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Author(s)	Sha, WEI; Choy, WCH; Chew, WC
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Comprehensive Study of Plasmonic Effects in Organic Solar Cells

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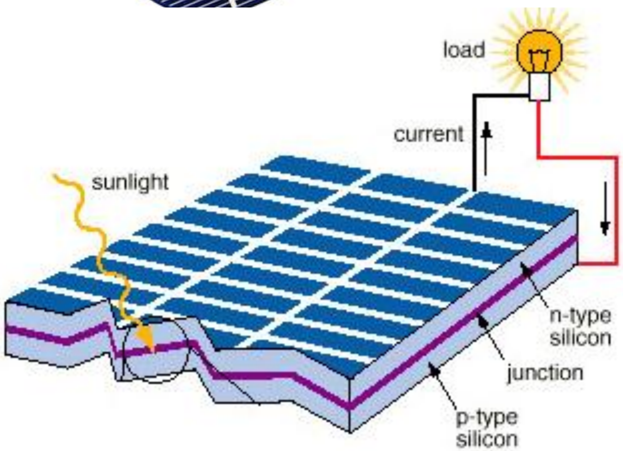
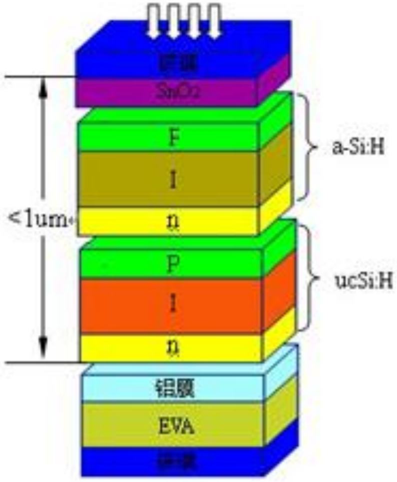
Organic Solar Cell (1)

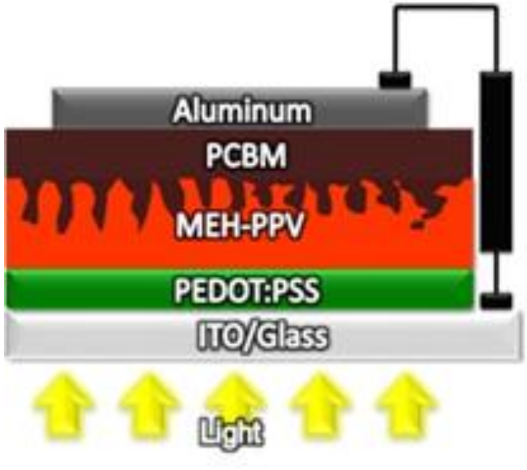
Advances of solar cell technology



monocrystalline silicon solar cell



amorphous/polycrystalline silicon solar cell

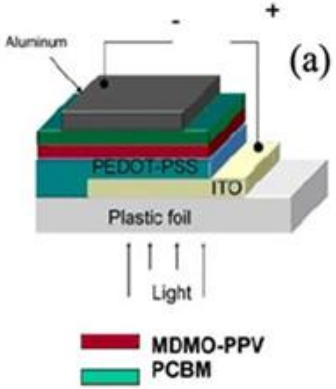


organic solar cell

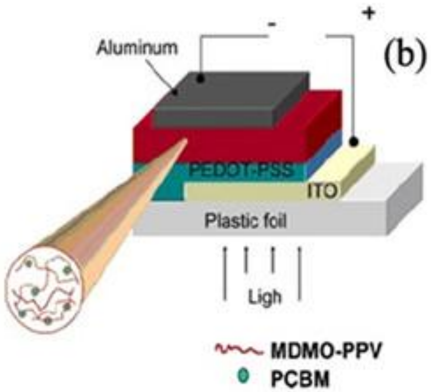
Organic Solar Cell (2)

Thin-film organic solar cell

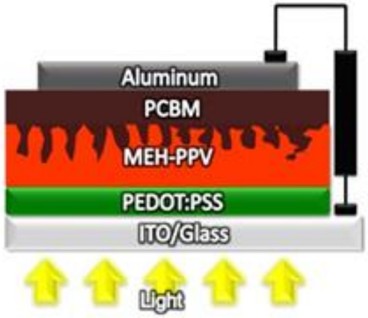
- ✓ *low-cost processing*
- ✓ *mechanically flexible*
- ✓ *large-area application*
- ✓ *environmentally friendly*
- X *low exciton diffusion length*
- X *low carrier mobility*



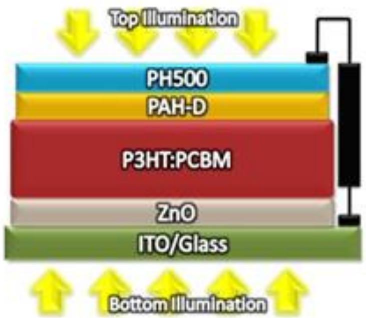
Bilayer PV Cell



Bulk Heterojunction PV Cell



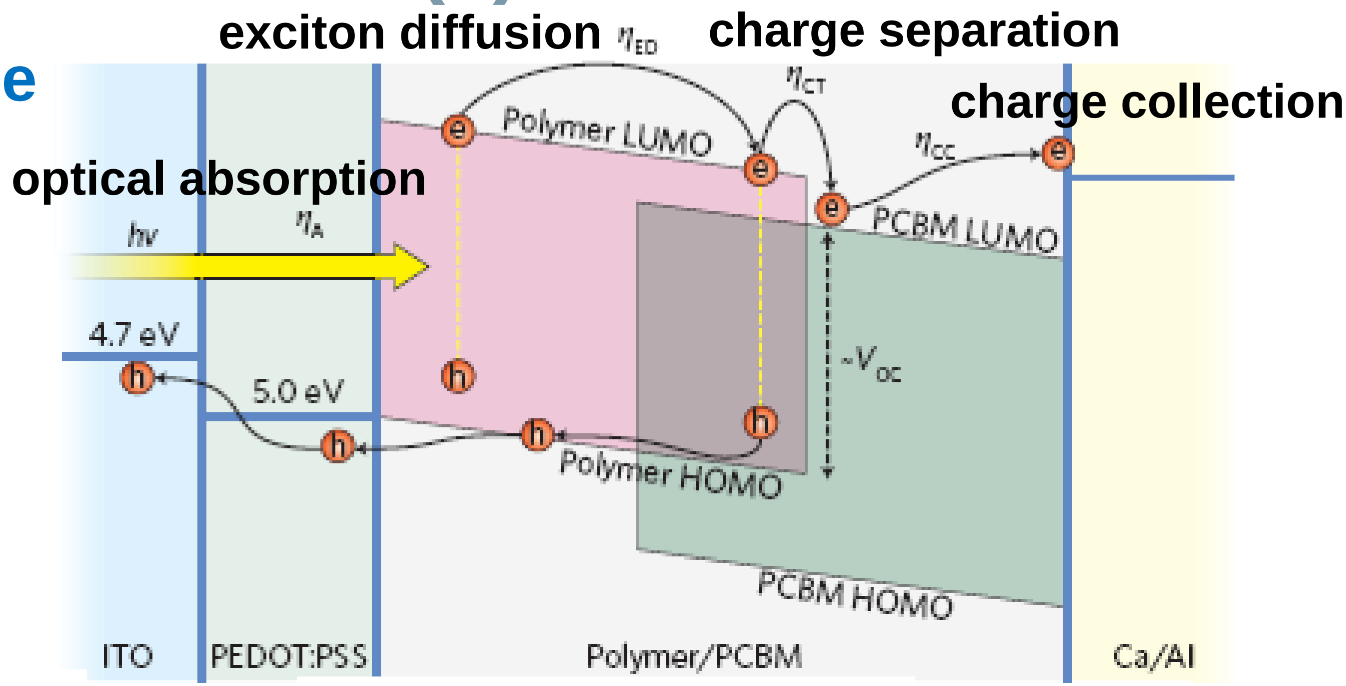
Planar-diffused PV Cell

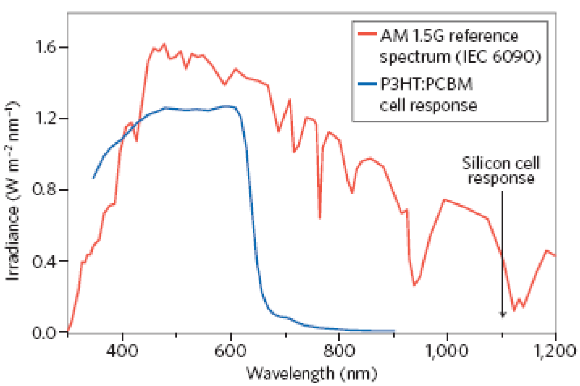


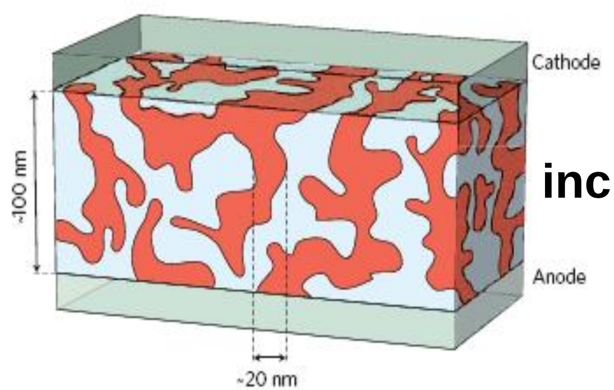
Inverted PV Cell

Organic Solar Cell (3)

Working principle





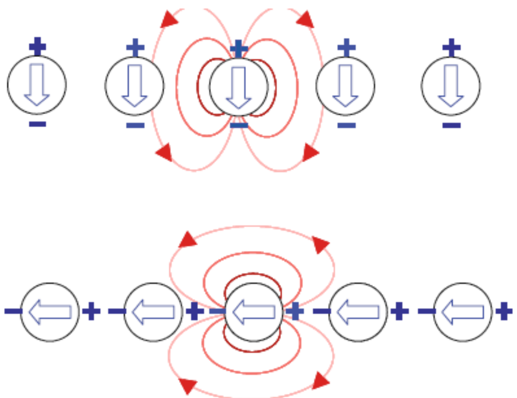


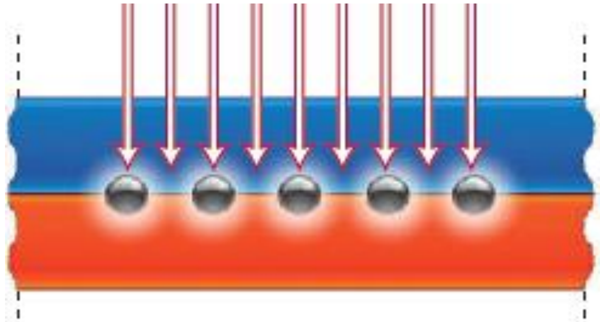
increase interface area

Plasmonic Organic Solar Cell

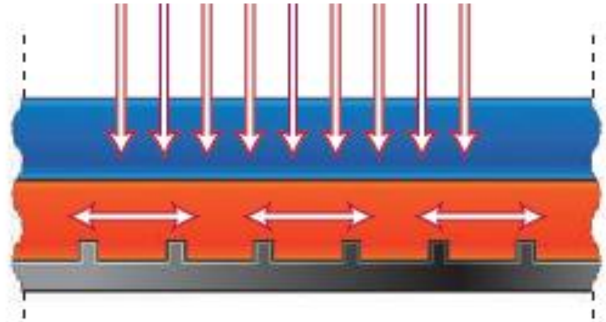
Why optical enhancement?

The thickness of the active layer must be smaller than the exciton diffusion length to avoid bulk recombination. As a result, the thin-film organic solar cell has poor photon absorption or harvesting. Plasmonic solar cell is one of emerging solar cell technologies to enhance the optical absorption.

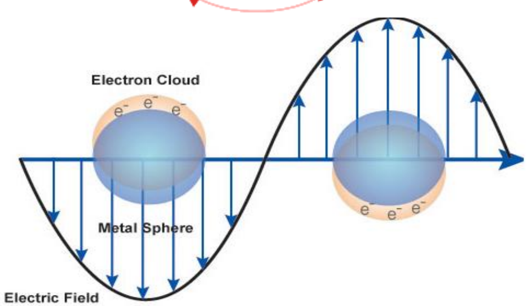


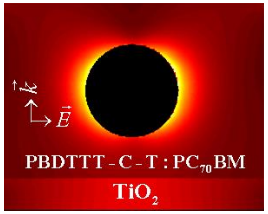


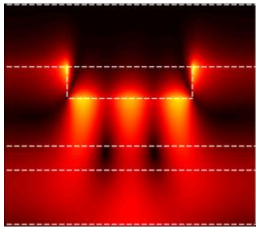
nanoparticles: local plasmon

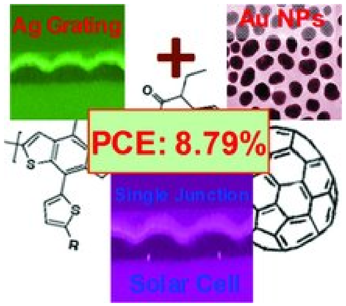


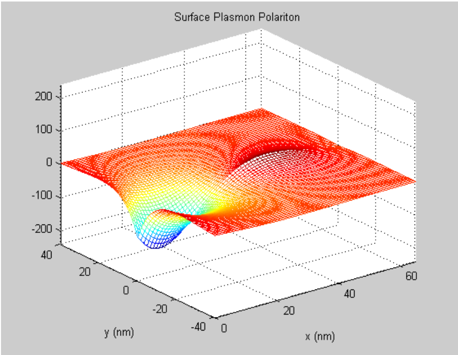
nanograting: surface plasmon





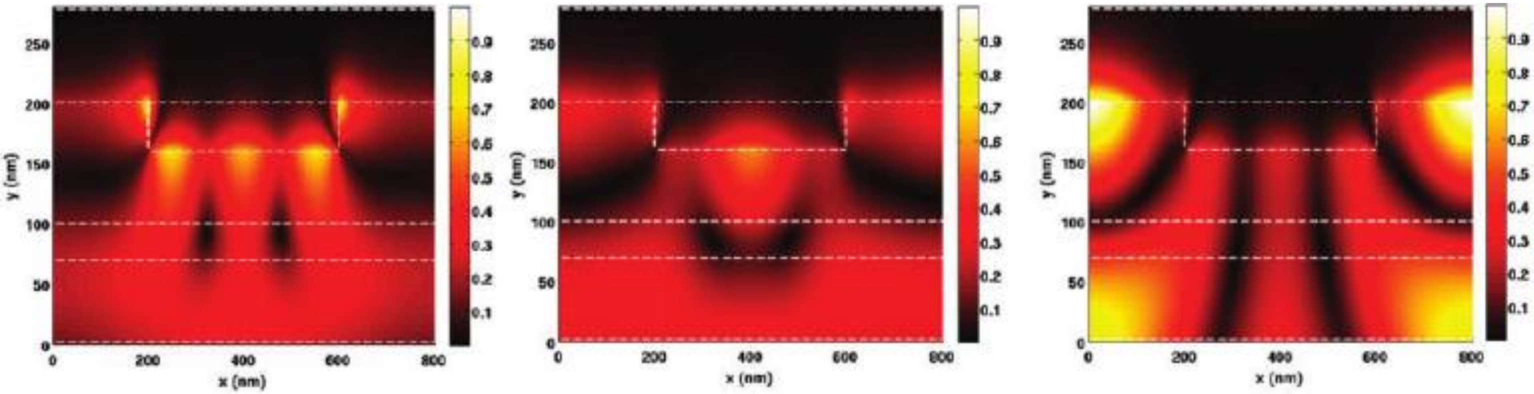


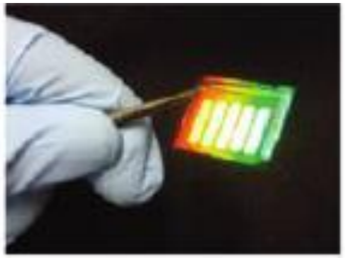




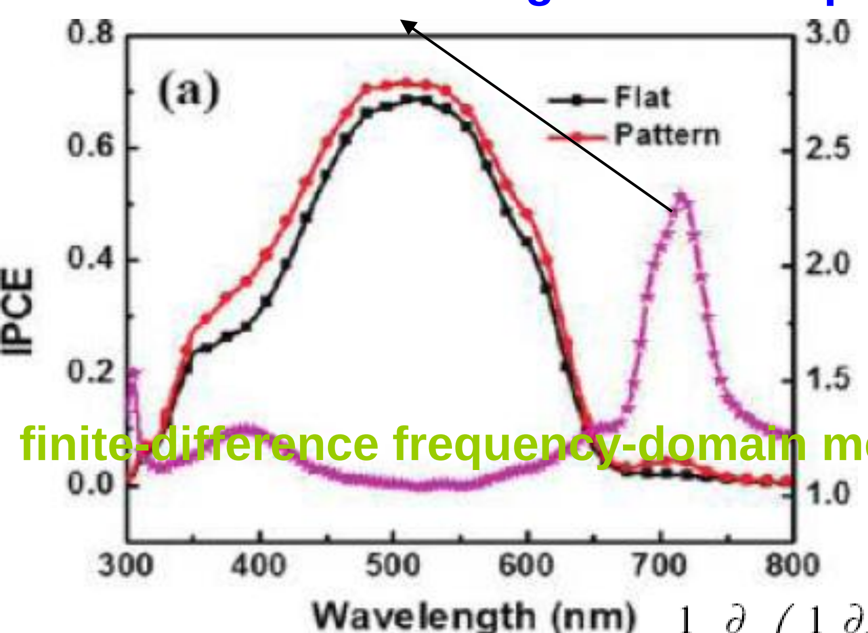
Comprehensive Study of Plasmonic Effects in Organic Solar Cells

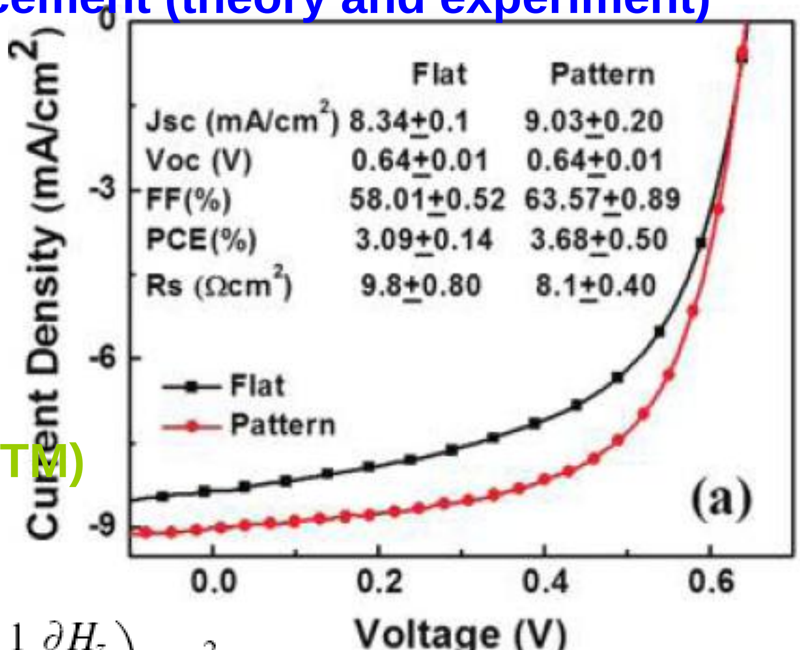
X.H. Li, W.E.I. Sha, W.C.H. Choy, etc, J. Phys. Chem. C, 116(12), 7200-7206, 2012.





Plasmonic band edge boosted optical enhancement (theory and experiment)





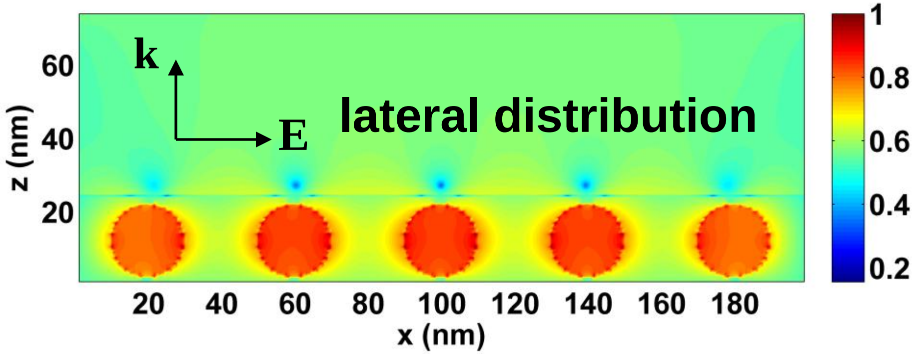
finite-difference frequency-domain method (TE&TM)

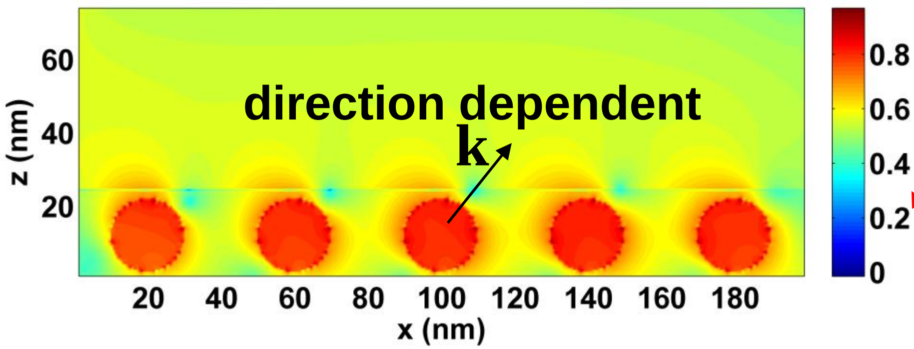
$$\frac{1}{\mu_r}\frac{\partial}{\partial x}\left(\frac{1}{\varepsilon_r}\frac{\partial H_z}{\partial x}\right)+\frac{1}{\mu_r}\frac{\partial}{\partial y}\left(\frac{1}{\varepsilon_r}\frac{\partial H_z}{\partial y}\right)+k_0^2H_z=0$$

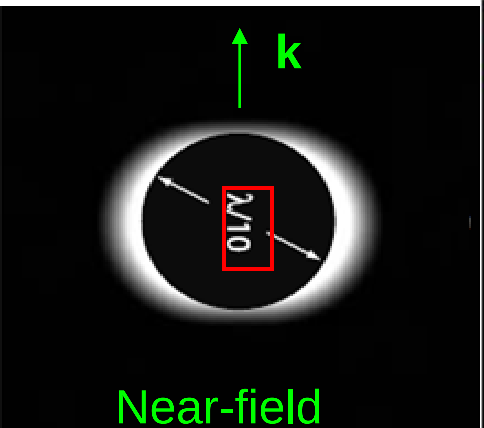
Comprehensive Study of Plasmonic Effects in Organic Solar Cells

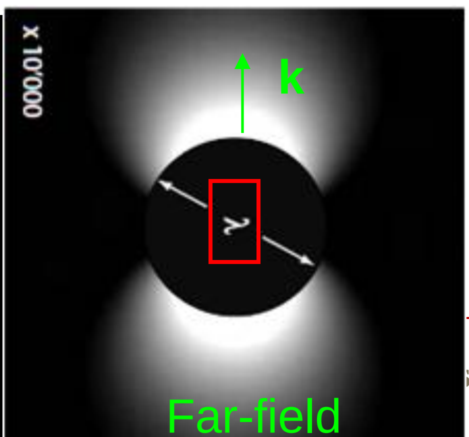
W.E.I. Sha, W.C.H. Choy, Y.P. Chen, and W.C. Chew, Appl. Phys. Lett., 99(11), 113304, 2011.

Bulk heterojunction polymer solar cell

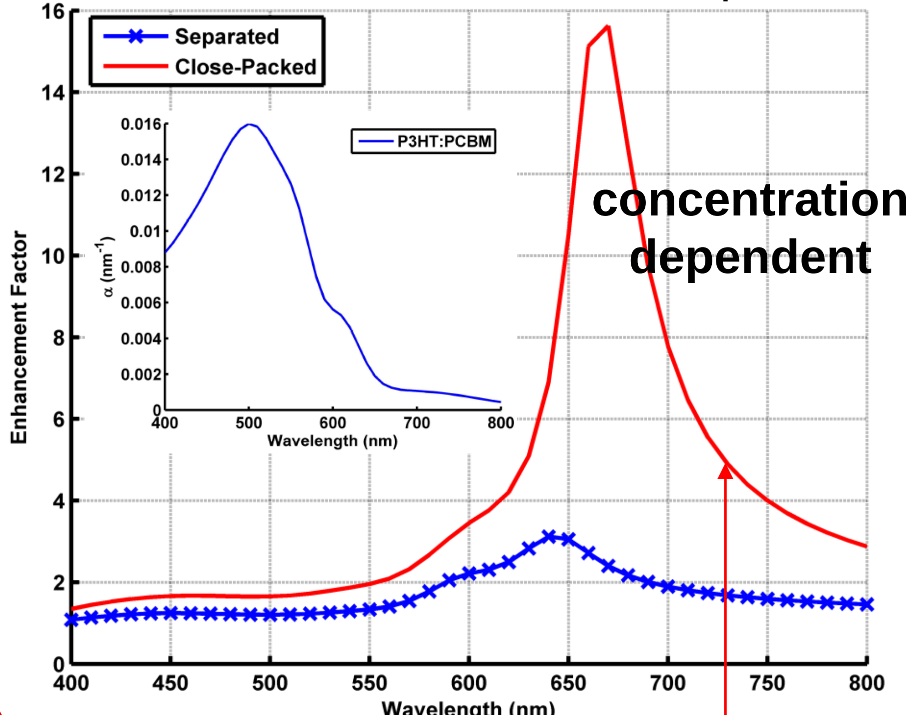


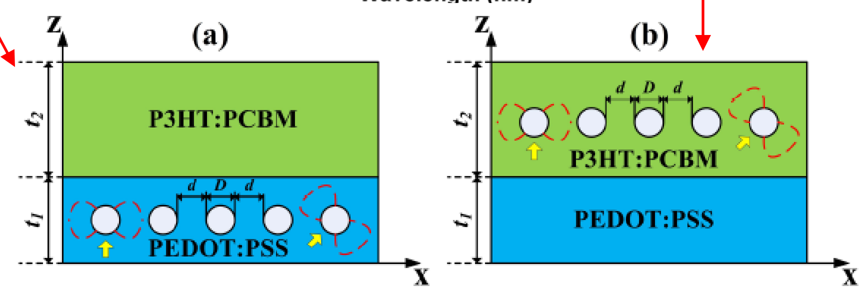






2 fold increase in total absorption!

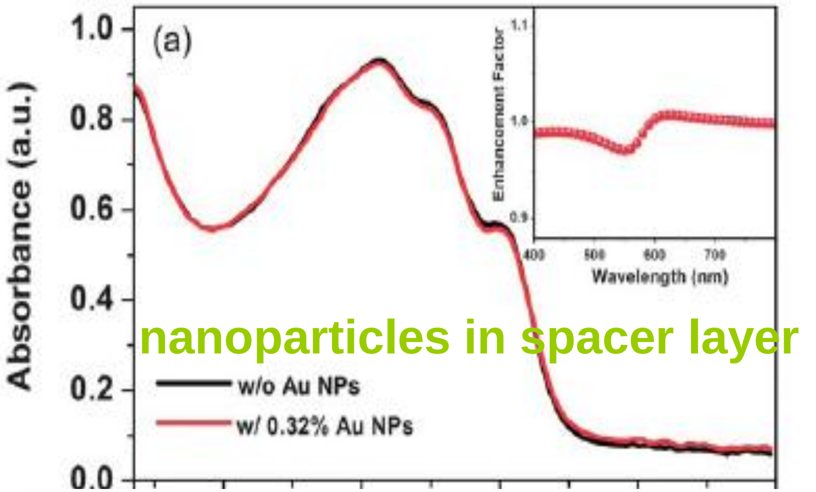


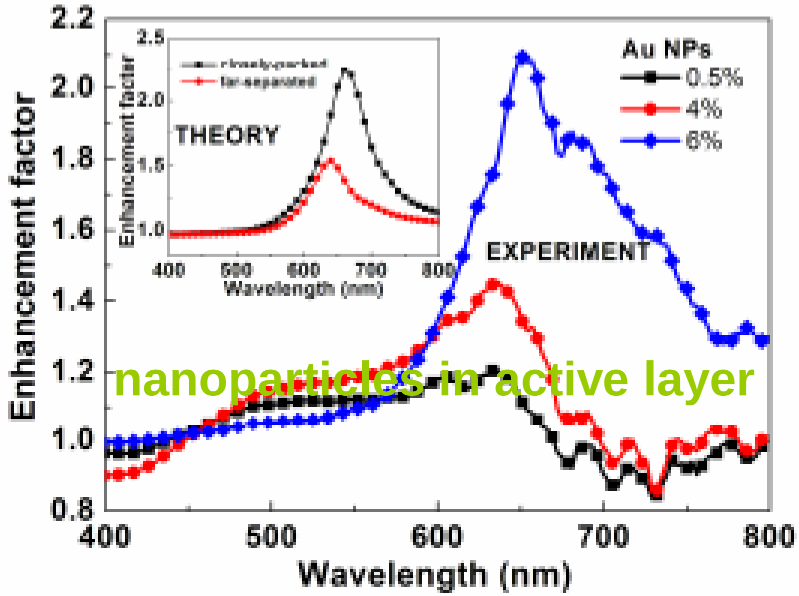


VIE-FFT method (BiCG-STAB)

$$\mathbf{E}^i(\mathbf{r}) = \frac{\mathbf{J}(\mathbf{r})}{j\omega\left(\epsilon(\mathbf{r})-\epsilon_0\right)} + j\omega\mu_0 \int_v \overline{\mathbf{G}}(\mathbf{r},\mathbf{r}')\cdot\mathbf{J}(\mathbf{r}')dr'$$

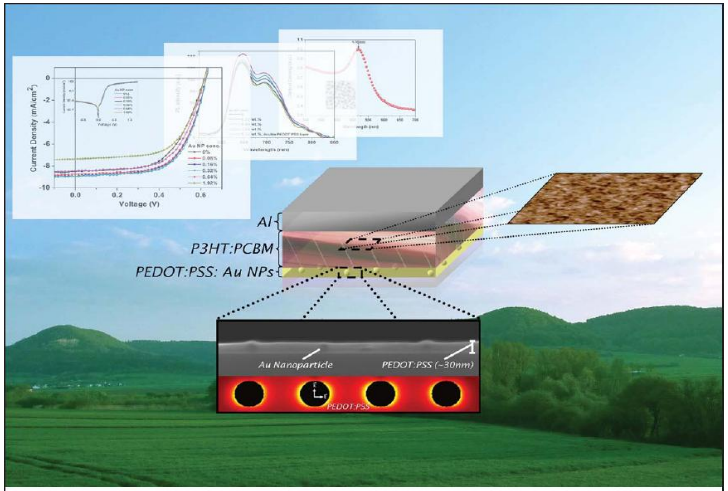
Comparisons with experimental results





C.C.D. Wang, W.C.H. Choy, etc, J. Mater. Chem., 22, 1206-1211, 2011.

D.D.S. Fung, L.F. Qiao, W.C.H. Choy, etc, J. Mater. Chem., 21, 16349-16356, 2011.



Highlighting joint research results from the labs of Department of Electrical and Electronic Engineering, Faculty of Engineering, the University of Hong Kong and Centre for Optical and Electromagnetic Research, State Key Laboratory of Modern Optical Instrumentations, Zhejiang University.

Title: Optical and Electrical Properties of Efficiency Enhanced Polymer Solar Cells with Au Nanoparticles in PEDOT-PSS Layer

Efficiency improvement of polymer solar cells with Au nanoparticles doped into PEDOT:PSS is achieved and attributed to increased interfacial area between P3HT:PCBM and PEDOT:PSS instead of plasmonic effects. New device physics was unveiled, as the very strong LSPR near field of Au nanoparticles was found to distribute laterally along PEDOT:PSS and does not significantly improve P3HT:PCBM active layer absorption.

As featured in:

Journal of Materials Chemistry

See Wallace C. H. Choy *et al.*, *J. Mater. Chem.*, 2011, **21**, 16349.

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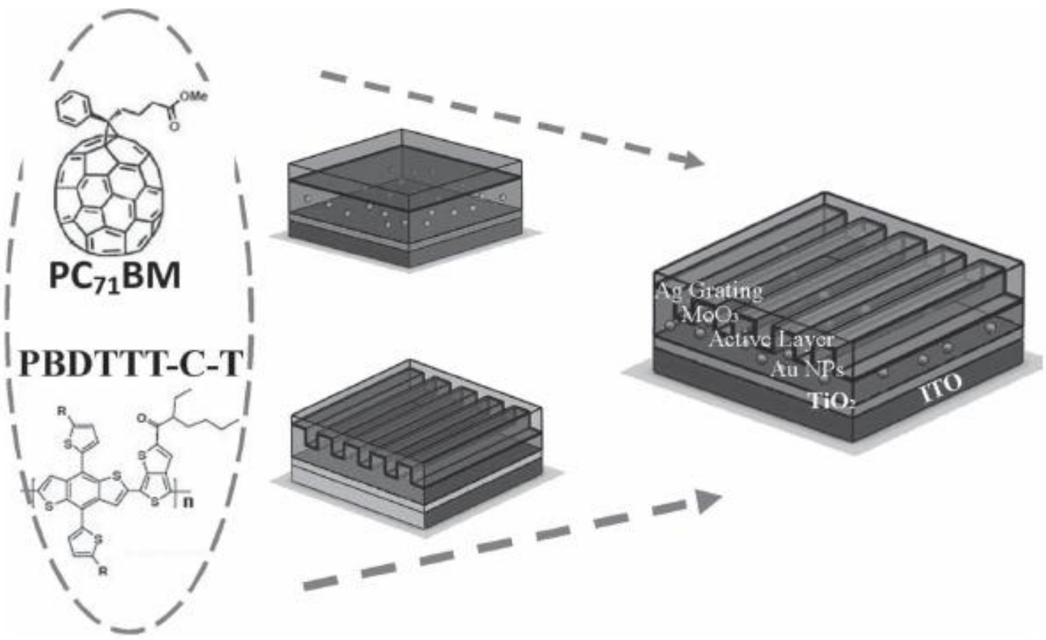
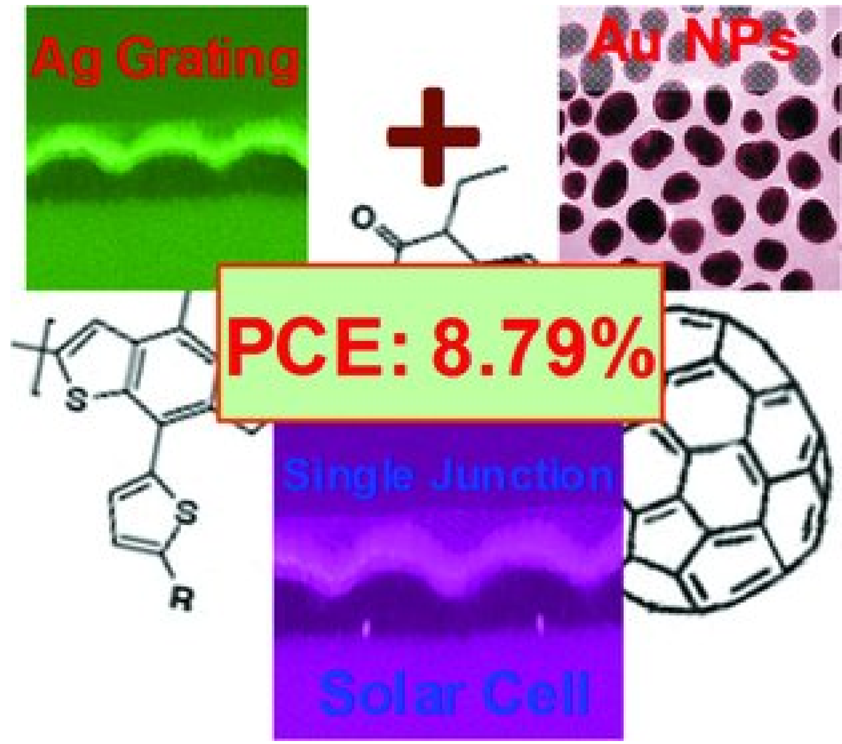
Selected as Back Cover and Hot Article in Journal of Material Chemistry

X.H. Li, W.C.H. Choy, L.J. Huo, F.X. Xie, W.E.I. Sha, B.F. Ding, X. Guo, Y.F. Li, J.H. Hou, J.B. You, and Y. Yang, Adv. Mater., 24, 3046–3052, 2012.

Dual Plasmonic Nanostructure (experimental results)
power conversion efficiency 8.79%

Spin-coating+nanoimprinting





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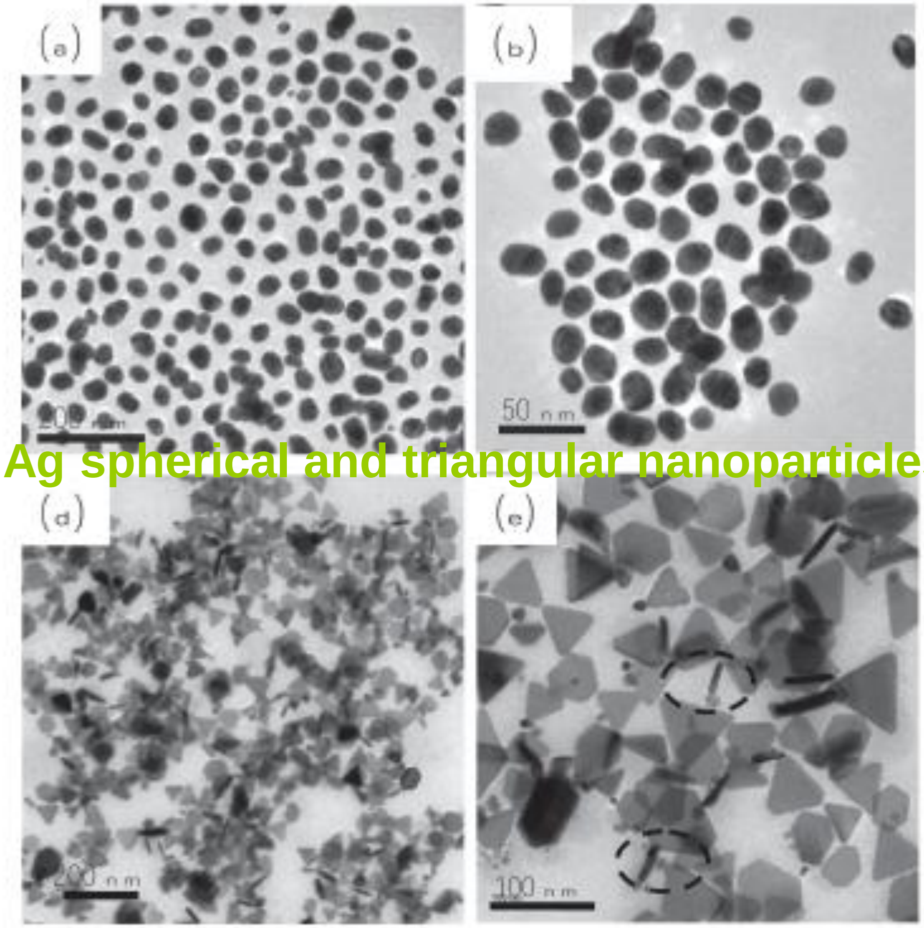
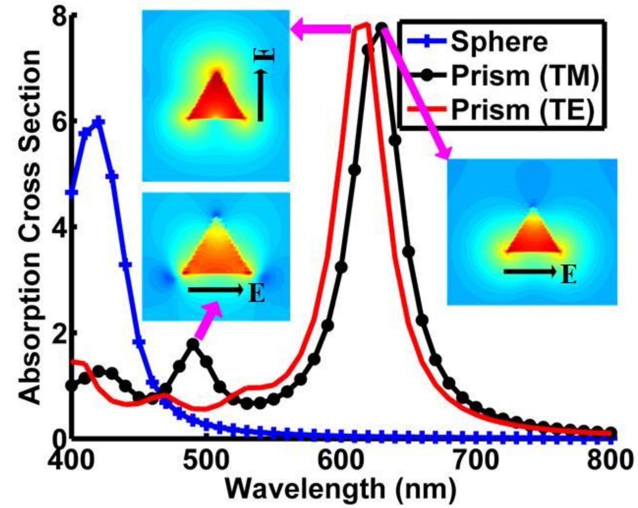
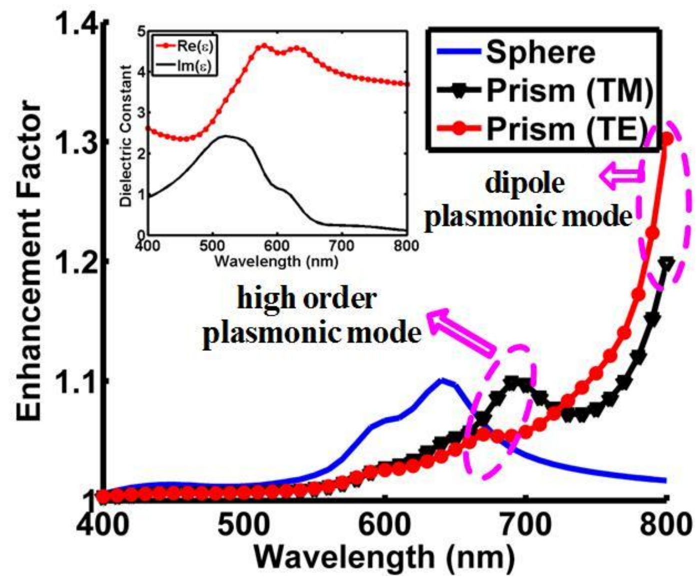
X.H. Li, W.C.H. Choy, H.F. Lu, W.E.I. Sha, and A.H.P Ho, Adv. Funct. Mater., 23(21), 2728–2735, 2013

Shape-Dependent Broadband Plasmonic Resonances

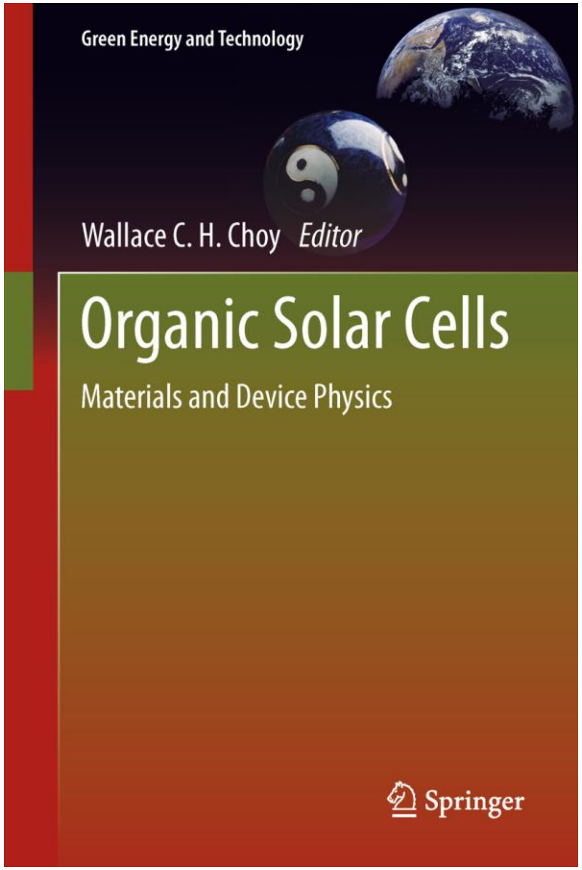


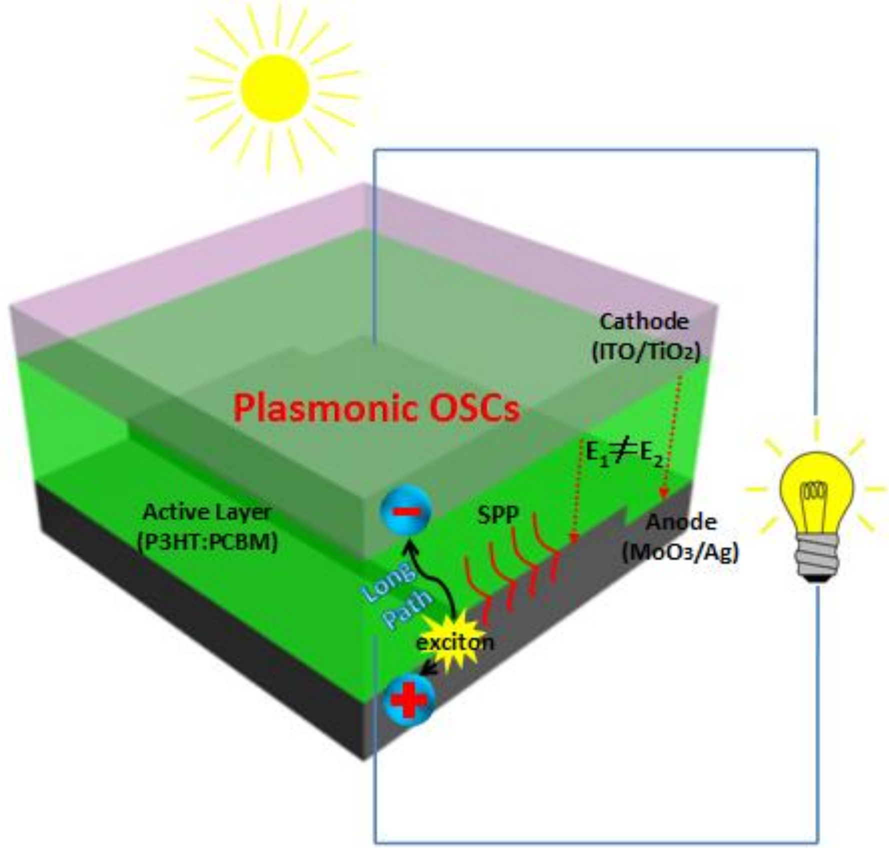
Ag spherical and triangular nanoparticles





Could electrical properties of OSCs be affected by introducing the metallic nanostructures?



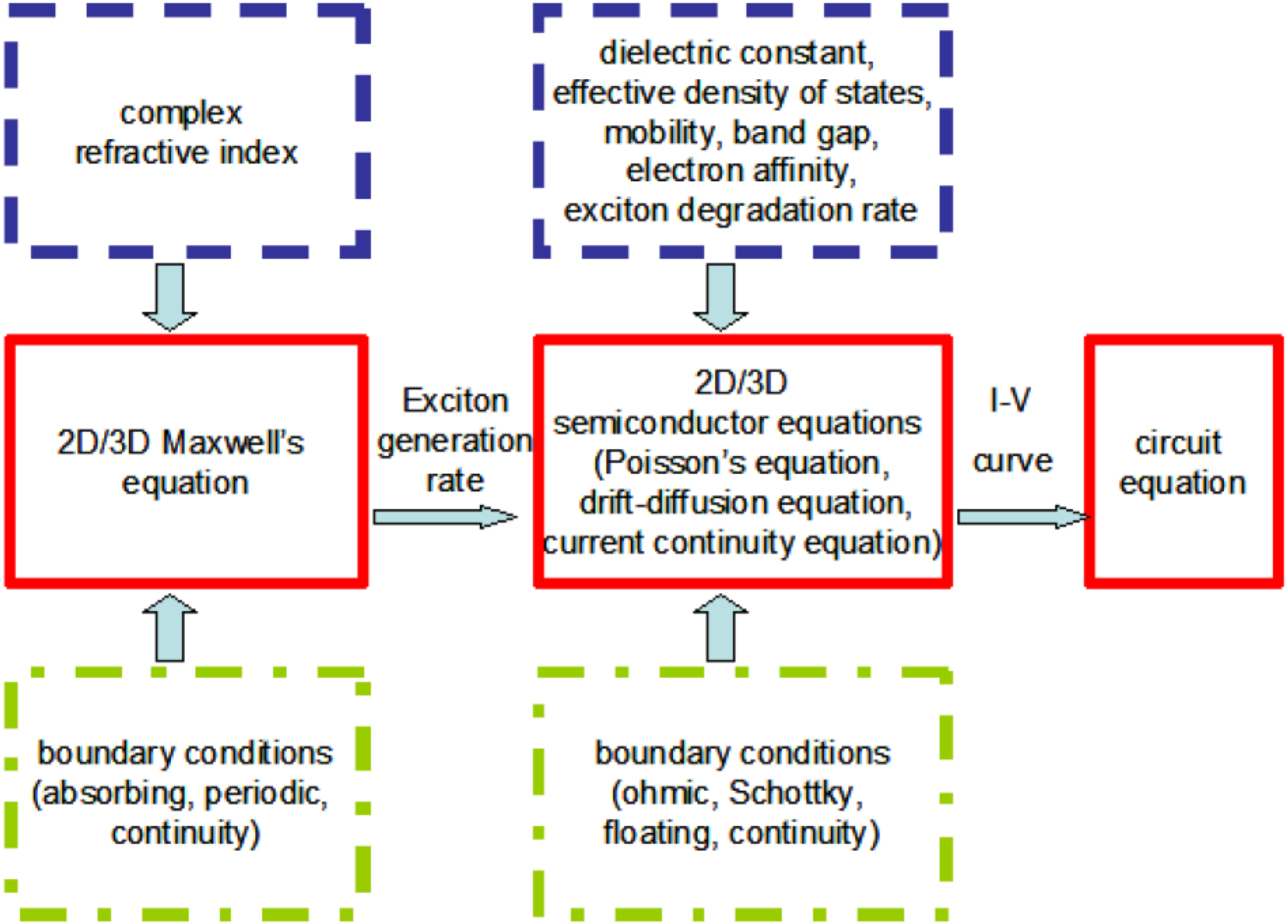


Wei E. I. Sha, Wallace C. H. Choy and Weng Cho Chew, "Theoretical Studies of Plasmonic Effects in Organic Solar Cells", Chapter 7, Organic Solar Cells: Materials and Device Physics, Pages 177-210, Wallace C.H. Choy (Ed.), ISBN 978-1-4471-4823-4, Springer, 2013.

Multiphysics Model (1)

Schematic diagram

W.E.I. Sha, W.C.H. Choy*, Y.M. Wu, and W.C. Chew, Opt. Express, 20(3), 2572-2580, 2012.



Multiphysics Model (2)

Governing equations

frequency dependent permittivity

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

Maxwell's equation

optical electric field

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

generation rate

Generation rate

electrostatic potential

electron density

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

bimolecular recombination rate

electrostatic dielectric constant

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

semiconductor equations

hole density *mobility* *Diffusion coefficients* *exciton dissociation probability*

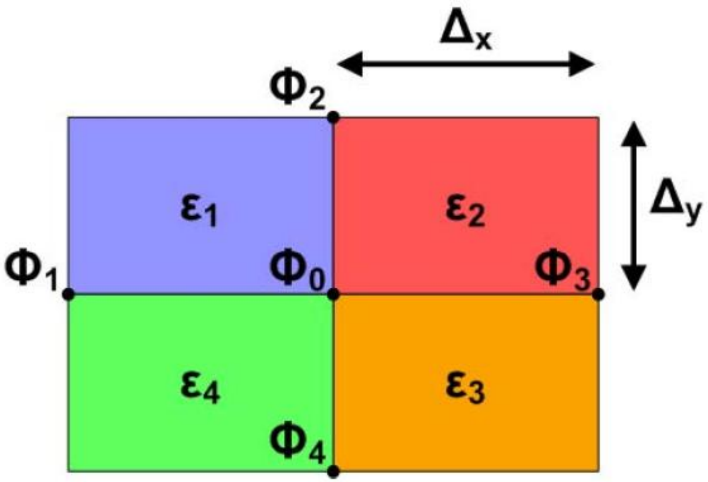
$$\frac{\partial p}{\partial t} = -\frac{1}{q} \nabla \cdot (-q\mu_p p \nabla \phi - qD_p \nabla p) + QG - (1-Q)R$$

Multiphysics Model (3)

Unified finite difference method

optical properties

spatial step depends on the dielectric wavelength and skin depth of surface plasmons



2D wave equations: TE & TM

$$2\left(\frac{1}{\Delta_x^2}+\frac{1}{\Delta_y^2}\right)\frac{\Phi_0}{\bar{\epsilon}}-k_0^2\Phi_0-\frac{\Phi_1+\Phi_3}{\bar{\epsilon}\Delta_x^2}-\frac{\Phi_2+\Phi_4}{\bar{\epsilon}\Delta_y^2}=0,\quad \Phi=E_z$$

$$2\left(\frac{1}{\Delta_x^2}+\frac{1}{\Delta_y^2}\right)\frac{\Phi_0}{\bar{\epsilon}}-k_0^2\Phi_0-\frac{\epsilon_1^{-1}+\epsilon_4^{-1}}{2\Delta_x^2}\Phi_1-\frac{\epsilon_2^{-1}+\epsilon_3^{-1}}{2\Delta_x^2}\Phi_3 -\frac{\epsilon_1^{-1}+\epsilon_2^{-1}}{2\Delta_y^2}\Phi_2-\frac{\epsilon_3^{-1}+\epsilon_4^{-1}}{2\Delta_y^2}\Phi_4=0,\quad \Phi=H_z$$

periodic boundary conditions
stretched-coordinate perfectly matched layer

$$\bar{\epsilon}=\begin{cases}\dfrac{\epsilon_1+\epsilon_2+\epsilon_3+\epsilon_4}{4}, & \Phi=E_z\\ 4(\epsilon_1^{-1}+\epsilon_2^{-1}+\epsilon_3^{-1}+\epsilon_4^{-1})^{-1}, & \Phi=H_z\end{cases}$$

Multiphysics Model (4)

electrical properties

spatial step depends on the Debye length

Poisson equation (Gummel's method)

$$\frac{1}{\Delta_x^2}\epsilon^d_{i+1/2,j}\phi^{t+1}_{i+1,j}+\frac{1}{\Delta_x^2}\epsilon^d_{i-1/2,j}\phi^{t+1}_{i-1,j}+\frac{1}{\Delta_y^2}\epsilon^d_{i,j+1/2}\phi^{t+1}_{i,j+1}+\frac{1}{\Delta_y^2}\epsilon^d_{i,j-1/2}\phi^{t+1}_{i,j-1}$$

$$-\left(\epsilon^d_{i+1/2,j}+\epsilon^d_{i-1/2,j}+\epsilon^d_{i,j+1/2}+\epsilon^d_{i,j-1/2}\right)\left(\frac{1}{2\Delta_x^2}+\frac{1}{2\Delta_y^2}\right)\phi^{t+1}_{i,j}-\frac{n^t_{i,j}+p^t_{i,j}}{U_t}\phi^{t+1}_{i,j}$$

$$=q(n^t_{i,j}-p^t_{i,j})-\frac{n^t_{i,j}+p^t_{i,j}}{U_t}\phi^t_{i,j}$$

scaling unit

cm	$\max\{\mathrm{DOS}\}^{1/3}$
s	10^{12}
V	1
C	$\frac{1}{1.602\times10^{-19}}$
K	$\frac{1}{300}$

drift-diffusion and continuity equations of electron (Scharfetter-Gummel scheme in spatial domain semi-implicit strategy in time domain)

$$\frac{n^{t+1}_{i,j}-n^t_{i,j}}{\Delta_t}=Q^t_{i,j}G_{i,j}-(1-Q^t_{i,j})R^t_{i,j}+\frac{D^n_{i+1/2,j}}{\Delta_x^2}B\left(\frac{\phi^{t+1}_{i+1,j}-\phi^{t+1}_{i,j}}{U_t}\right)n^{t+1}_{i+1,j}$$

$$+\frac{D^n_{i-1/2,j}}{\Delta_x^2}B\left(\frac{\phi^{t+1}_{i-1,j}-\phi^{t+1}_{i,j}}{U_t}\right)n^{t+1}_{i-1,j}+\frac{D^n_{i,j+1/2}}{\Delta_y^2}B\left(\frac{\phi^{t+1}_{i,j+1}-\phi^{t+1}_{i,j}}{U_t}\right)n^{t+1}_{i,j+1}$$

$$+\frac{D^n_{i,j-1/2}}{\Delta_y^2}B\left(\frac{\phi^{t+1}_{i,j-1}-\phi^{t+1}_{i,j}}{U_t}\right)n^{t+1}_{i,j-1}-\left[\frac{D^n_{i+1/2,j}}{\Delta_x^2}B\left(\frac{\phi^{t+1}_{i,j}-\phi^{t+1}_{i+1,j}}{U_t}\right)\right.$$

$$+\frac{D^n_{i-1/2,j}}{\Delta_x^2}B\left(\frac{\phi^{t+1}_{i,j}-\phi^{t+1}_{i-1,j}}{U_t}\right)+\frac{D^n_{i,j+1/2}}{\Delta_y^2}B\left(\frac{\phi^{t+1}_{i,j}-\phi^{t+1}_{i,j+1}}{U_t}\right)$$

$$\left.+\frac{D^n_{i,j-1/2}}{\Delta_y^2}B\left(\frac{\phi^{t+1}_{i,j}-\phi^{t+1}_{i,j-1}}{U_t}\right)\right]n^{t+1}_{i,j}$$

Dirichlet and Neumann boundary conditions

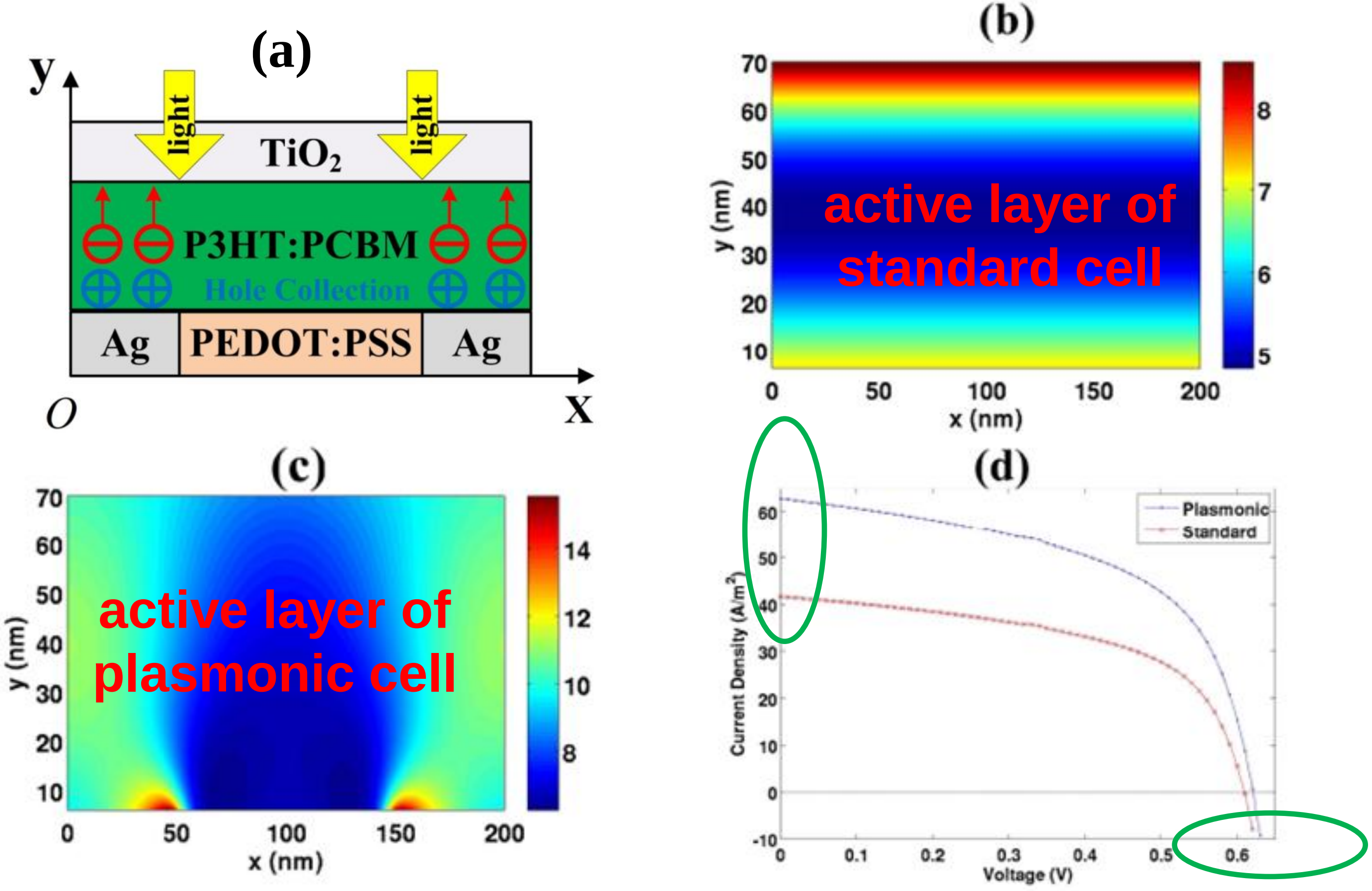
time step for stable algorithm

$$\Delta_t<\min\left(\frac{C\varepsilon}{\mu_n\cdot n+\mu_p\cdot p}\right)$$

Multiphysics Model (5)

Beyond optical absorption enhancement: facilitating hole collection!

schematic pattern of nanostrip plasmonic cell



Model settings

active layer thickness
70 nm
periodicity
200 nm
PEDOT:PSS width
100 nm
anode
ohmic
cathode barrier height
0.2 eV
hole mobility
*0.1*electron mobility*
effective band gap
1.1 eV

Multiphysics Model (6)

Characteristic parameters

Plasmonic	J_{sc} (A/m^2) ↑	V_{oc} (V)	MP (W)	FF	PCE (%) ↑
	62.84	0.62	21.47	0.55	2.15
Standard	J_{sc} (A/m^2)	V_{oc} (V)	MP (W)	FF	PCE (%)
	41.67	0.61	14.03	0.55	1.40

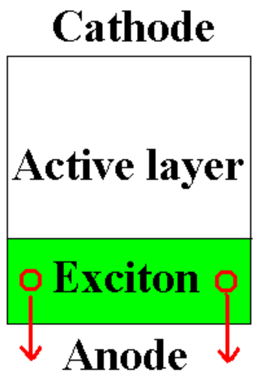
Plasmonic	V (V)	J (A/m^2)	⟨Diss⟩ (%)	⟨Rec loss⟩ (%)
SC	0	62.84	66.96	2.62
MP	0.48	44.73	58.97	14.55 ↓
OC	0.62	0	55.47	80.88
Standard	**V (V)**	**J (A/m^2)**	**⟨Diss⟩ (%)**	**⟨Rec loss⟩ (%)**
SC	0	41.67	66.96	3.18
MP	0.47	30.42	59.19	14.93
OC	0.61	0	55.75	81.91

- **reduce recombination loss**
- **increase short-circuit current**
- **improve open-circuit voltage**
- **boost power conversion efficiency**

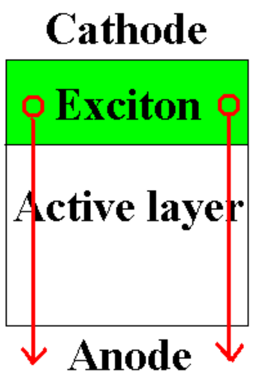
Multiphysics Model (7)

Dummy case for further illustrating physics (hole transport and collection)

$$G_{grating} = \begin{cases} G_c, & d_3 \le y \le d_3 + L_g \\ 0, & \text{else} \end{cases}$$

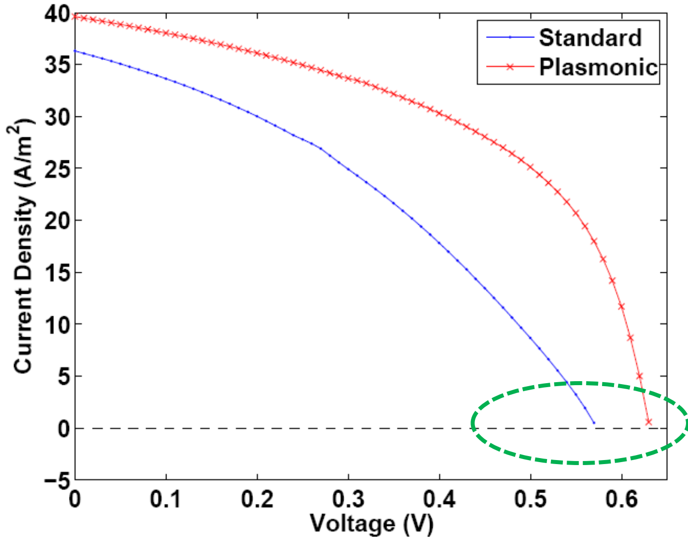


$$G_{planar} = \begin{cases} G_c, & d_3 + d_2 - L_g \le y \le d_3 + d_2 \\ 0, & \text{else} \end{cases}$$



hole mobility is set to be two order of magnitude lower than electron mobility

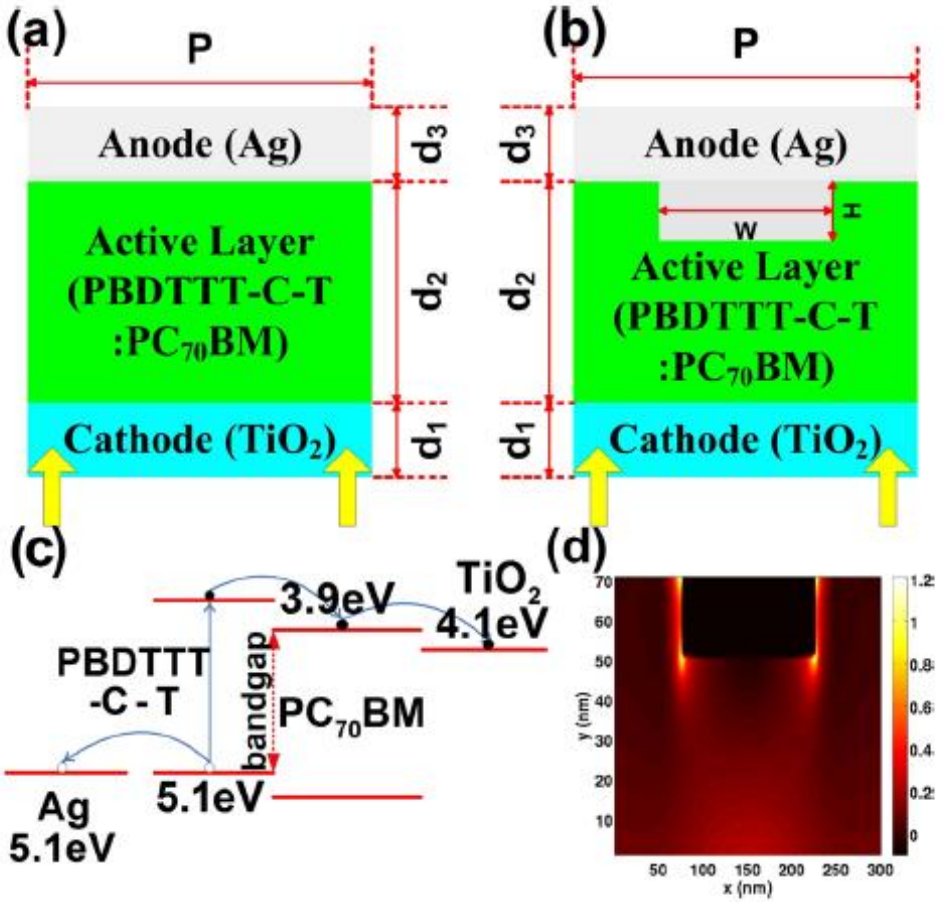
J-V curve



inhomogeneous exciton generation significantly affects fill factor and open-circuit voltage

Multiphysics Model (8)

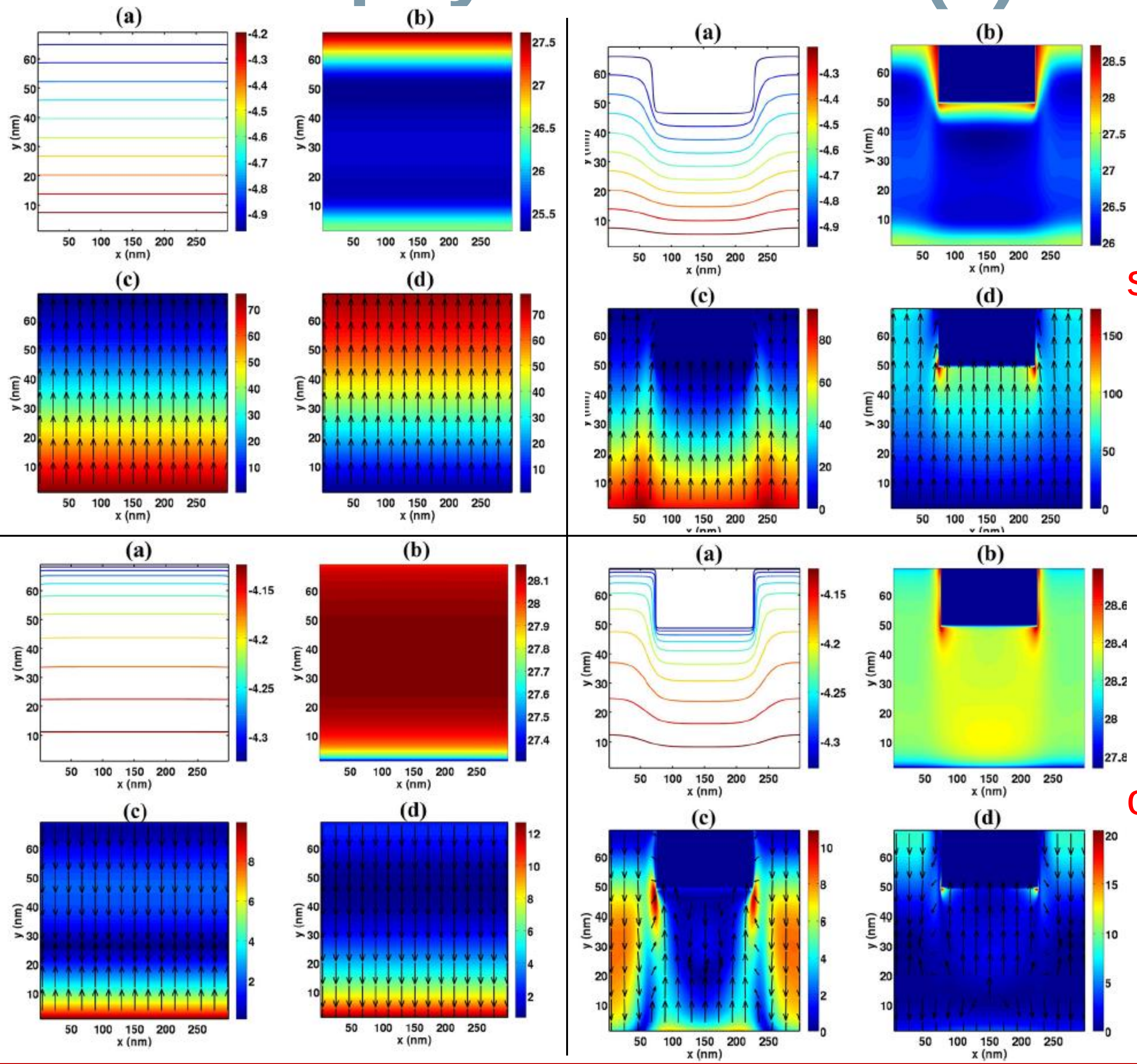
The nanograting structure v.s. flat standard structure



Simulation parameters

E_g	$1.2\ eV$
μ_n	$7.4 \times 10^{-7}\ m^2/(V \cdot S)$
μ_p	$7.4 \times 10^{-8}\ m^2/(V \cdot S)$
N_c	$2.5 \times 10^{19}\ cm^{-3}$
N_v	$2.5 \times 10^{19}\ cm^{-3}$
ϵ^d	$3.4\epsilon_0\ F/m$
a	$1.12\ nm$
k_r	$3 \times 10^5\ s^{-1}$
ψ_b^n	$0.2\ eV$
ψ_b^p	$0\ eV$

Multiphysics Model (9)

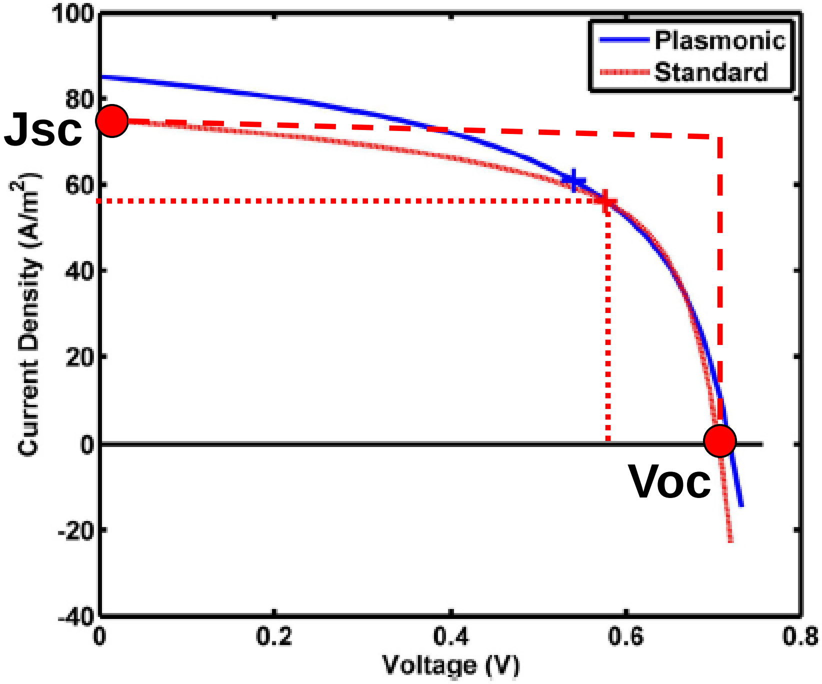


short-circuit

open-circuit

(a) equipotential lines; (b) recombination rate; (c,d) electron and hole current densities.

Multiphysics Model (10)



$$FF = \frac{P_{MAX}}{P_T} = \frac{I_{MP} \cdot V_{MP}}{I_{SC} \cdot V_{OC}}$$

The grating anode induces nonuniform optical absorption and inhomogeneous internal E-field distribution. Thus uneven photocarrier generation and transport are formed in the plasmonic OSC leading to the dropped FF.

TABLE II. The characteristic parameters of the standard and plasmonic OSCs involving short-circuit J_{sc}, open-circuit voltage V_{oc}, MP, FF, and PCE.

	J_{sc} (A/m^2)	V_{oc} (V)	MP (W)	FF (%)	PCE (%)
Standard	75.18	0.706	32.34	60.91	3.23
Plasmonic	85.12	0.719	32.91	53.77	3.29

	SC (Diss)	SC (Rec)	MP (Diss)	MP (Rec)	OC (Diss)	OC (Rec)
Standard (%)	69.83	0.88	62.34	9.19	59.69	82.56
Plasmonic (%)	70.52	2.5	63.38	16.63	59.63	92.75

recombination and exciton dissociation

W.E.I. Sha, W.C.H. Choy*, and W.C. Chew,
Appl. Phys. Lett., 101, 223302, 2012.

Conclusion

- ✓ Environmentally friendly organic solar cell (OSC), which has a bright outlook to meet the urgent demand in clean energy, draws much attention in recent years due to their merits of large-area production, low-cost processing and mechanical flexibility. Proposing and optimizing new device architectures plays a key role in designing high-performance OSCs.

- ✓ A multiphysics study carries out on plasmonic OSCs by solving Maxwell's equations and semiconductor (Poisson, drift-diffusion, and continuity) equations simultaneously with a unified finite-difference framework.

- ✓ Nonuniform distributions of optical near-fields induced by plasmonic nanostructures will significantly affect the carrier transport in OSCs. Besides their optical effects, the electrical effects induced by plasmonic resonances will open up a new way to design emerging plasmonic organic photovoltaics.

Acknowledgement

Thanks for your attention!