P3HT:PCBM only)



<u>Other OPV device model</u>

- 1D electronic model from University of Groningen, The Netherlands developed by Koster et al (PRB 72, 085205, 2005) for BHJ solar cells
  - Constant optical generation in active layer assumed
- 2D optoelectronic model from University of Bath, UK by J. Williams et al (Nanotechnology 19, 424011, 2008)
  - Only single wavelength illumination demonstrated
- 3D optoelectronic model by Koh et al
  - Reduced recombination factor (IEEE Journal of PV, 1, 84, 2011)
  - Non-germinate recombination due to traps (SPIE Photonic West OPTO Symposium 2013)

Optical

❖ Solve the Frequency-Domain Maxwell Equations:

$$\nabla \times \overrightarrow{H}_{opt} = j2\pi\nu\varepsilon_r\varepsilon_0 \overrightarrow{E}_{opt}$$

$$\nabla \times \overrightarrow{E}_{opt} = -j2\pi\nu\mu_0 \overrightarrow{H}_{opt}$$

where $\overrightarrow{H}_{opt}$ = magnetic field vector

$\overrightarrow{E}_{opt}$ = electric field vector

ν = frequency

$\varepsilon_r = \varepsilon_1 - j\varepsilon_2$ = relative permittivity

❖ Spectral absorbed energy density in the photoactive layer (P3HT:PCBM) at each position (x, y, z) [1]:

$$Q(\nu, x, y, z) = \frac{1}{2} c\varepsilon_0\alpha\eta E_{opt}^{\;2}$$

where c = speed of light

$\alpha = \frac{2\pi\kappa}{\lambda}$ = absorption coefficient

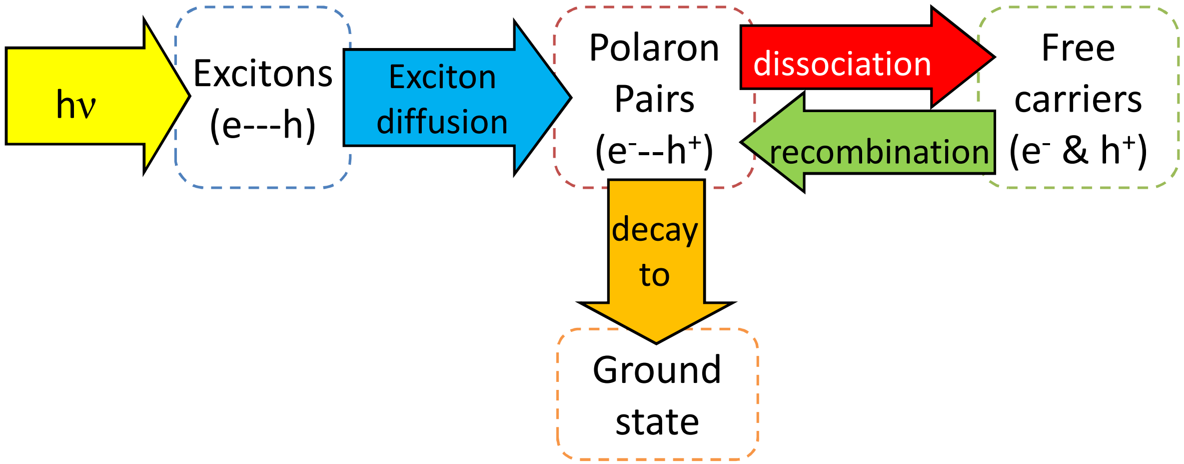
λ = wavelength of incoming light

κ = imaginary part of refractive index

η = real part of refractive index

1) J. Williams et al, Nanotechnology, 19, 424011 (2008)

Polaron Generation & Carrier Recombination



❖ Generation of polarons at each frequency ν and position (x, y, z)

$$G(\nu, x, y, z) = \frac{Q}{h\nu} = \frac{\pi\varepsilon_2\varepsilon_0}{h} E_{opt}{}^2$$

❖ Integrate the frequency dependent G over the AM1.5G solar spectrum

$$G_{tot}(x, y, z) = \int_{AM1.5G} G(\nu, x, y, z)\, S(\nu)\ d\nu$$

where $S(\nu)$ = spectral density of the AM1.5G solar spectrum

Polaron Generation & Carrier Recombination

- At steady state and at each position (x, y, z) in the active layer (P3HT:PCBM), the net free carriers generated [2] is

$$k_d X = G - k_f X + R$$

where X = polaron concentration

k_d = polaron dissocation rate constant

k_f = polaron decay rate constant

R = carrier bimolecular recombination rate constant

- From Osnager & Braun's germinate theory,

$$k_d(a,T,E) = \frac{3\gamma}{4\pi a^3} e^{-\frac{E_b}{k_b T}} \frac{J_1\left(2\sqrt{-2b}\right)}{\sqrt{-2b}}$$

where a = mean polaron (bound e & h) separation distance

T = temperature

E = electrostatic electric field in organic semiconductor

$E_b = \frac{q^2}{4\pi\varepsilon_r\varepsilon_0 a}$ = polaron binding energy

k_b = Boltzmann constant

$b = \frac{q^3 E}{8\pi\varepsilon_r\varepsilon_0 k_b^2 T^2}$

J_1 = Bessel function of first order

$\gamma = \frac{q}{\varepsilon_r\varepsilon_0}(\mu_n + \mu_p)$ = Langevin factor

$\mu_{n(p)}$ = mobility of electrons (holes)

[2] L. J. A. Koster et al, PRB, 72, 085205 (2005)

Polaron Generation & Carrier Recombination

- The decay rate constant k_f can also be derived from Osnager and Braun's model with the following relation to k_d:

$$k_f = \frac{1-P}{P} k_d$$

where $P = \int_{\infty}^{0} p(r,T,E)\, f(r,a)\, dr =$ average probability of polaron dissociation

$p = \frac{k_d}{k_d + k_f} =$ probability of dissocation of polarons with e - h separation r

$\mathrm{f} = \frac{4}{\sqrt{\pi a^3}} r^2 e^{\frac{r^2}{a^2}} =$ Gaussian distribution for r as the polymer is a disordered material [3]

- The recombination rate of free carriers to polarons $R_{n,p}$ can be described by the using a trap model which will enable us to account for the dark current generated due to traps [4]:

$$R_n = \gamma\left[n_f p_t - n_i p_i\right]$$

$$R_p = \gamma\left[p_f n_t - n_i p_i\right]$$

where $n_t(p_t) =$ trapped electron(hole) concentration

$n_f(p_f) =$ free electron(hole) concentration

$n_i(p_i) =$ intrinsic carrier concentration

3) J. A. Barker et al, PRB, 67, 075205 (2003)
4) N. C. Giebink et al, PRB 82, 155305 (2010)

Device Model: Charge Transport

- Drift diffusion equations

$$J_n = -en_f \mu_n \nabla V + eD_n \nabla n_f$$

$$J_p = -ep_f \mu_p \nabla V + eD_p \nabla p_f$$

- Poisson equation

$$\nabla^2 V = \frac{q}{\varepsilon_0 \varepsilon_r}\left(n_f + n_t - p_f - p_t\right)$$

- Continuity equation

$$\frac{dn}{dt} = \frac{1}{q}\nabla J_n + k_d X - R_n = 0 \quad \text{(steady state)}$$

$$\frac{dp}{dt} = \frac{1}{q}\nabla J_p + k_d X - R_p = 0 \quad \text{(steady state)}$$

Boundary Conditions

- **At hole-ohmic PEDOT:PSS**

$$n_{f,cathode} = N_{LUMO} \exp\left(-\frac{E_{gap}}{k_B T}\right)$$

$$p_{f,cathode} = P_{HOMO}$$

$$V_{cathode} = V_a - \frac{E_{gap}}{q}$$

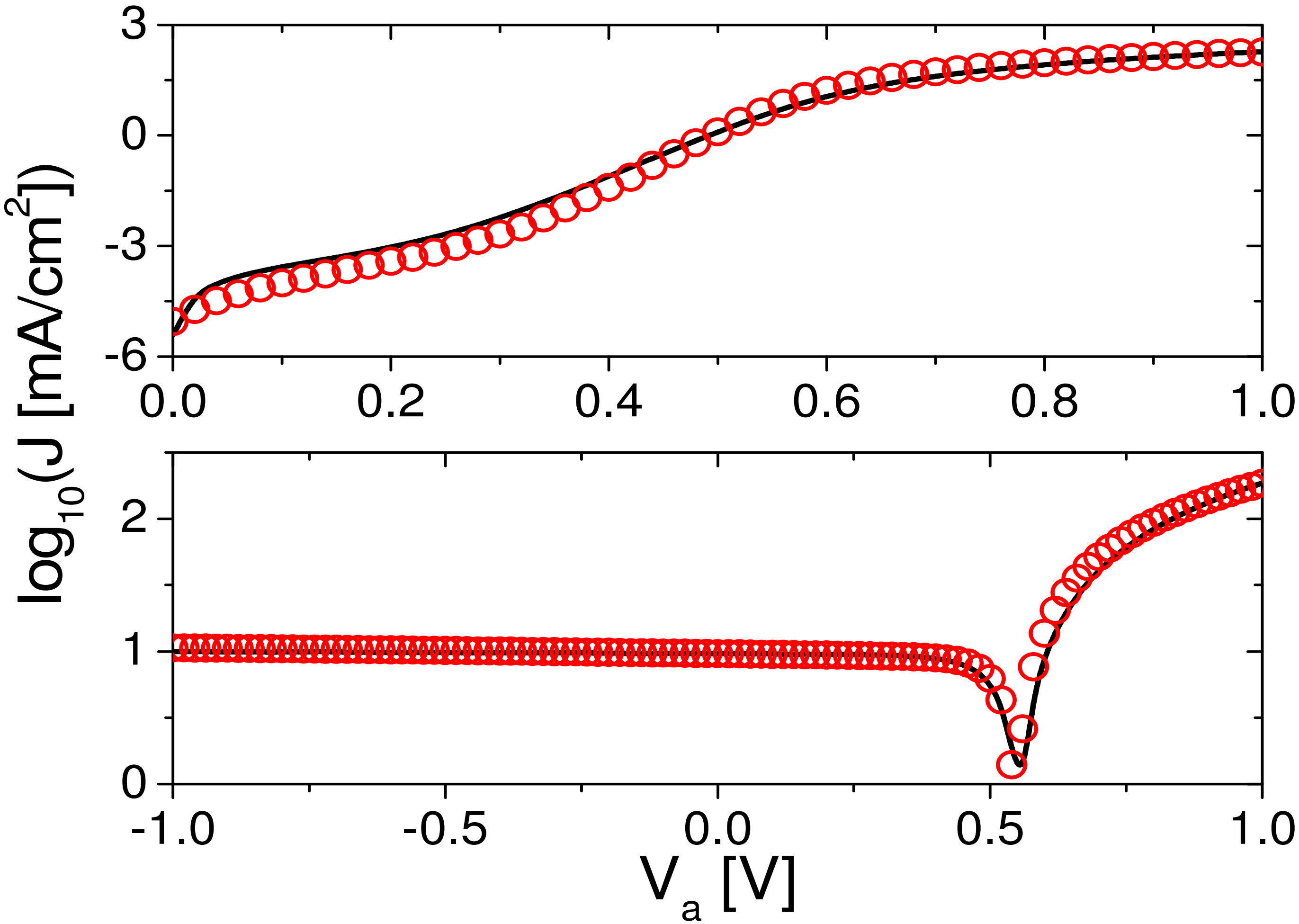
- **At electron-ohmic Ca**

$$n_{f,anode} = N_{LUMO}$$

$$p_{f,anode} = P_{HOMO} \exp\left(-\frac{E_{gap}}{k_B T}\right)$$

$$V_{anode} = 0$$

Validation and Calibration of Simulation Model with Experiment



*Simulated J-V curves (symbols)

*Experimental J-V curves courtesy of IMRE (solid line)

Simulation Parameters

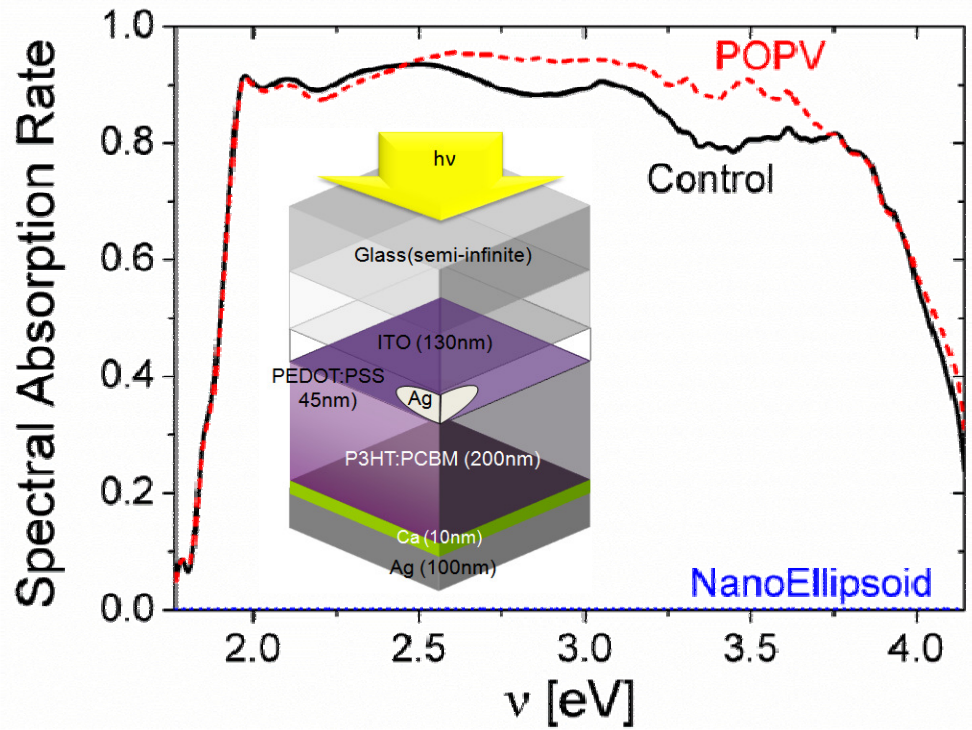
Parameter	Symbol	Simulation Value	Remarks
Bandgap	E_{gap}	1.1eV	LUMO (PCBM=-4eV) [5], HOMO (P3HT)=-5.1eV [6]
E-h pair separation	a	1.15nm	Related to k_d [from Ref 7]
Electron mobility	μ_n	0.7 x10^{-4} cm^2/Vs	Experimental Measurement=~10^{-4} cm^2/Vs
Hole mobility	μ_p	0.7 x10^{-4} cm^2/Vs	Experimental Measurement=~10^{-4} cm^2/Vs
Decay rate	k_f	3x10^4	Constrained Fitting Parameter
E-h pair separation	a	1.15nm	Related to k_d [from Ref 7]
P3HT:PCBM relative permittivity	ε_r	3.4	Average Value of P3HT & PCBM
Characteristic temperature of trapped electrons (holes)	$T_{t,A}$ ($T_{t,D}$)	1200K	**Unique fitting parameter for dark current**
Density of states of free electrons (holes)	N_{LUMO} (P_{HOMO})	4.2x10^{22} cm^{-3}	Constrained Fitting Parameter related to $T_{t,A}$ ($T_{t,D}$)
Density of states of trapped electrons (holes)	H_A (H_D)	2x$10^{13}$$cm^{-3}$	Constrained Fitting Parameter related to $T_{t,A}$ ($T_{t,D}$)
Series Resistance	R_s	1.8Ω	Experimental measurement is ~1-2Ω

5) M. D. Irwin et al, PNAS, 105, 2783-2787 (2007)
6) M. C. Scharber et al, Advanced Materials, 18, 789-794 (2006)
7) W. S. Koh et al, IEEE J. Photovoltaics, 1, 84-92 (2011)

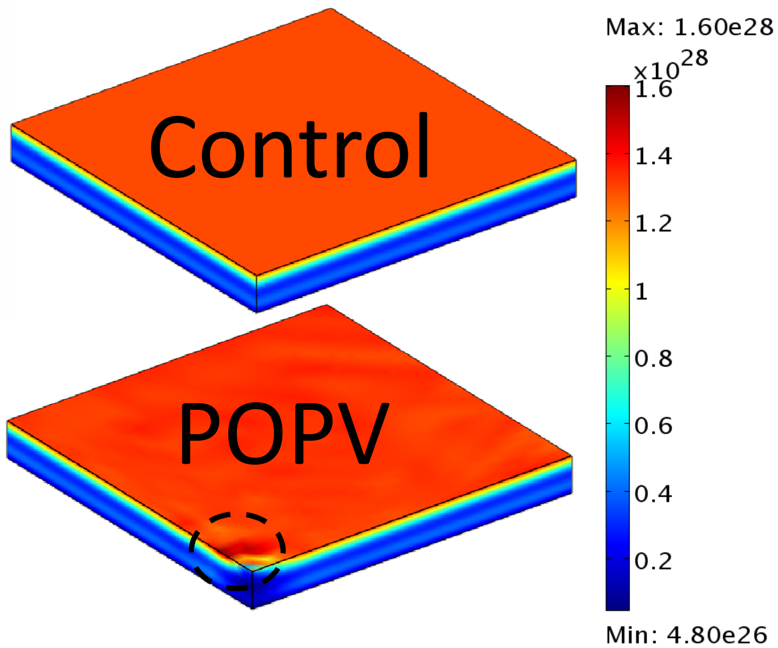
Plasmonic OPV (POPV) Device: Optical & Polaron Generation

- Structure with 200nm (long axis) by 40nm (short axis) Ag nanoellipsoid in PEDOT:PSS @ 1% coverage is illuminated by AM1.5G spectrum

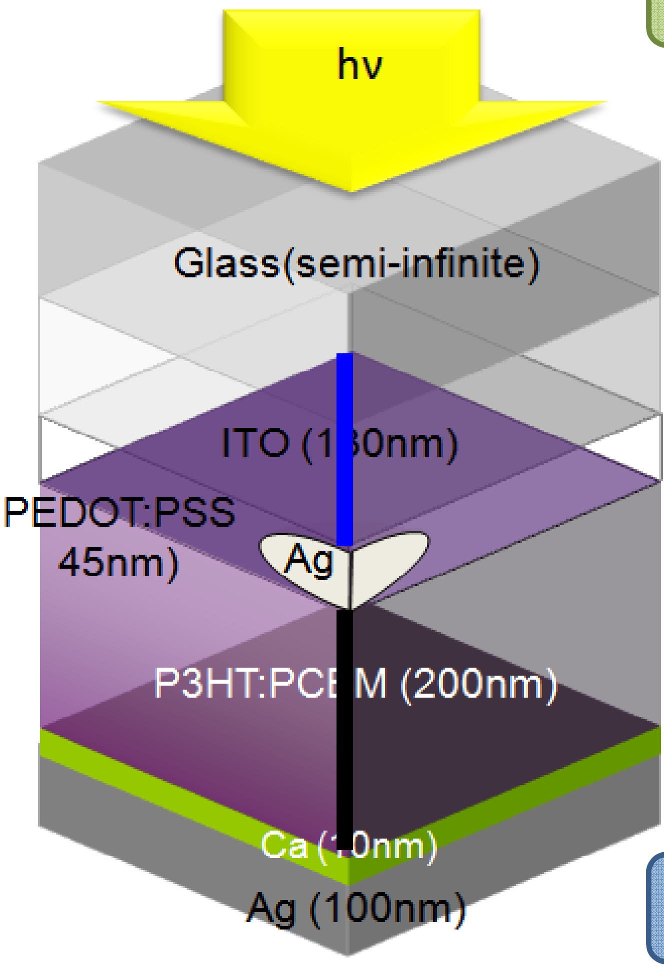
Absorption Rate

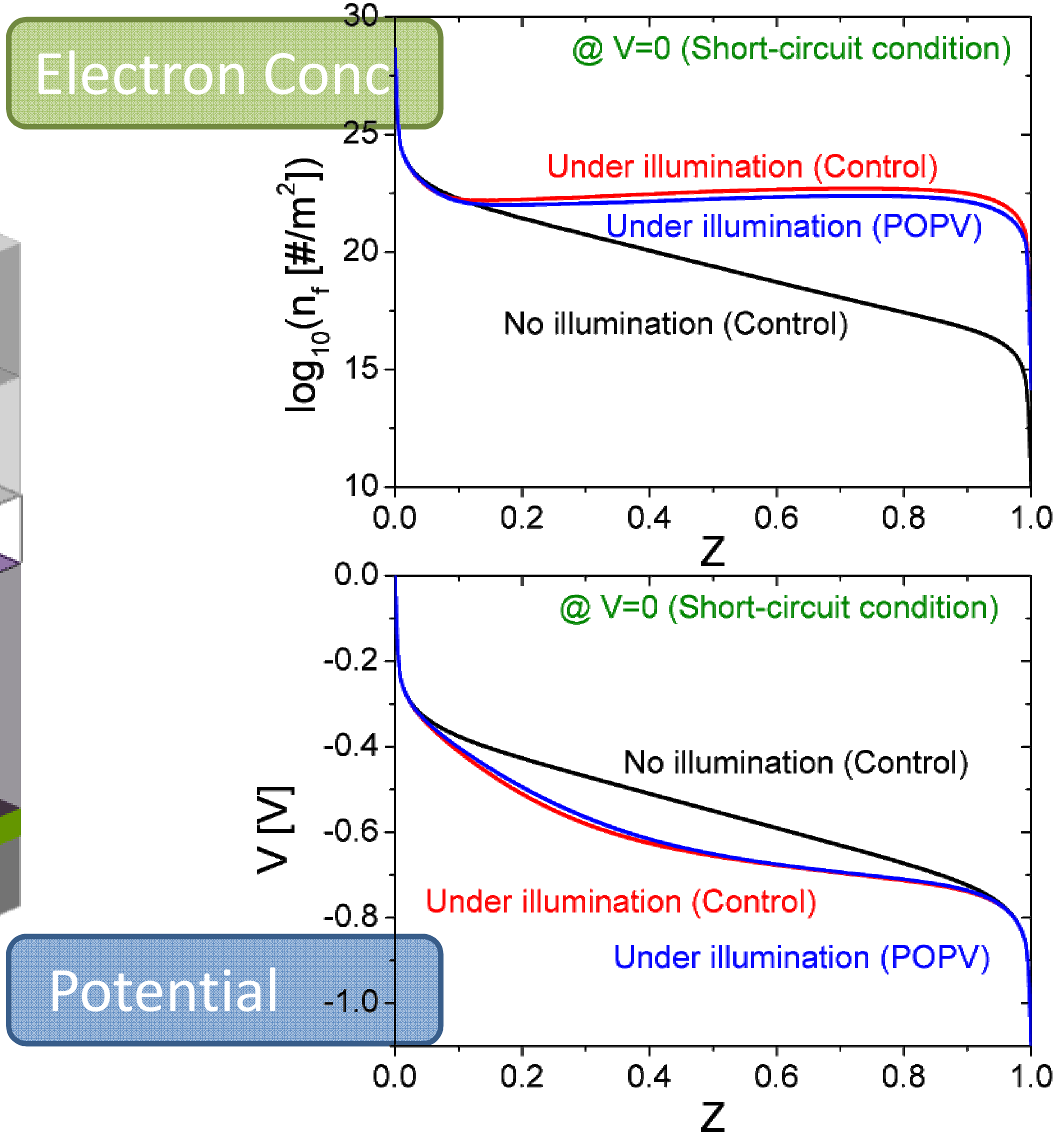


Generation of Polarons

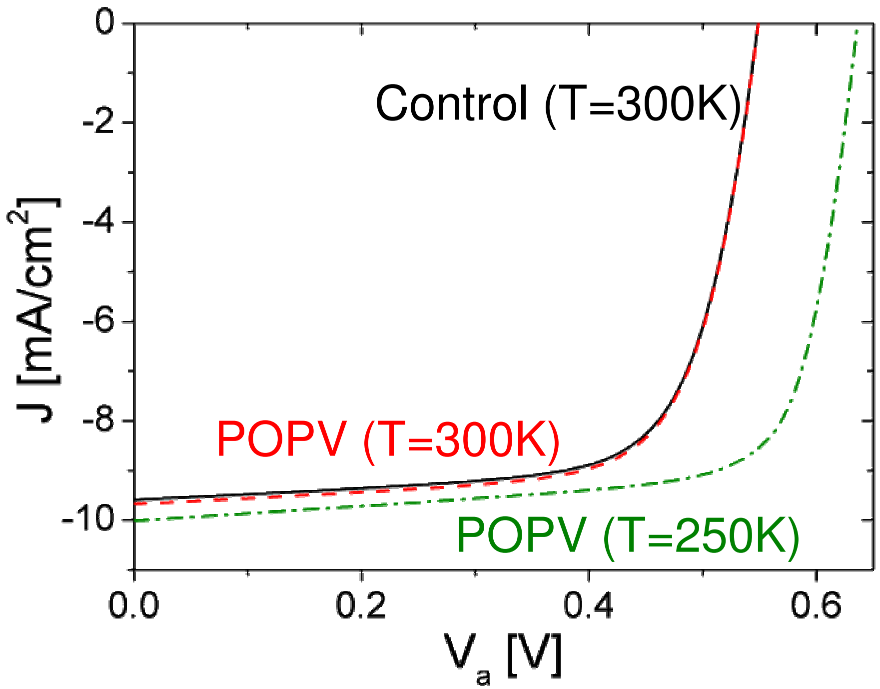


POPV Device: Carrier Transport





POPV Device: J-V Characteristics



- % enhancement in Jsc is approx % ↑ in optical absorption
- ↓ temperature → ↑Voc is consistent with experimental behavior small molecule OPV device by Giebink et al. [4]

Device Characteristic	Control Cell (Experiment)	Control Cell (T=300K)	POPV Cell (T=300K)	POPV Cell (T=250K)
V_{oc} (V)	0.55	0.55	0.55	0.64
J_{sc} (mA/cm^2)	9.61	9.61	9.76	10
Efficiency (%)	3.6	3.76	3.82	4.6
Fill Factor	0.68	0.71	0.71	0.72

Summary

- Developed a full 3D optoelectronic model for organic bulk-heterojunction solar cell
- Validated our model with experiment for a control structure
- Illustrate and predict both optical and electrical characteristics of a 3D Plasmonic OPV device
- Open up possibilities to design and simulate nanostructure enhanced organic bulk-heterojunction solar cells.
- Device physics is applicable for both polymer and small molecule-based organic bulk-heterojunction solar cells.

Thank You for your Attention

Any Questions?