

Breaking the Space Charge Limit in Organic Semiconductors by Novel Plasmon-Electrical Concept

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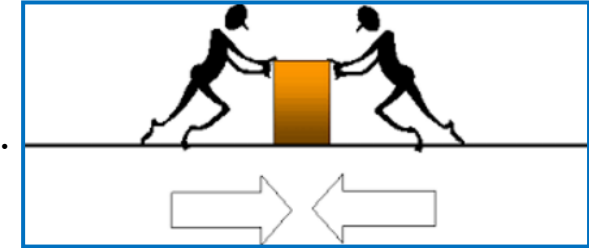
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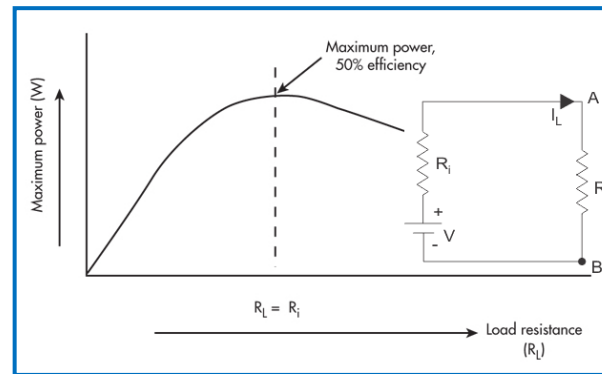
FUNDAMENTAL BALANCE LAW

Fundamental balance laws have rich applications:

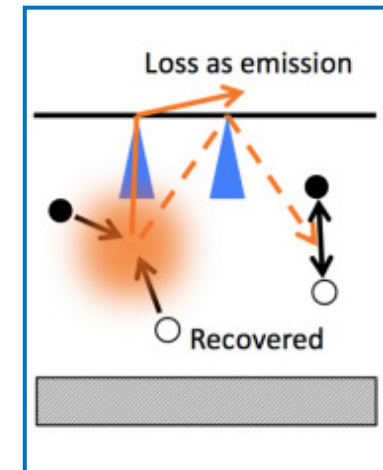
1. If the force is balanced, an object maintains its state of motion.



2. If load resistance balances with internal resistance of a source, the load will gain a maximum power from the source.



3. If the emitted photons balance with incoming photons, the solar cell achieves its limiting efficiency.

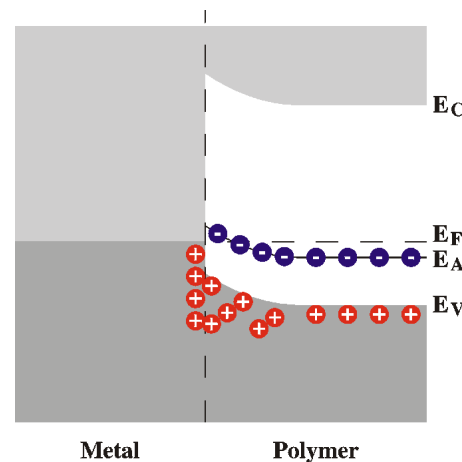


A proper balancing design reduces unwanted losses by unbalanced configurations. Here, we will show balancing the transport time of electrons and holes by plasmonic-electrical effect will break the space charge limit (SCL) in organic photovoltaics (OPVs) caused by unbalanced mobility.

WHAT IS SCL EFFECT?

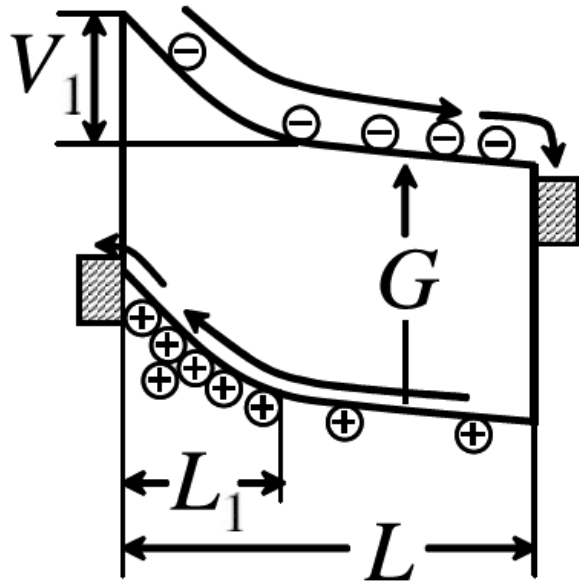
1. Unbalanced mobility
2. Active layer is thicker than mean drift length of low-mobility holes
3. High light intensity
4. Moderate reverse bias

Positive space charges are accumulated due to the unbalanced carrier mobility and a long transport path of holes. As a result, the short-circuit current and fill factor of OPVs will drop significantly due to both the bulk recombination and space charge formation.



density of free carriers injected into the active region is larger than the number of acceptor levels
(by Peter Stallinga, Universidade do Algarve)

WHAT IS CHARACTERISTICS OF SCL EFFECT?



Mean drift length of holes

$$L_1 = \mu_h \tau_h V_1 / L_1$$

Photocurrent

$$J_{Ph} = qGL_1 = qG(\mu_h \tau_h V_1)^{1/2}$$

Space-charge limited current (Mott-Gurney law)

$$\epsilon \frac{dE}{dx} = \frac{J}{\mu_h E} \quad \longrightarrow \quad J_{SCL} = \frac{9}{8} \epsilon \mu_h \frac{V_1^2}{L_1^3}$$

$$V_1 = \int_0^{L_1} E(x) dx$$

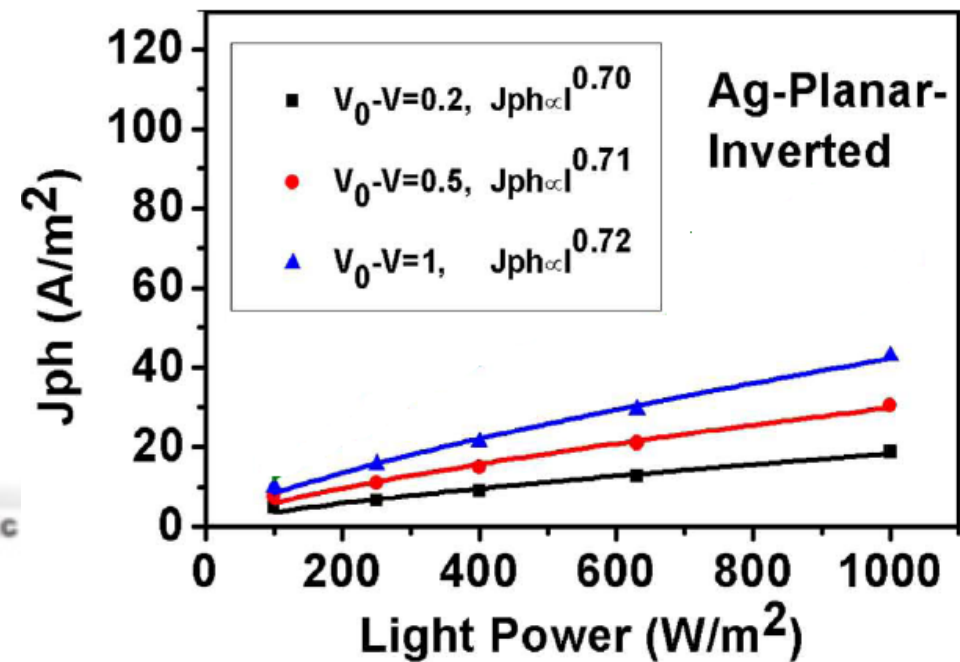
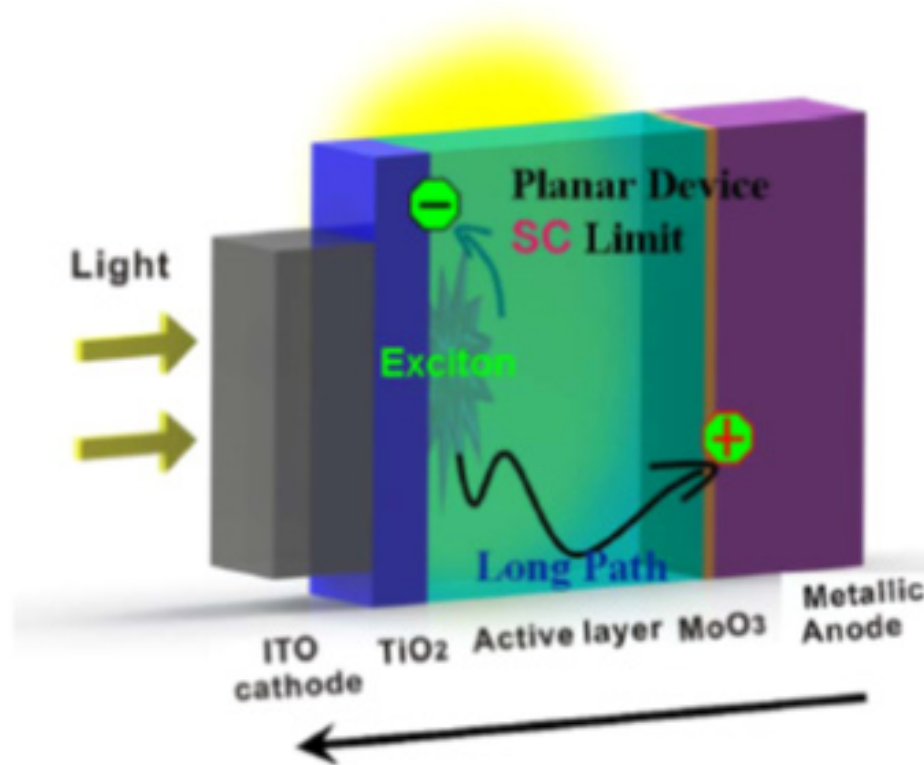
Current density-voltage characteristics ($J_{SCL} = J_{Ph}$)

$$J_{normal} = qGL$$

$$J_{SCL} = q \left(\frac{9\epsilon\mu_h}{8q} \right)^{1/4} G^{3/4} V^{1/2}$$

V. D. Mihailetschi, J. Wildeman, and P.W. M. Blom, *Physical Review Letters* **94**, 126602 (2005).

SCL FOR PLANAR INVERTED OPVS



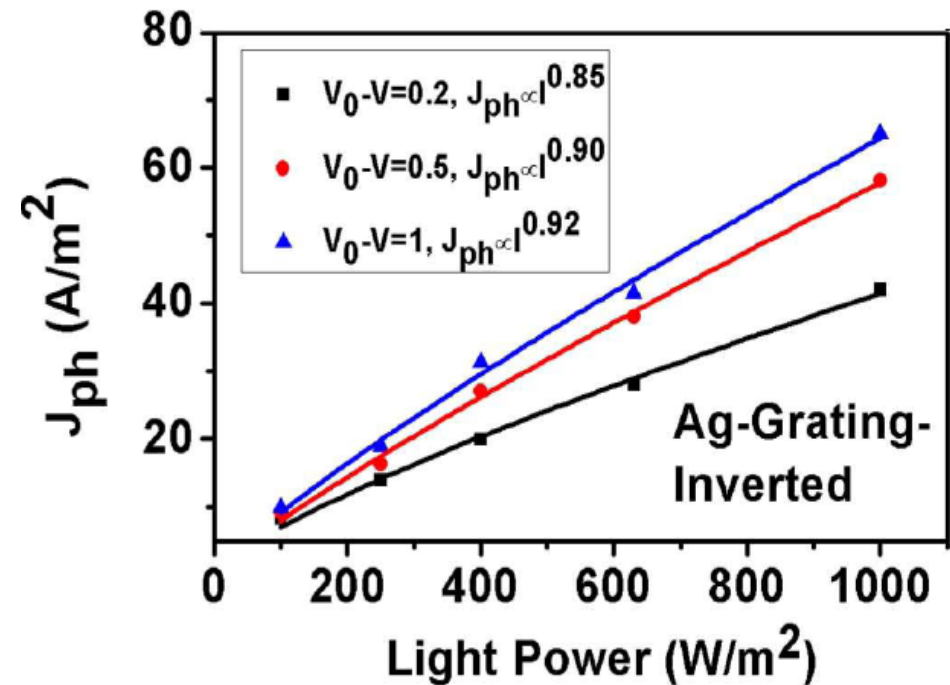
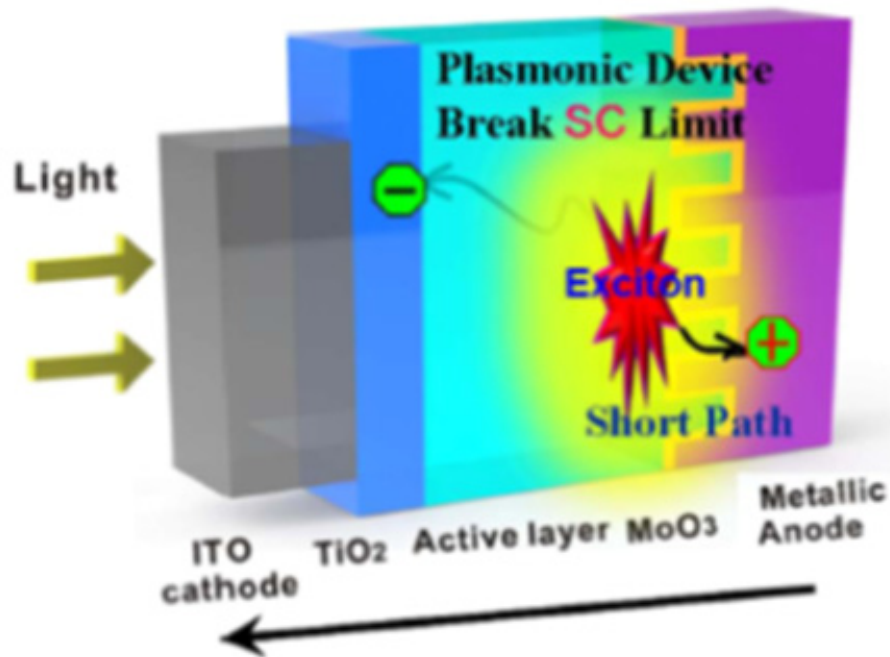
Light distribution mainly concentrates around cathode.

Low-mobility holes travel a long distance with a long transport time.

High-mobility electrons travel a short distance with a short transport time.

SCL effect occurs due to unbalanced transport time!

SCL BREAKING FOR GRATING INVERTED OPVS



Light distribution concentrates around anode due to plasmonic effects.

Low-mobility holes travel a short distance and high-mobility electrons travel a long distance.

Carriers have balanced transport times.

SCL effect is broken!

Plasmonic-electrical effect: manipulate electrical properties of OPVs by plasmonic effect.

HOW DOES LIGHT SPATIALLY DISTRIBUTE?

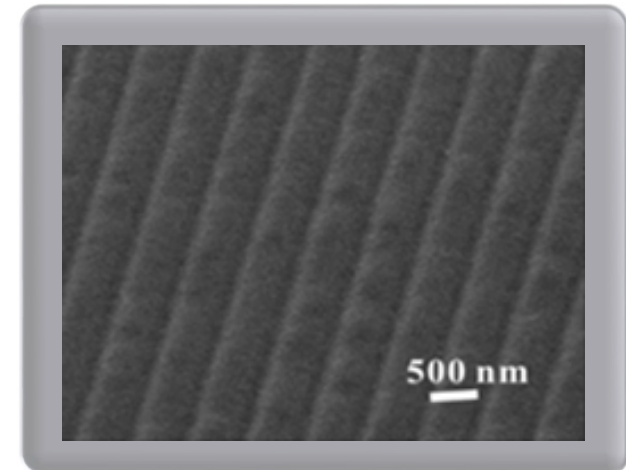
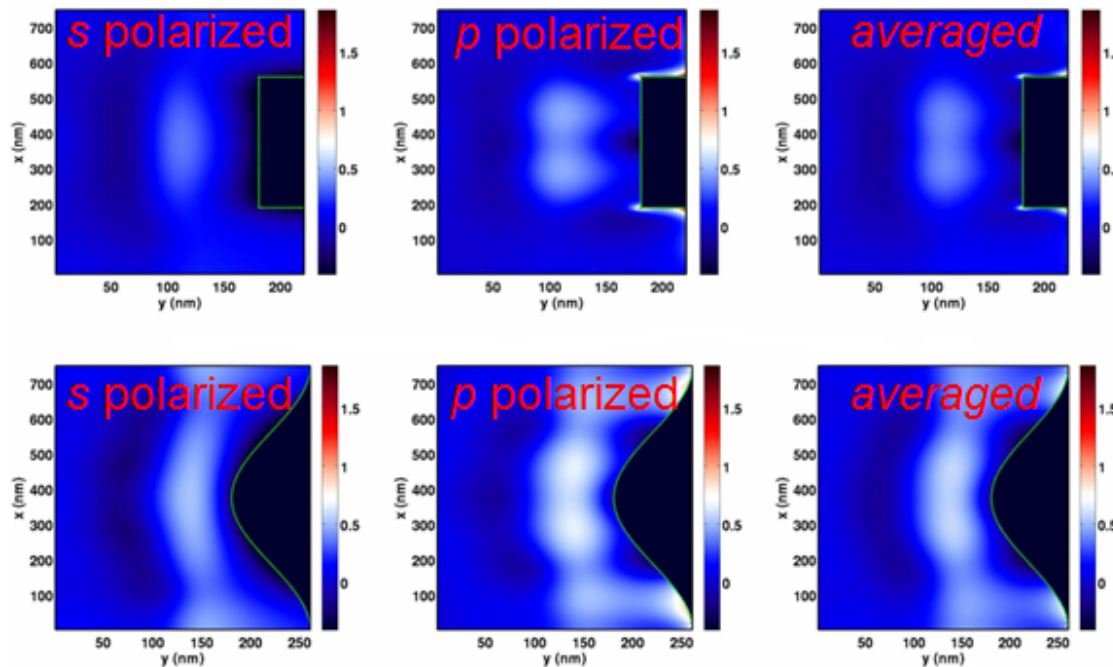
$$\nabla \times \mathbf{E} = -j\omega\mu_0 \mathbf{H}, \quad \nabla \times \mathbf{H} = j\omega\overset{\text{permittivity}}{\varepsilon(\omega)} \mathbf{E}$$

$$\boxed{G(\mathbf{r})} = \int_{400}^{800} \frac{\lambda}{hc} A(\mathbf{r}, \lambda) d\lambda, \quad A(\mathbf{r}, \lambda) = \omega\varepsilon_0 n_r k_i |\boxed{\mathbf{E}(\mathbf{r})}|^2$$

optical E-field

Maxwell's equations

generation rate



exciton generation of grating-inverted OPVs over that of planar inverted ones

HOW DO CARRIERS TRANSPORT?

electrostatic potential

$$\nabla \cdot (\epsilon \nabla \phi) = -q(p - n)$$

electron density

dielectric constant

hole density

mobility

Diffusion coefficients

recombination rate

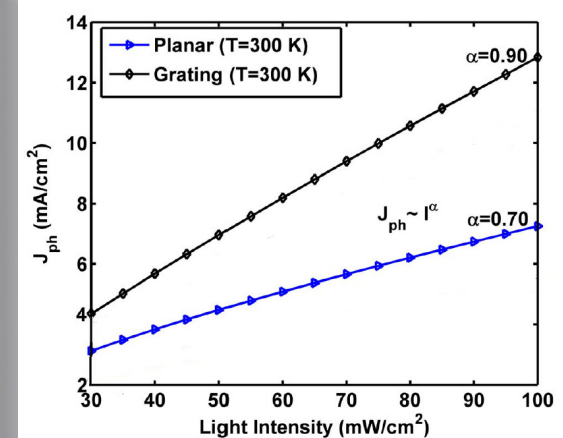
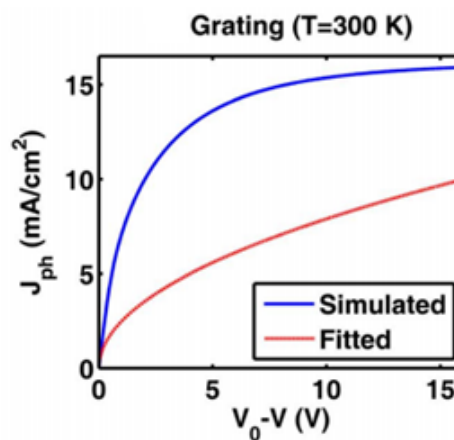
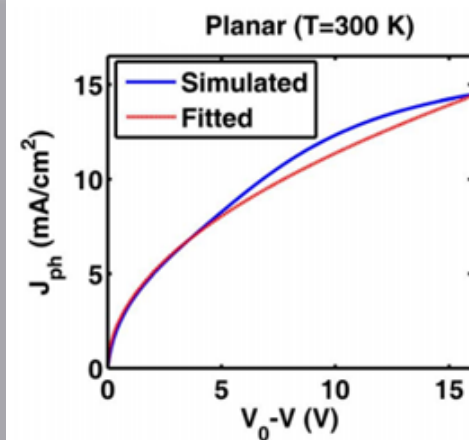
Generation rate

$$\frac{\partial n}{\partial t} = \frac{1}{q} \nabla \cdot (-q\mu_n n \nabla \phi + qD_n \nabla n) + G - R$$

$$\frac{\partial p}{\partial t} = -\frac{1}{q} \nabla \cdot (-q\mu_p p \nabla \phi - qD_p \nabla p) + G - R$$

Poisson equation

drift-diffusion & current continuity equation



A UNIVERSAL BALANCING RULE

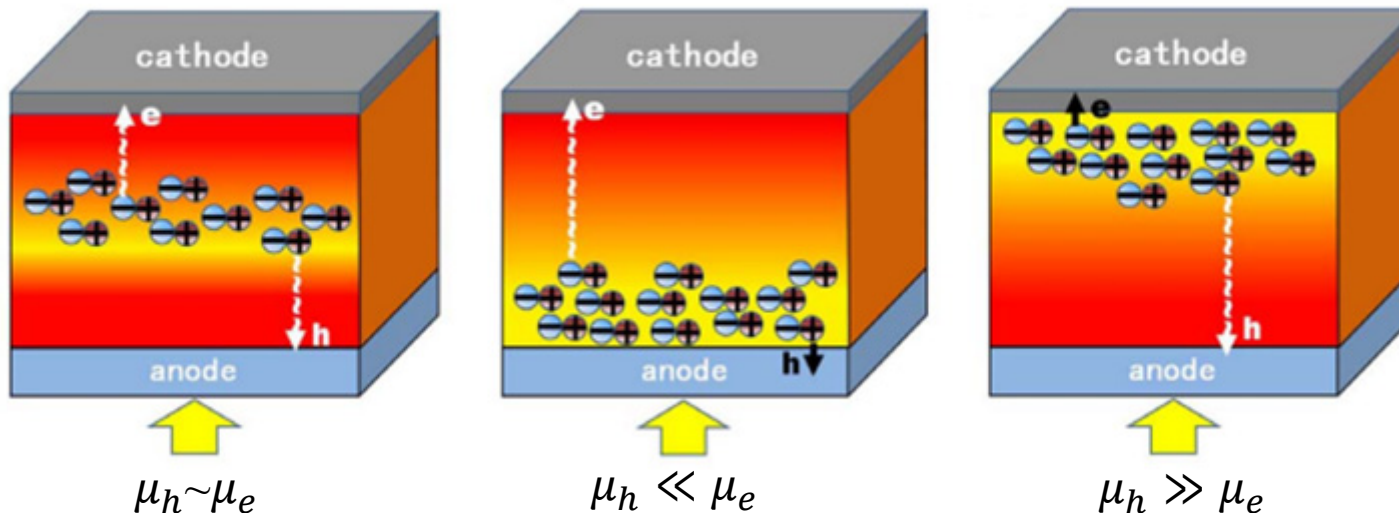
The total transport lengths of electrons and holes are equal to active layer thickness.

$$L_e + L_h \approx L$$

Transport time of electrons and holes are required to be balanced.

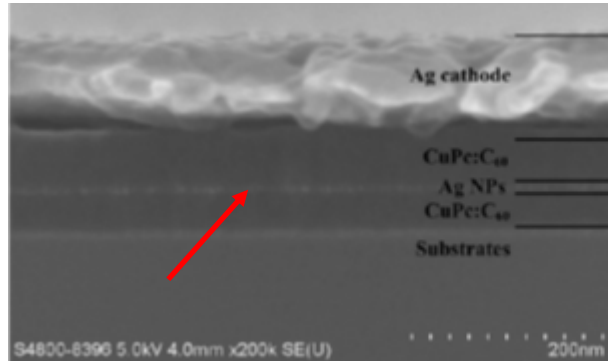
$$\frac{L_e}{\mu_e} \approx \frac{L_h}{\mu_h}$$

Mobility dependent optical designs

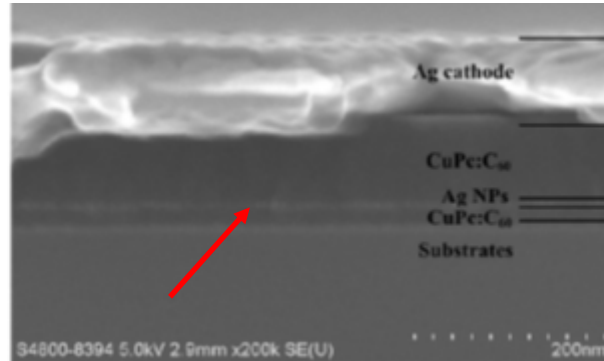


EXPERIMENTAL AND NUMERICAL RESULTS

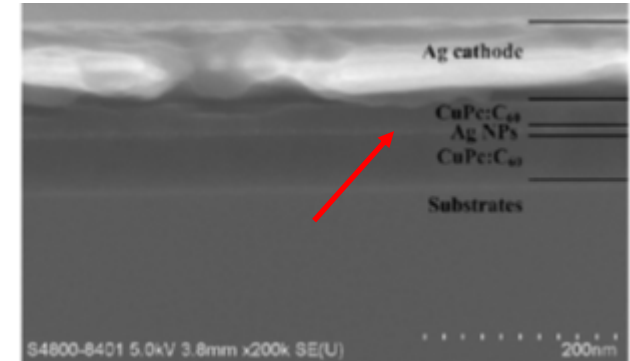
middle



near-anode



near-cathode



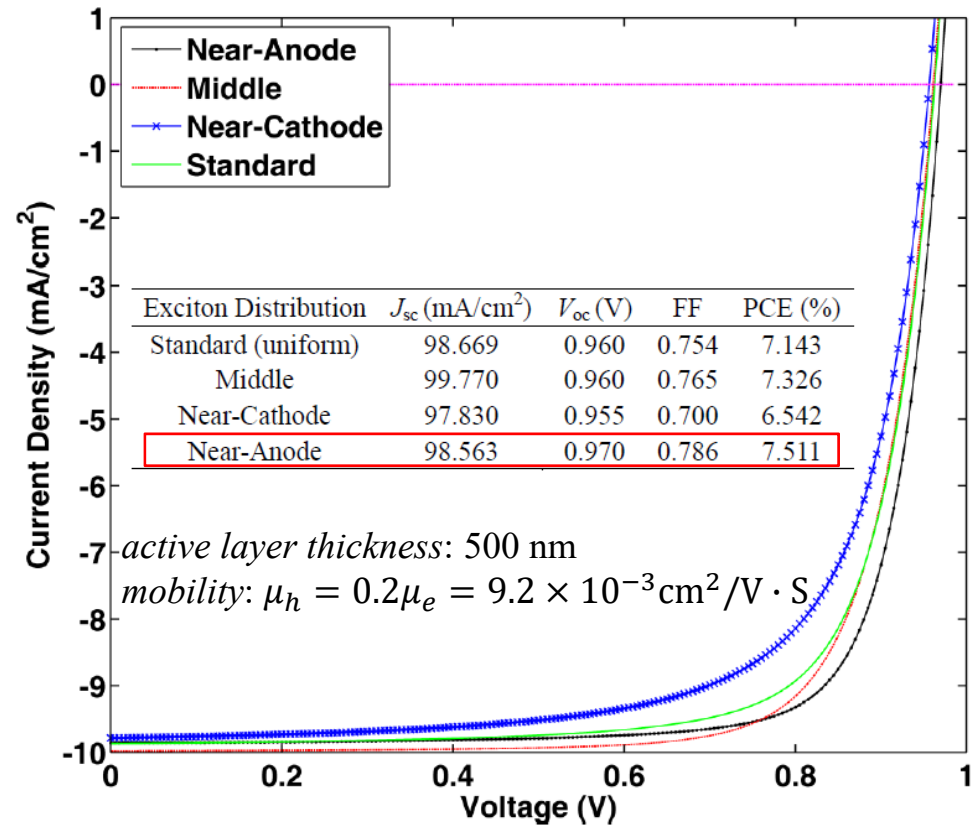
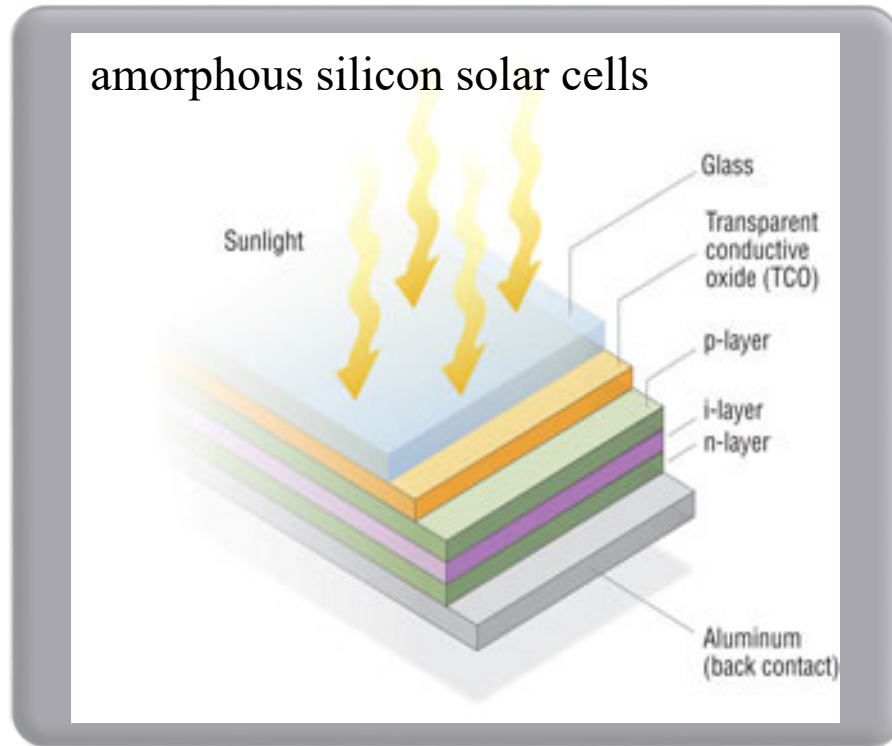
Types	J_{sc} (mA.cm ⁻²)	V_{oc} (V)	FF	PCE (%)
Near-anode	2.98±0.077	0.48±0.015	0.42±0.011	0.60±0.034
Middle	3.44±0.064	0.44±0.023	0.39±0.005	0.59±0.032
Near-cathode	3.21±0.240	0.36±0.023	0.32±0.004	0.37±0.010

experimental

NPs position	Mobility	J_{sc} (mA/cm ²)	FF	V_{oc} (V)	PCE (%)
N-Anode	$\mu_h = 0.02\mu_e$	7.953	0.535	0.549	2.33
Middle	$\mu_h = 0.02\mu_e$	8.494	0.480	0.523	2.13
N-Cathode	$\mu_h = 0.02\mu_e$	4.578	0.278	0.464	0.59

theoretical

IS IT UNIVERSAL FOR OTHER SOLAR CELLS?



$$G_{pl}^m(z) = \begin{cases} 0, & 0 \leq z < 2L/5 \\ 5\bar{G}_p, & 2L/5 \leq z < 3L/5 \\ 0, & 3L/5 \leq z < L \end{cases} \quad G_{pl}^a(z) = \begin{cases} 0, & 0 \leq z < 4L/5 \\ 5\bar{G}_p, & 4L/5 \leq z < L \end{cases} \quad G_{pl}^c(z) = \begin{cases} 5\bar{G}_p, & 0 \leq z < L/5 \\ 0, & L/5 \leq z < L \end{cases}$$

middle

near-anode

near-cathode



PUBLICATIONS

1. Wei E.I. Sha, Xuanhua Li, and Wallace C.H. Choy, “Breaking the Space Charge Limit in Organic Solar Cells by a Novel Plasmonic-Electrical Concept,” *Scientific Reports*, vol. 4, pp. 6236, Aug. 2014.
2. Wei E.I. Sha, Hugh L. Zhu, Luzhou Chen, Weng Cho Chew, and Wallace C.H. Choy, “A General Design Rule to Manipulate Photocarrier Transport Path in Solar Cells and Its Realization by the Plasmonic-Electrical Effect,” *Scientific Reports*, vol. 5, pp. 8525, Feb. 2015.
3. Wei E.I. Sha, Wallace C.H. Choy, Yumao Wu, and Weng Cho Chew, “Optical and Electrical Study of Organic Solar Cells with a 2D Grating Anode,” OSA, *Optics Express*, vol. 20, no. 3, pp. 2572-2580, Jan. 2012.



CONCLUSION

1. Balancing transport time of carriers with different mobility is essential to electrical properties of semiconductor devices including carrier transport, recombination, and collection.
2. A universal design rule is proposed to determine the transport paths of carriers via balancing the transport time.
3. Plasmonic effects concentrate light at an ultra-small region/volume and thus could spatially redistribute light at the active layer.
4. Through plasmonically induced modifications of carrier transport paths, the electrical performance of optoelectronic devices will be improved.

ACKNOWLEDGEMENT



Any Questions and Discussions?