Addressing the fundamental drawbacks of organic photovoltaics

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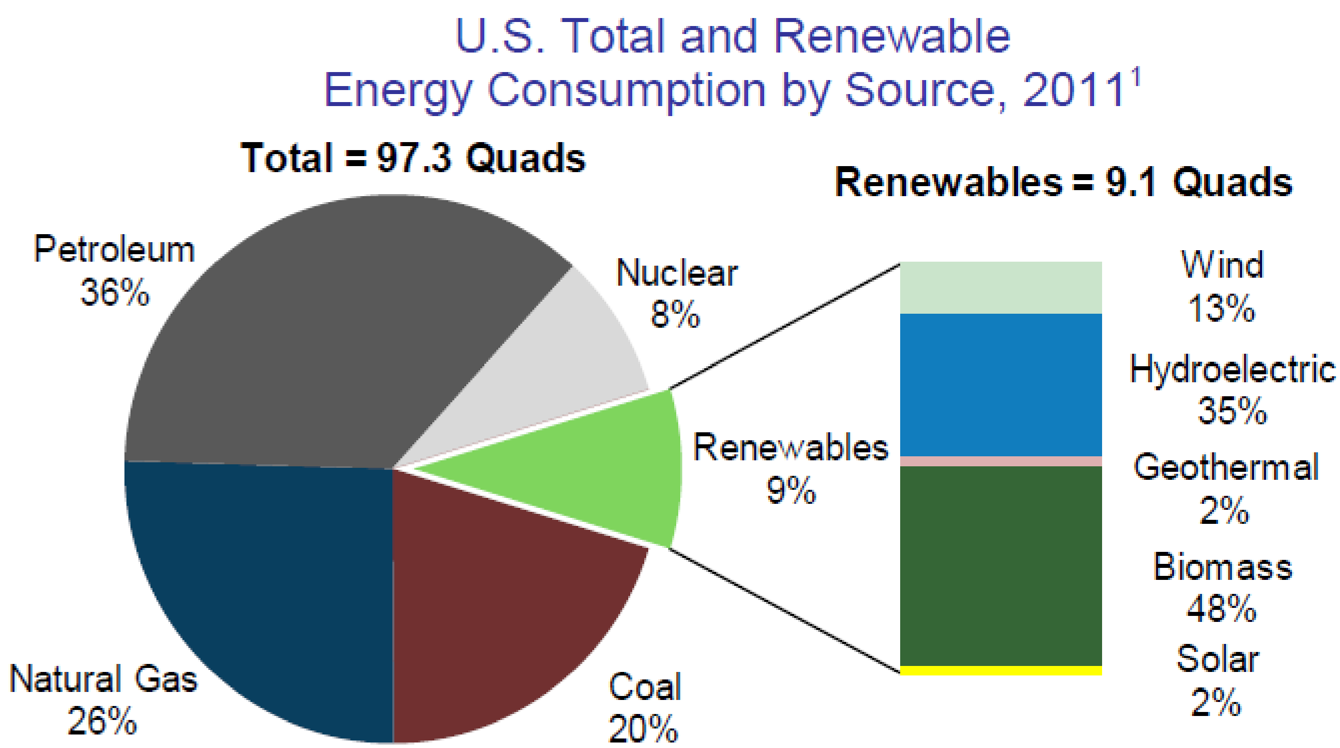
Solar Energy In Development

- Renewable
- Potential for High coverage
- Low emission



[1] US DOE Energy Information Administration (2012), *Annual Energy Review 2011*
U. Mich., *Center for Sustainable Systems.* 2012. "U.S. Renewable Energy Factsheet". Pub No. CSS03-12

Organic Photovoltaics (OPVs)

Solar power offers unique advantages

- no mech. parts
- flexible & customizable

- *relatively expensive*
- *storage*

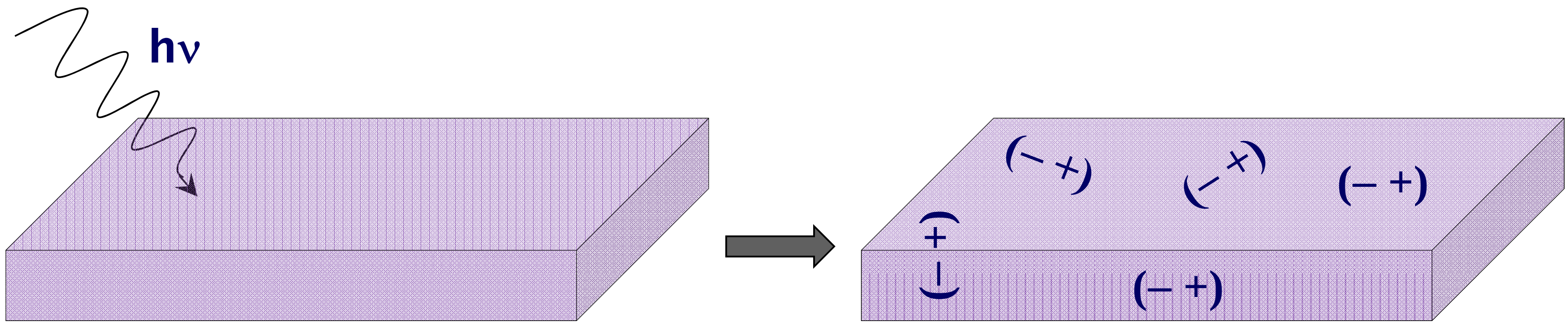
IIIa generation - Si & Ge cells are efficient but expensive

OPVs are of IIIb type: low to moderate efficiency

- processed at lower T
- versatile manufacturing
- distinctive mechanical & optical properties
- tunability
- **cheap**

- *low efficiency*
- *inadequate spectral coverage*
- *poor mobility of charges*

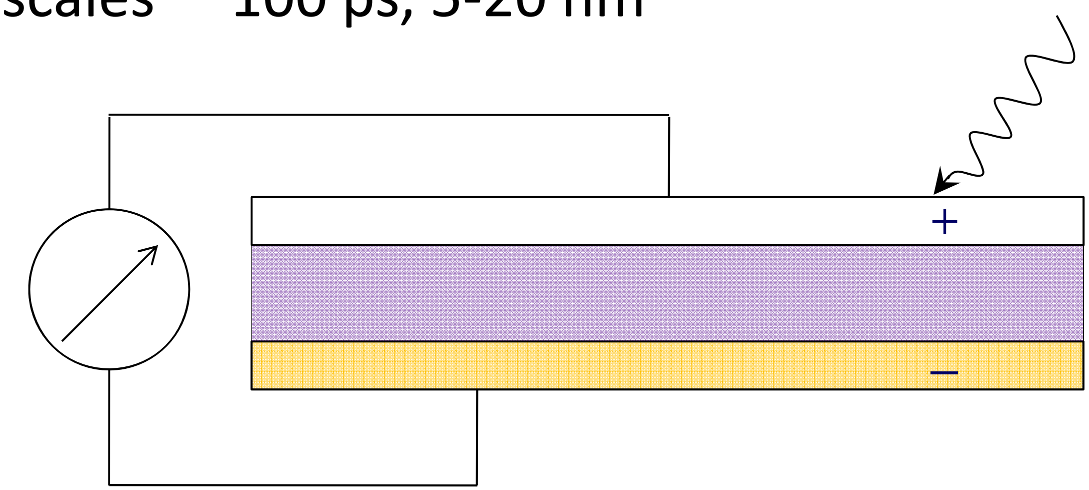
Functioning of OPVs



Incident radiation produces e-h pairs (excitons)

Exciton motion length & time scales ~ 100 ps, 5-20 nm

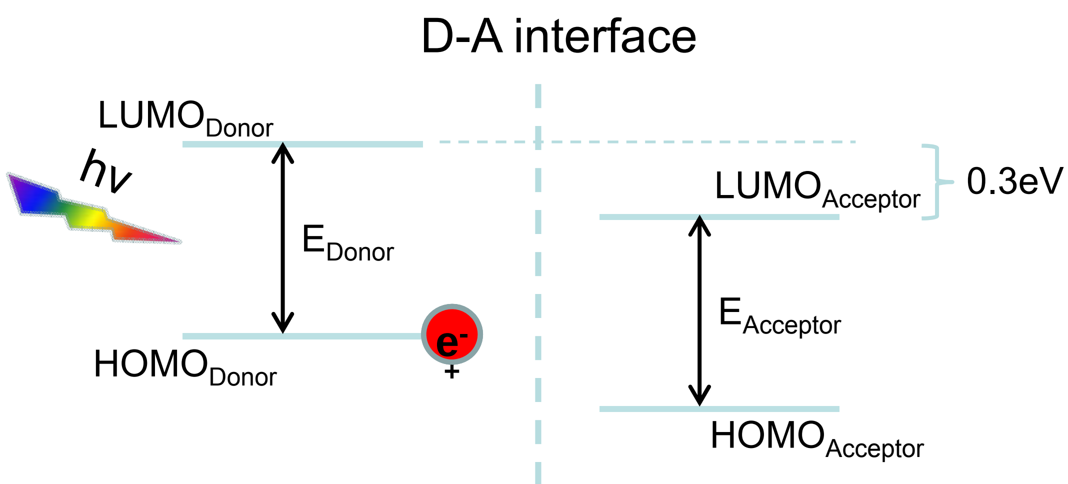
<u>Morphology of active material is KEY</u>



OPV Materials

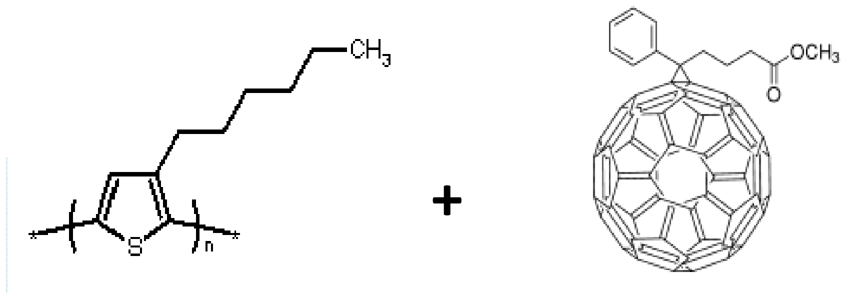
- Blend of polymer(s) and/or additive – bulk heterojunction (BHJ)
- Traditional BHJs have about 50% of polymer, and 50% PCBM (fullerene derivative)
- PCBM only for charge conduction and exciton dissociation
- **Critical Issues**
  - Increase fraction of conjugated polymer
    - Helps capture more sunlight
    - Improves efficiency
  - Improve charge transport

Importance of interfaces in OPV devices

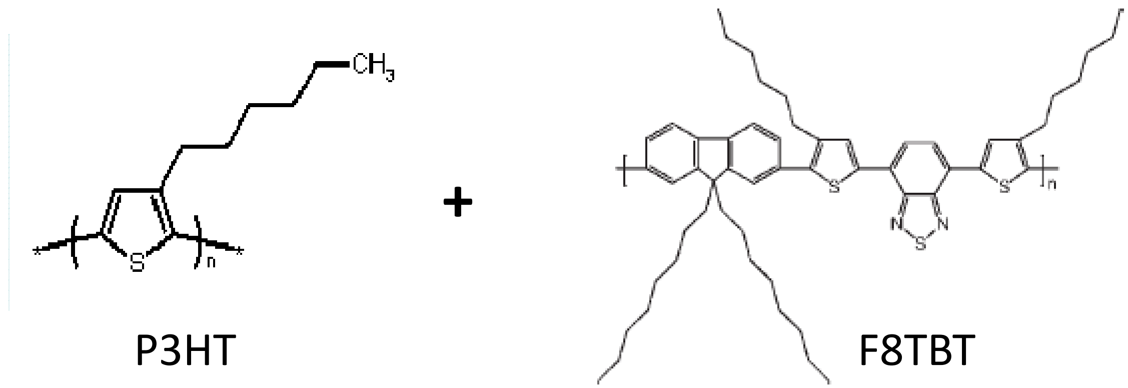


- D-A interface facilitates exciton dissociation
- Electron transfer from donor(semiconducting polymer) to acceptor
- Exciton dissociation is energetically favorable
- Exciton diffusion length(~10 nm)
- D-A interfacial area is determined by morphology

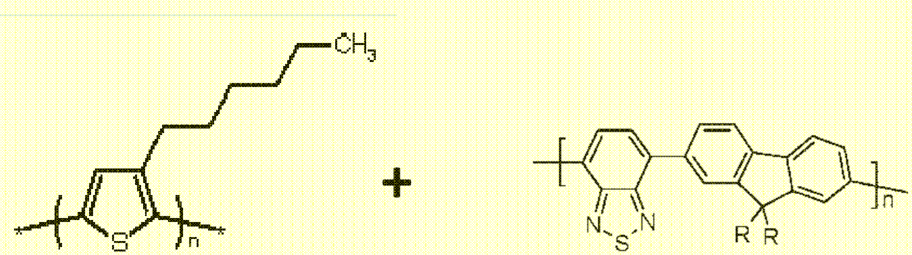
Typical OPVs



P3HT PCBM



P3HT



R=C_8H_{17}

P3HT F8BT

McNeill & Greenham, Adv. Mater. 2009 **21**, 3840
Kim *et al.,* Chem. Mater 2004 **16**(23), 4813

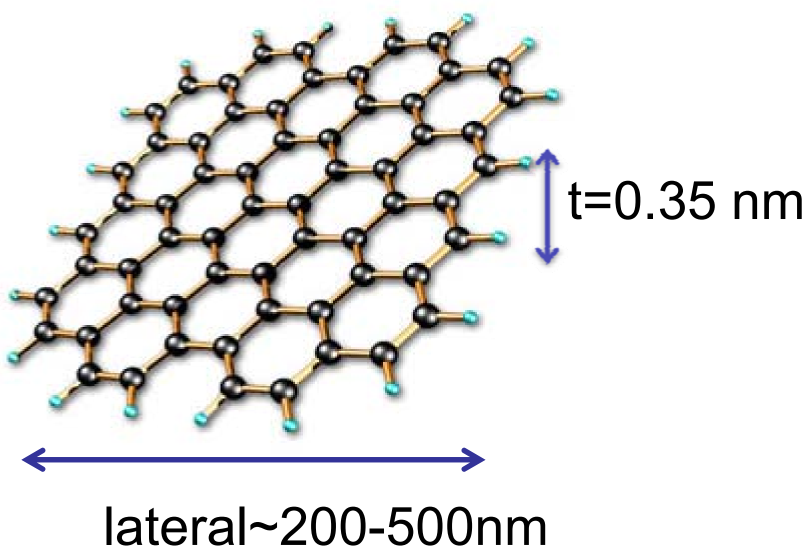
Polymer Blend OPVs

- Mix of semiconducting polymers
- Both components active & capture sunlight
- Morphology control is again key
- Critical Issues
    - Poor charge mobilities persist
        - Greater recombination losses
    - Crystallization of polymers and blend miscibility ?
        - Free charge formation and transport
        - Voltage

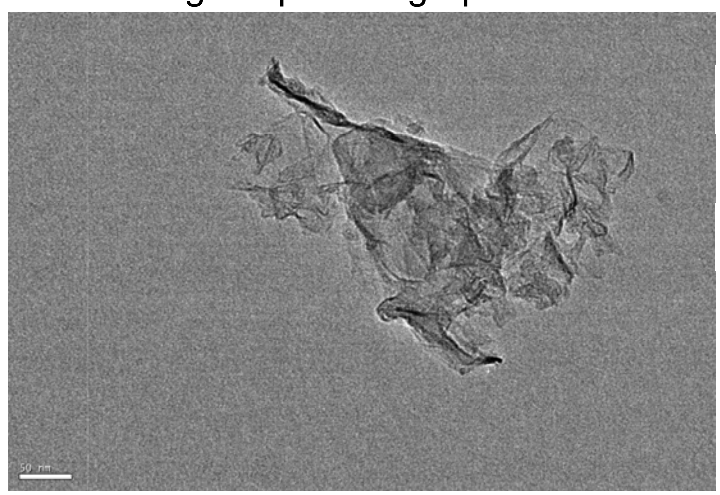
Solution ?

Pristine graphene

- Excellent conductivity and high aspect ratio
- Percolation paths at very low concentration
- OPVs with chemically modified graphenes were reported*
- Functionalized sheets show poor electronic behavior



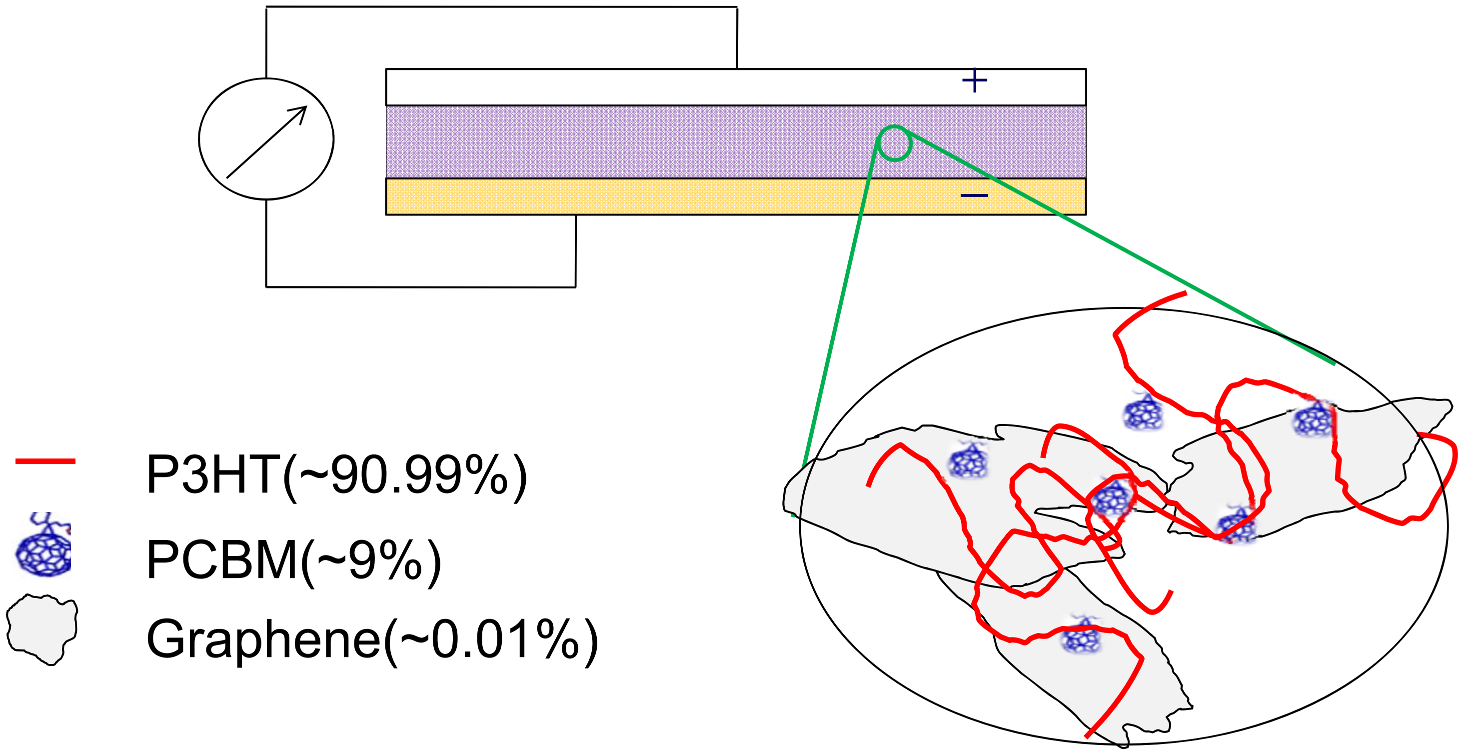
TEM image of pristine graphene flake



Scale bar=50nm

*Liu, Z. *et al.*, Adv. Mater., 2008 **20**(20), 3924
Yu, D. *et al.*, ACS Nano, 2010 **4**(10), 5633; Yu, D. *et al.*, J. Phys. Chem. Lett., 2011 **2**(10), 1113

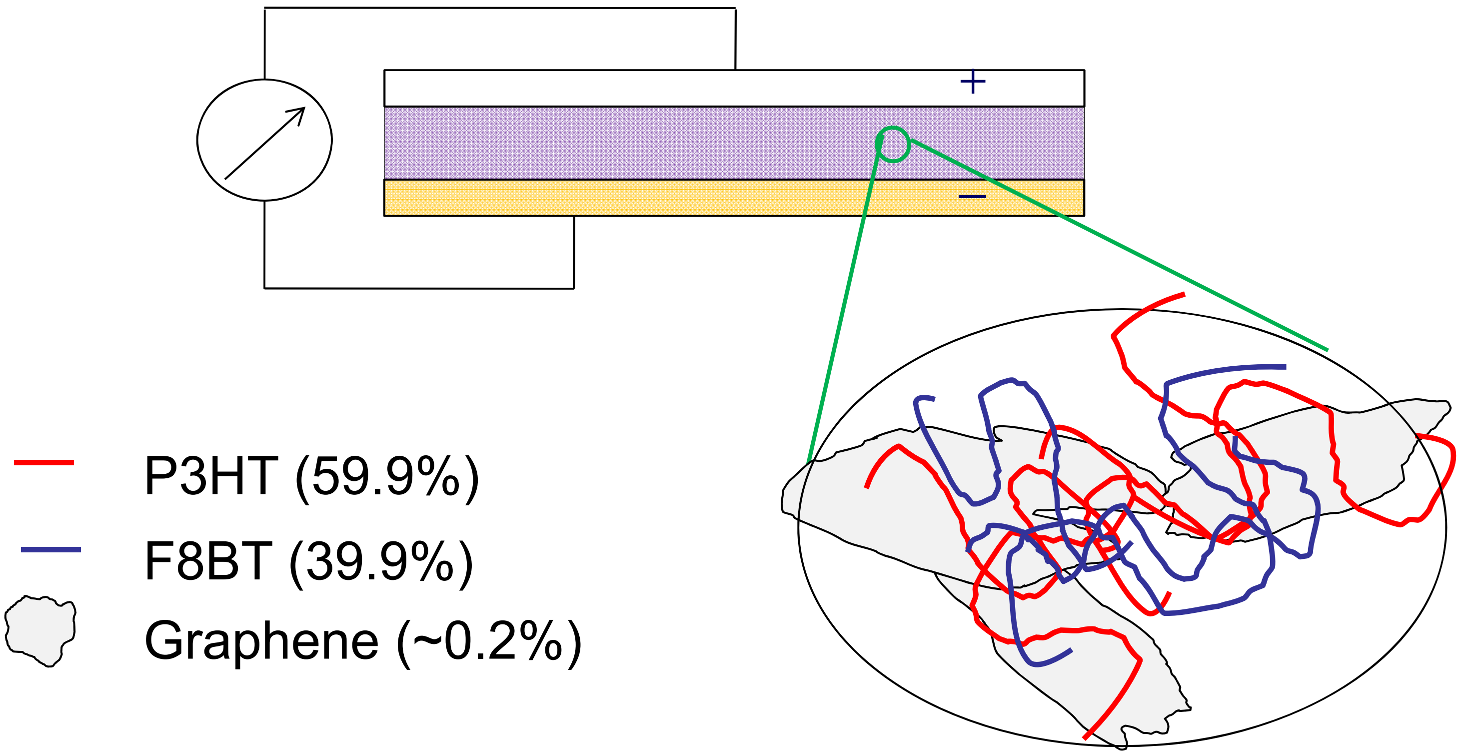
Graphene-based OPVs



— Three-fold enhancement in efficiency
— Increase in current – better mobility
— Novel device physics

Yu, Bahner & Kuppa, Key Engr. Mater. 2012 **21**, 3840
Yu & Kuppa, Mater. Lett. 2013 **99**, 72

Current focus - ternary blends



Device Fabrication

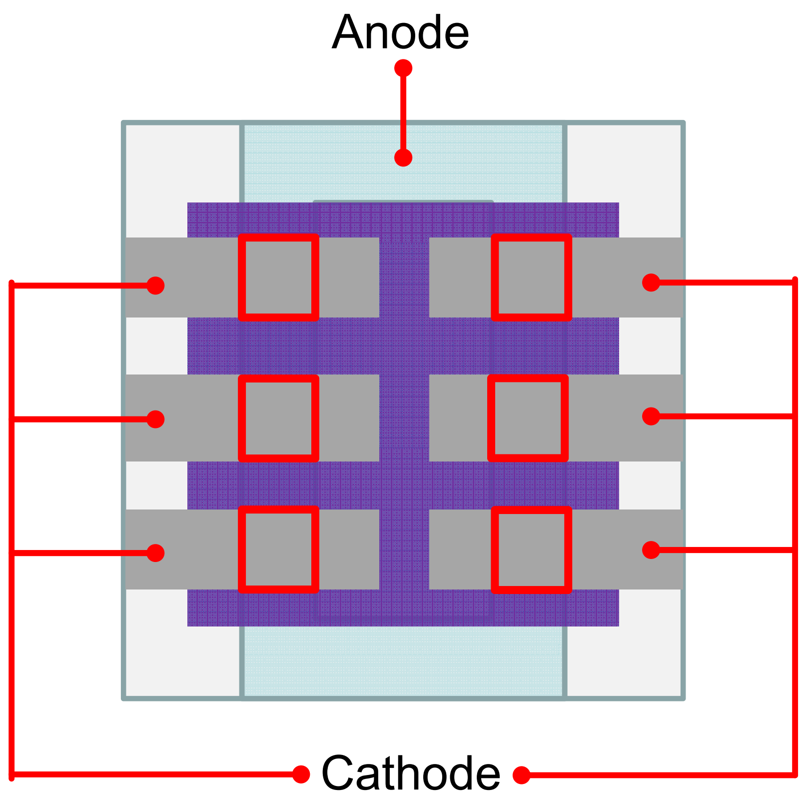
— Patterned ITO as bottom electrode

— PEDOT:PSS by spin coating

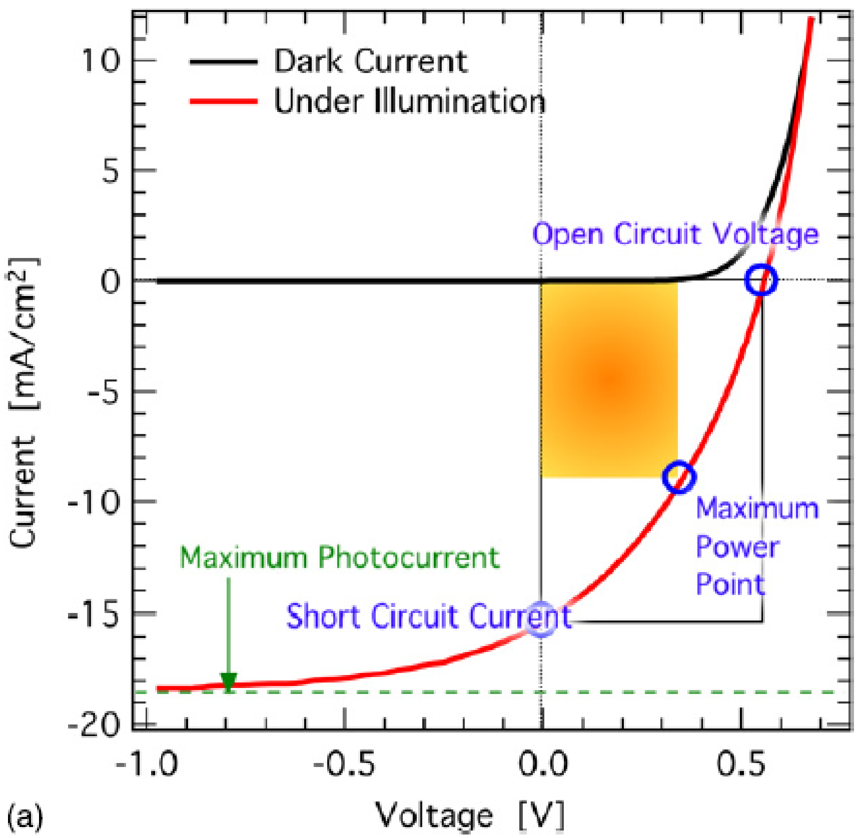
— Active layer with graphene by spin coating

— LiF and Aluminum

— Fabricated and annealed in N_2



Solar Cell Parameters



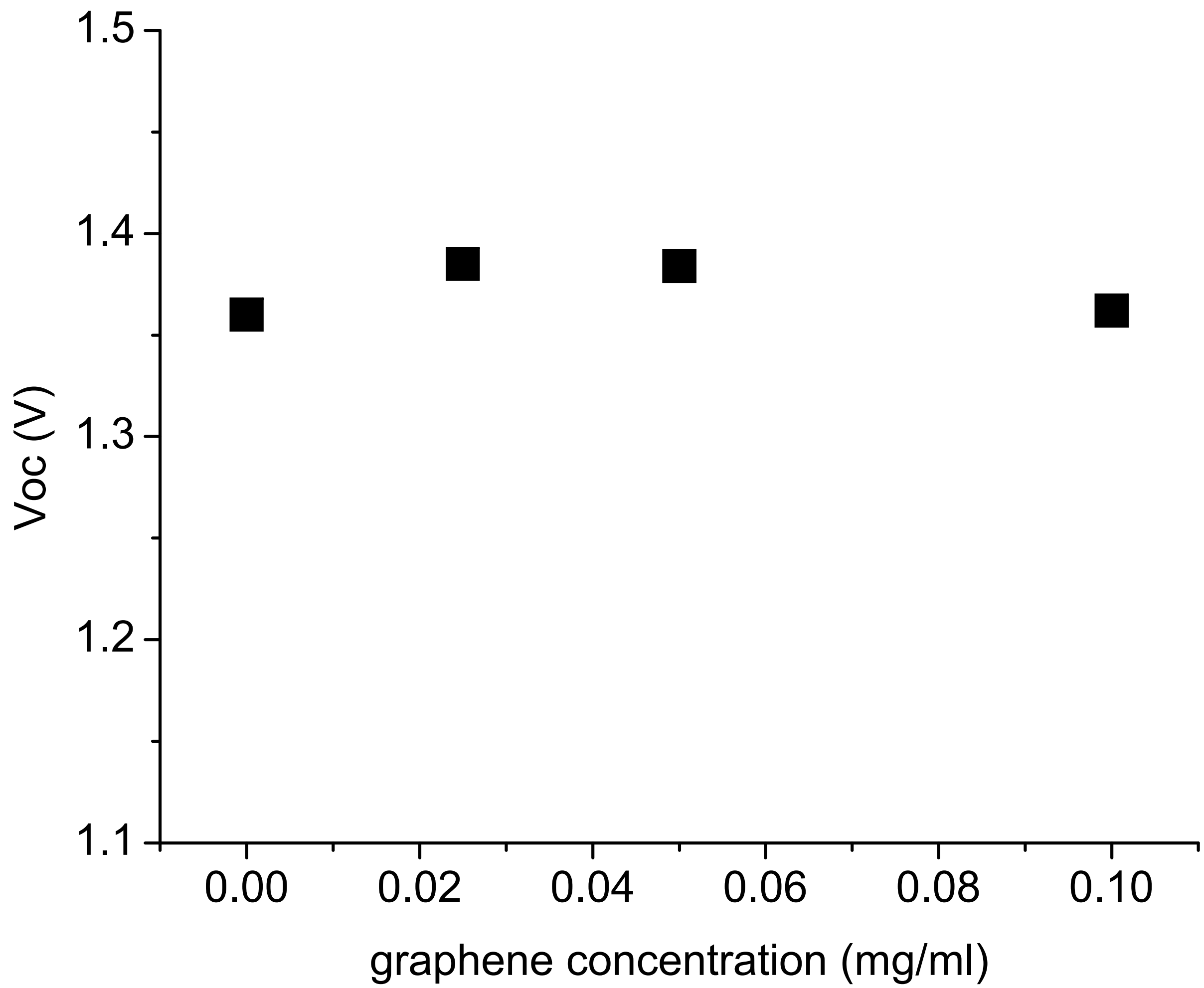
- J_{SC}: Short-circuit current density
- V_{OC}: Open-circuit voltage
- P_{max}: Maximum output power
- FF: Fill factor
- **Power conversion efficiency (η)**

$$\eta = \frac{P_{max}}{P_{in}}$$

Deibel and Dyakonov, Rep. Prog. Phys., 2010 **73**(9), 096401

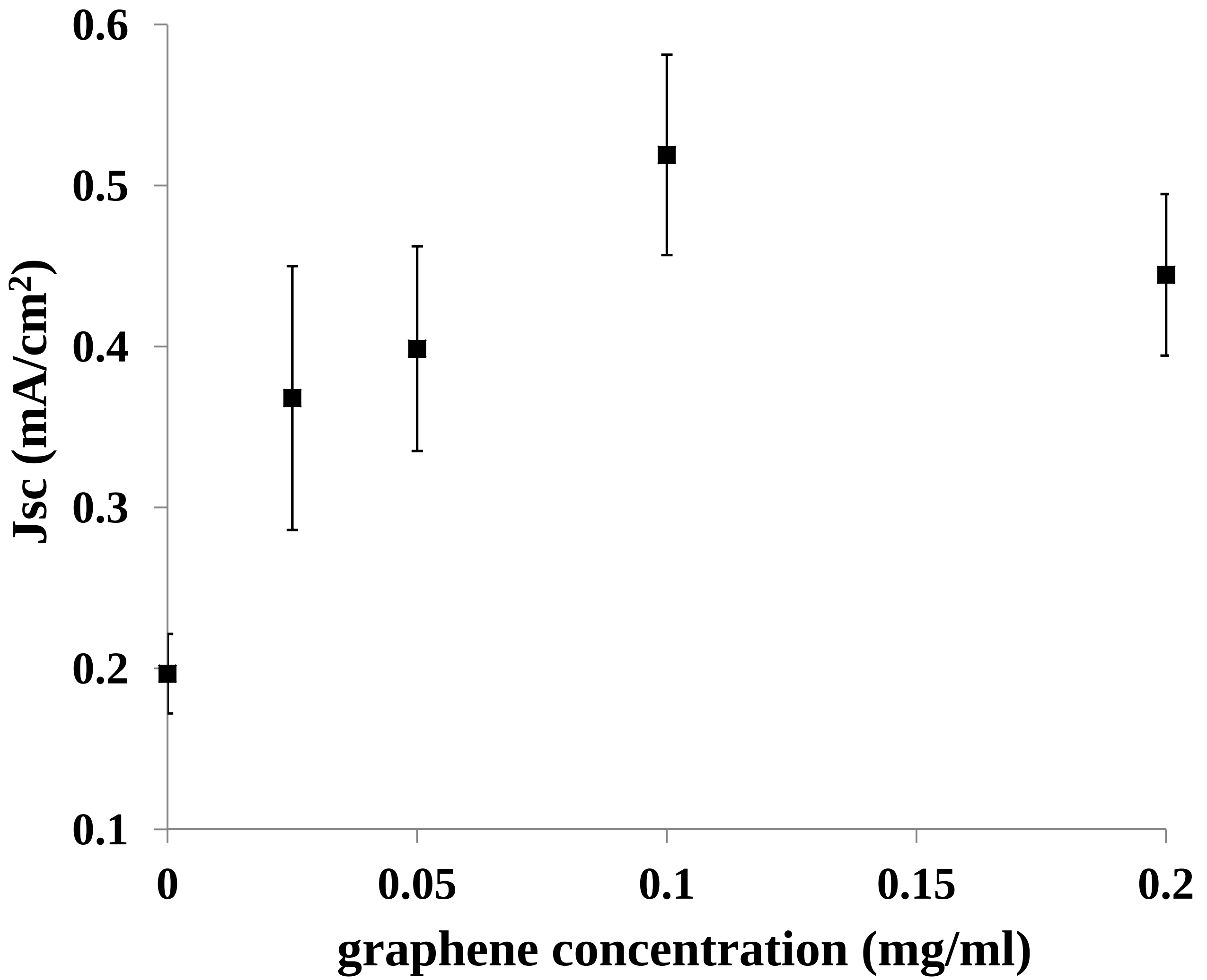
Cell Performance

Open circuit voltage - V_{oc}



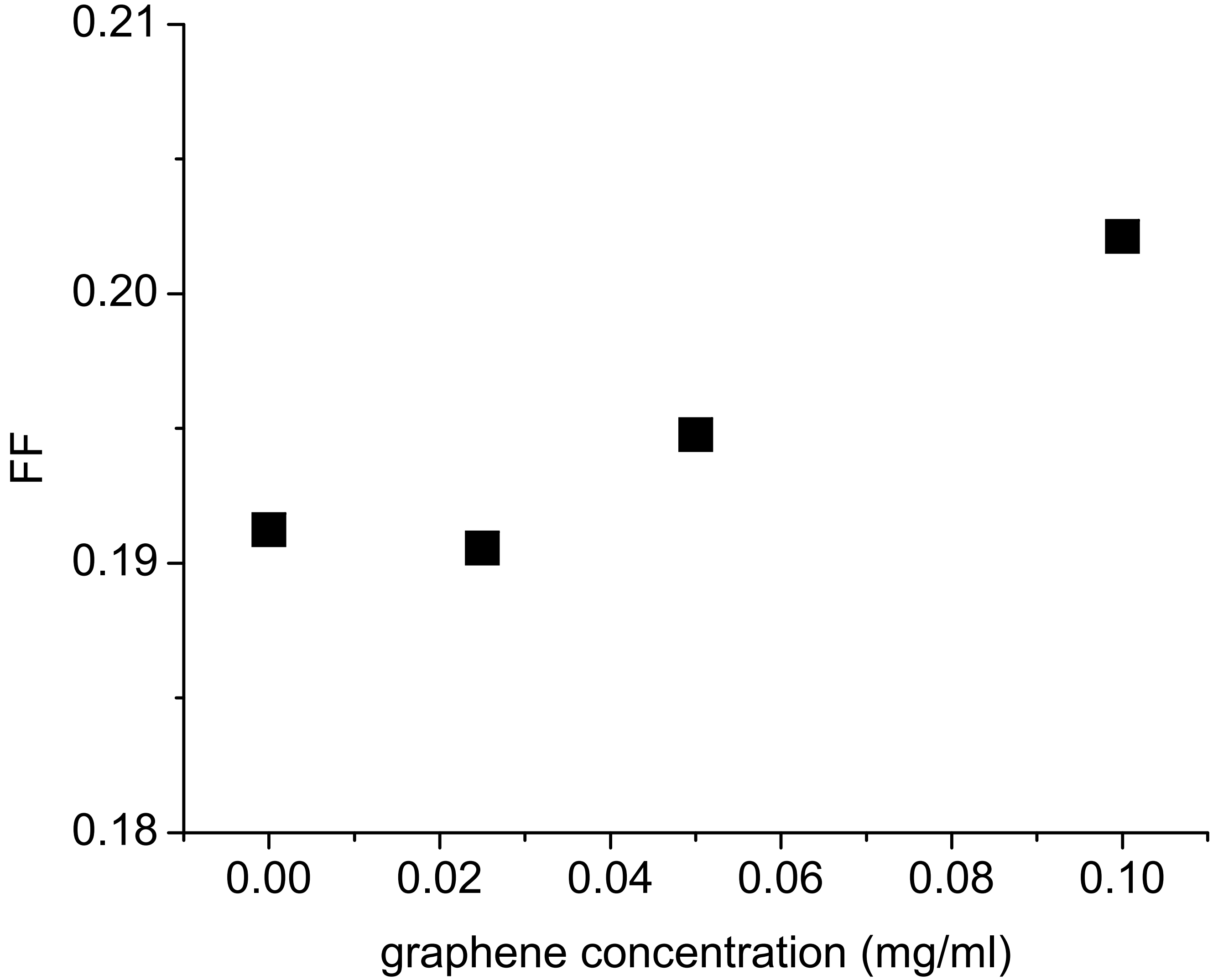
Cell Performance

Short circuit current - J_{sc}

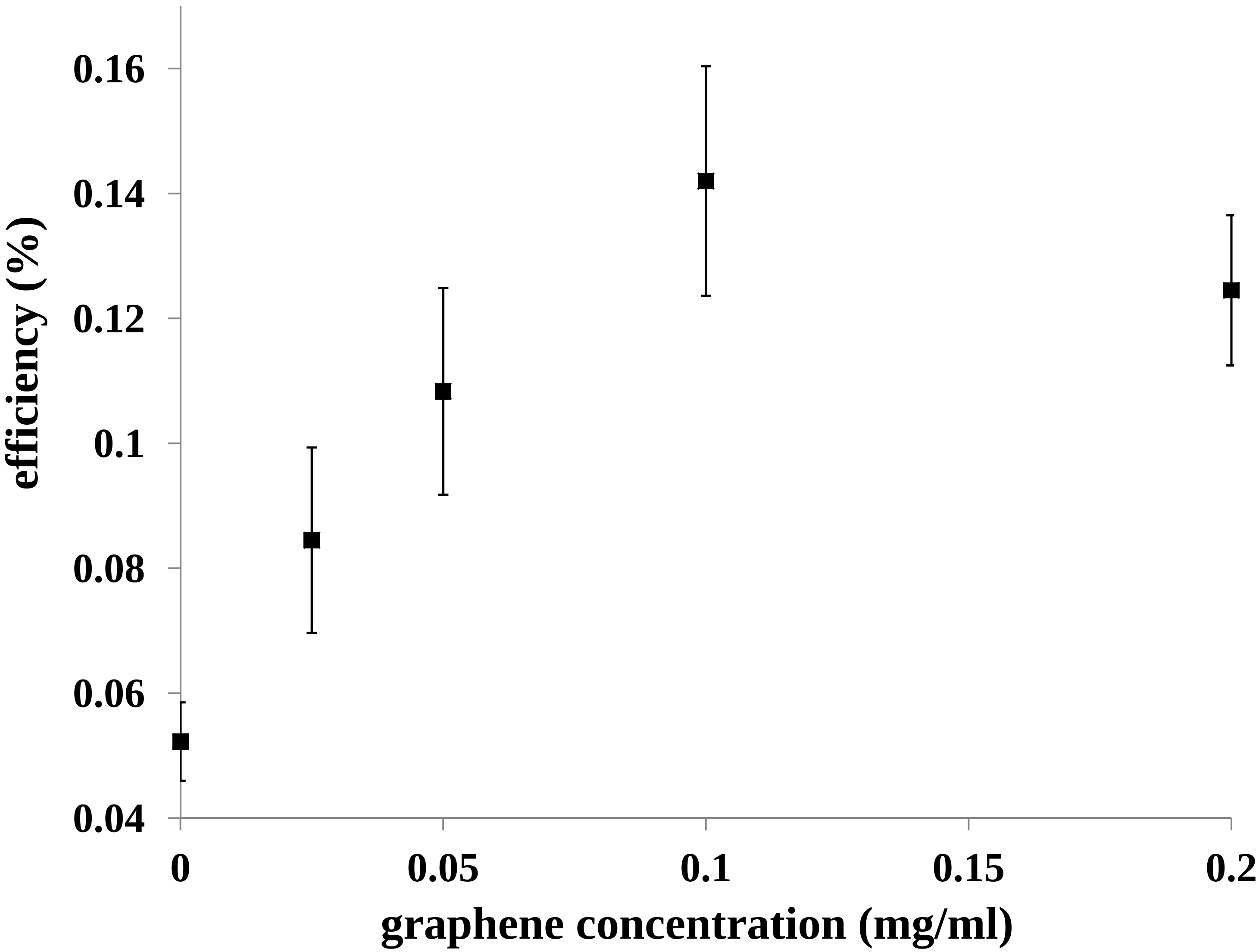


Cell Performance

Fill factor - FF

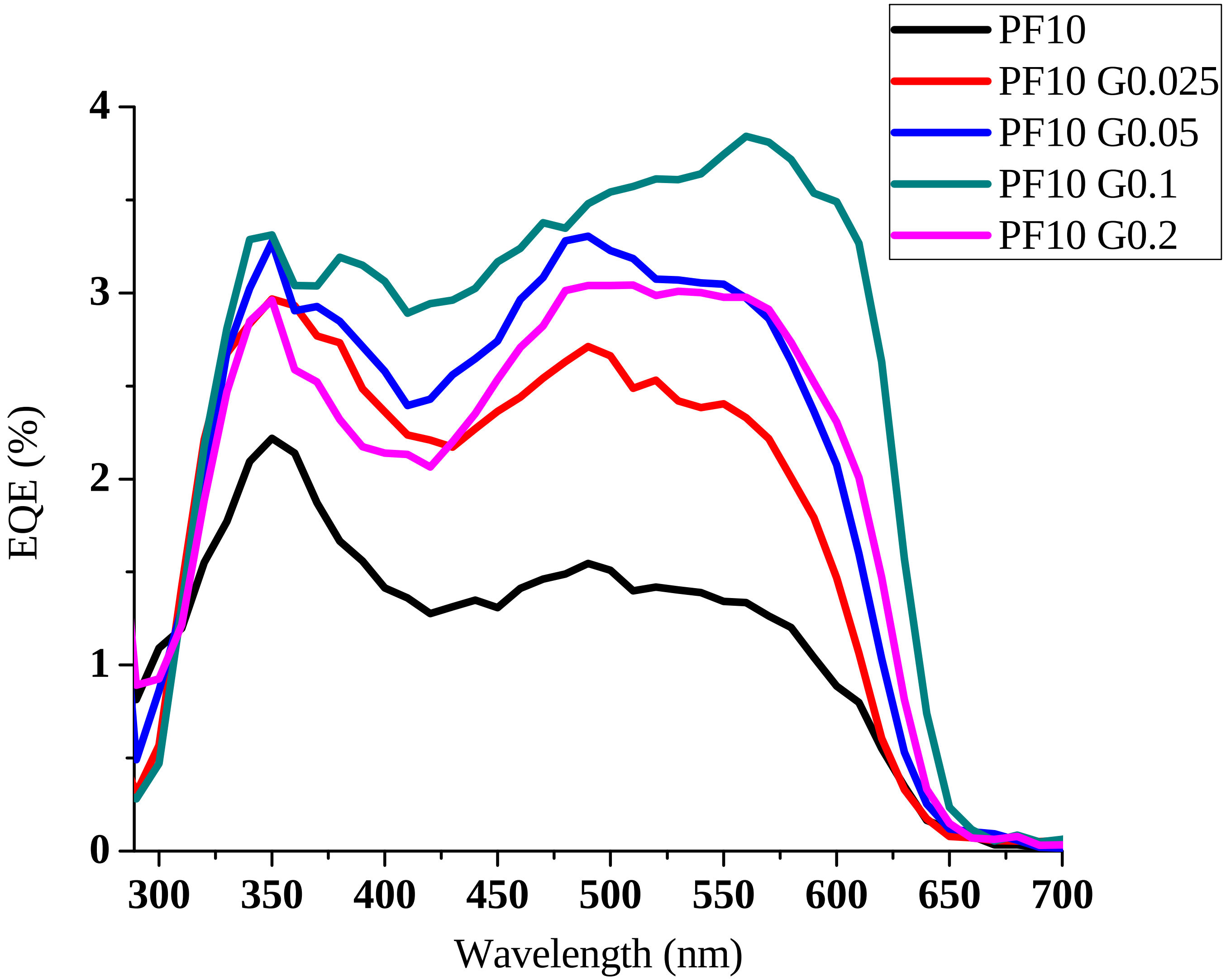


Cell Performance

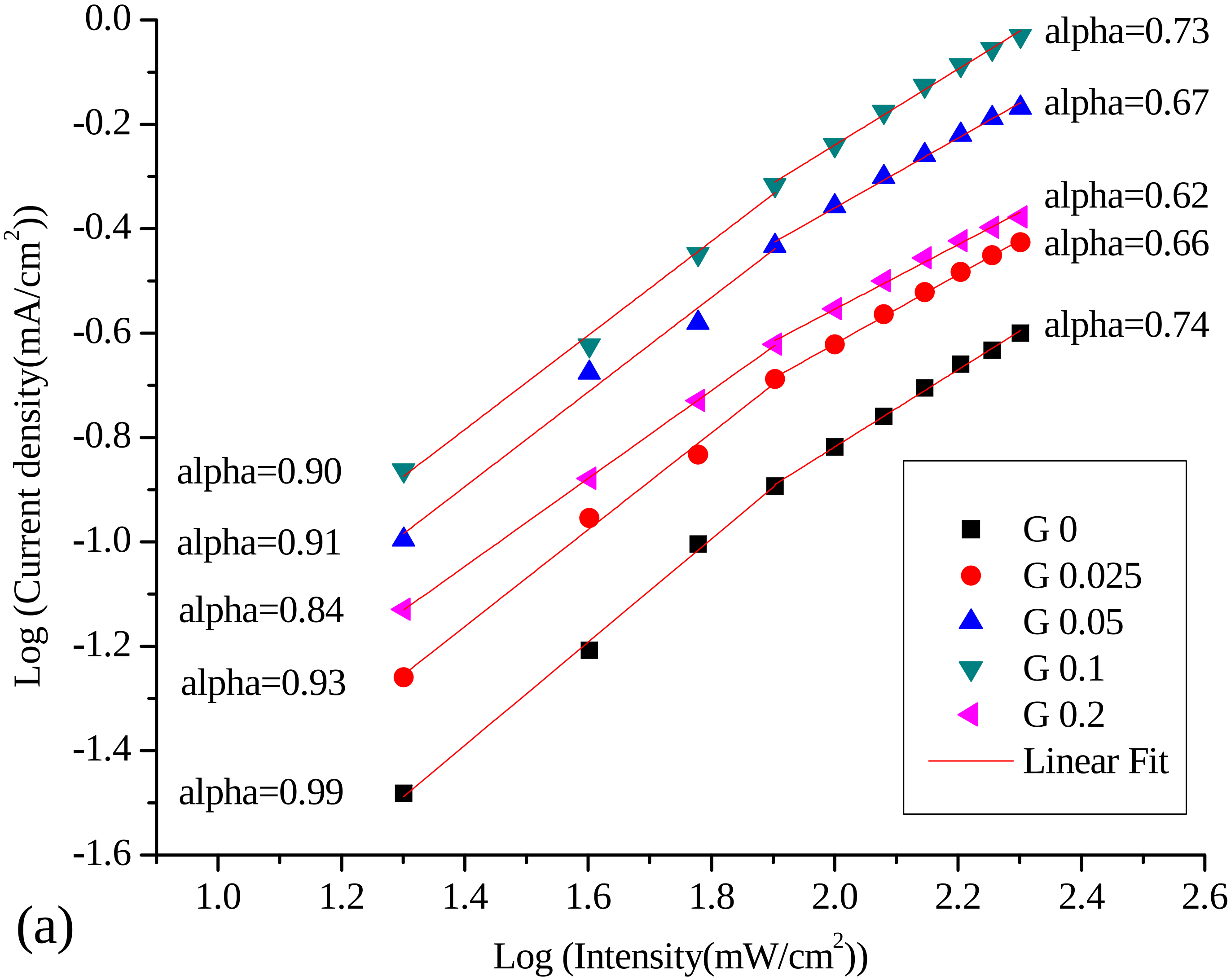


Cell Performance

External quantum efficiency - EQE



Device physics - recombination

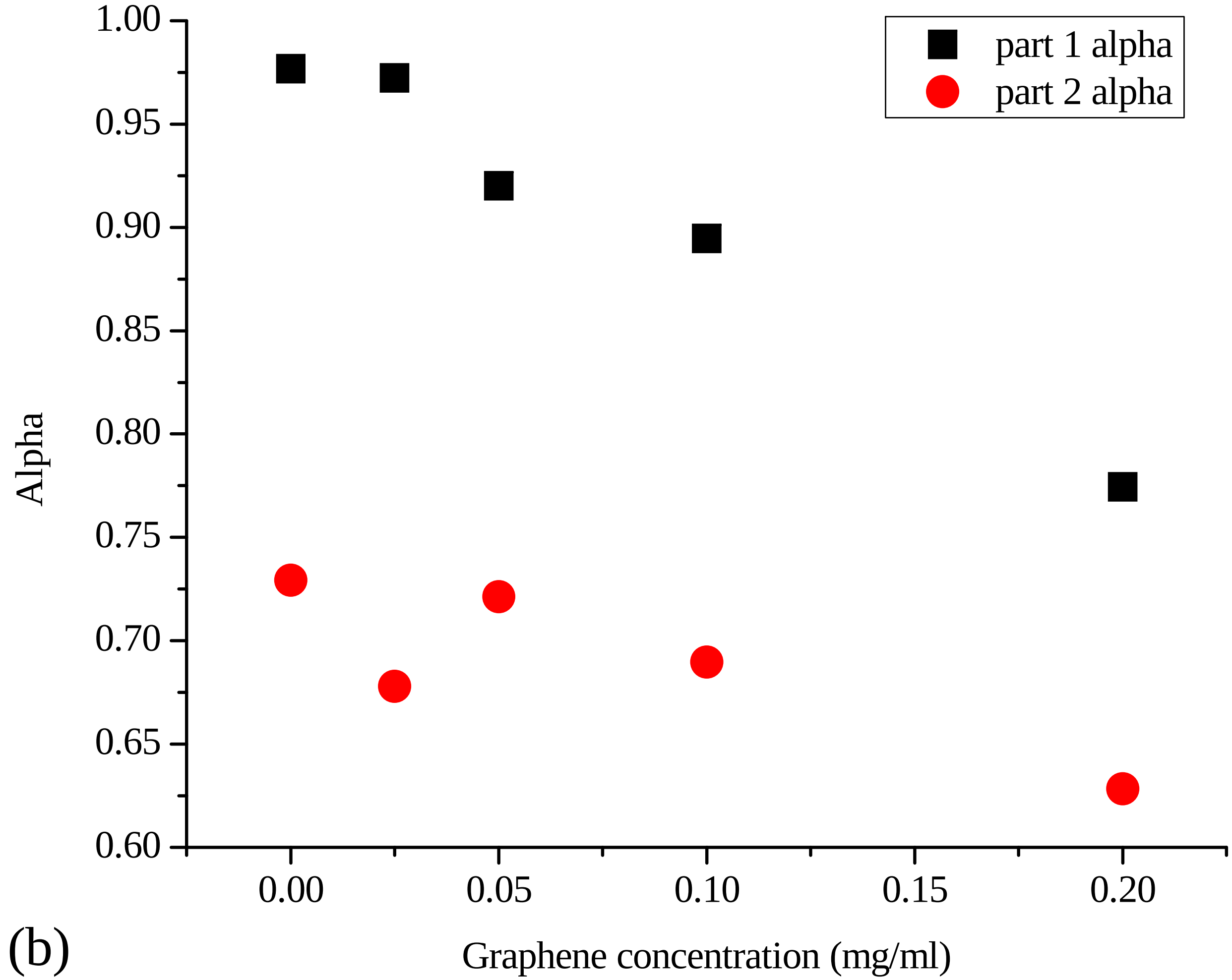


$J_{sc} \sim I^{\alpha}$

α = 1 for geminate

α = 0.5 for bimolecular

graphene dependence of α



$J_{sc} \sim I_{\alpha}$

Role of Graphene

Extrinsic

Morphology of blend

Structure of P3HT & F8BT

Crystallization & Aggregation

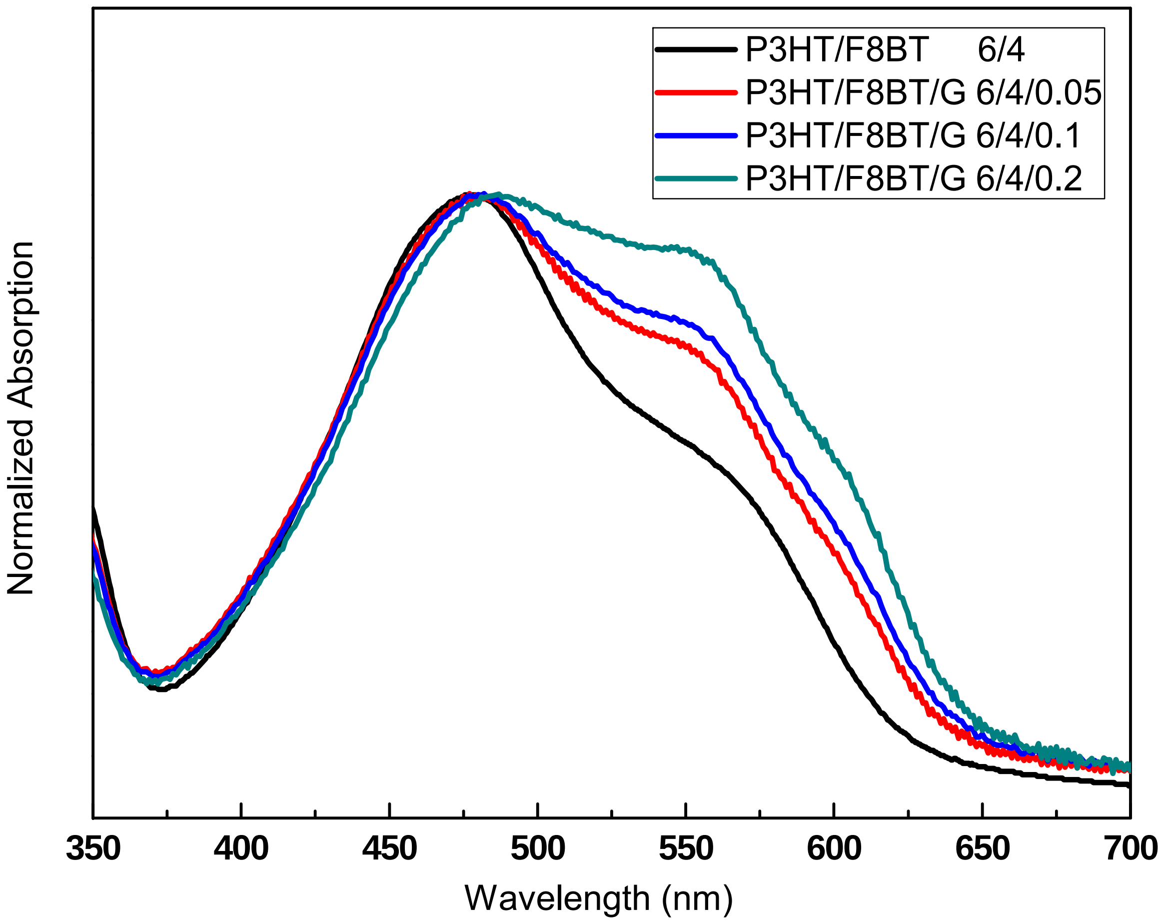
Intrinsic

Charge transport

Mobility

Recombination

UV-VIS of thin films

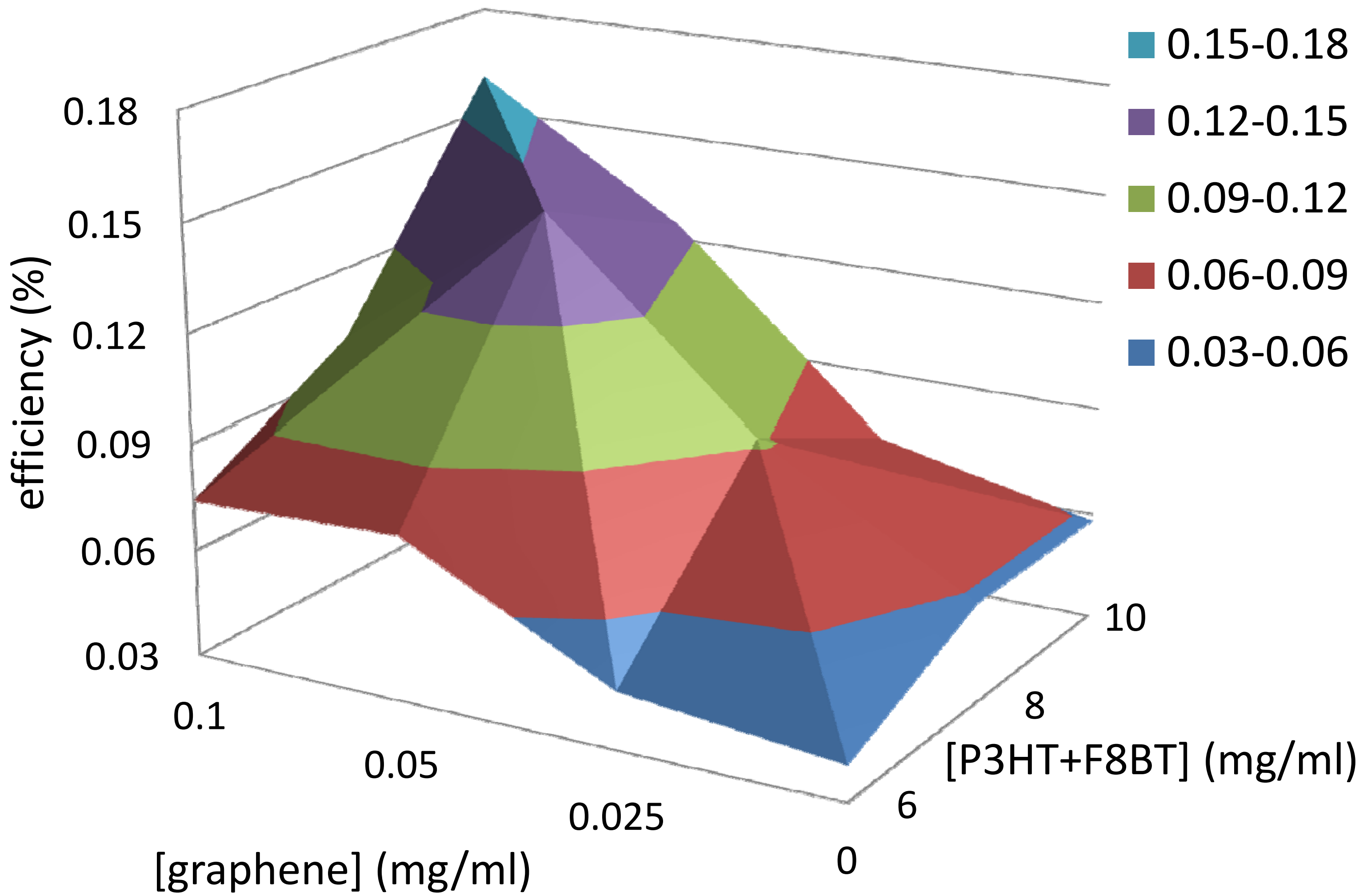


Peaks at 550-600nm w/ Increasing [Gr]

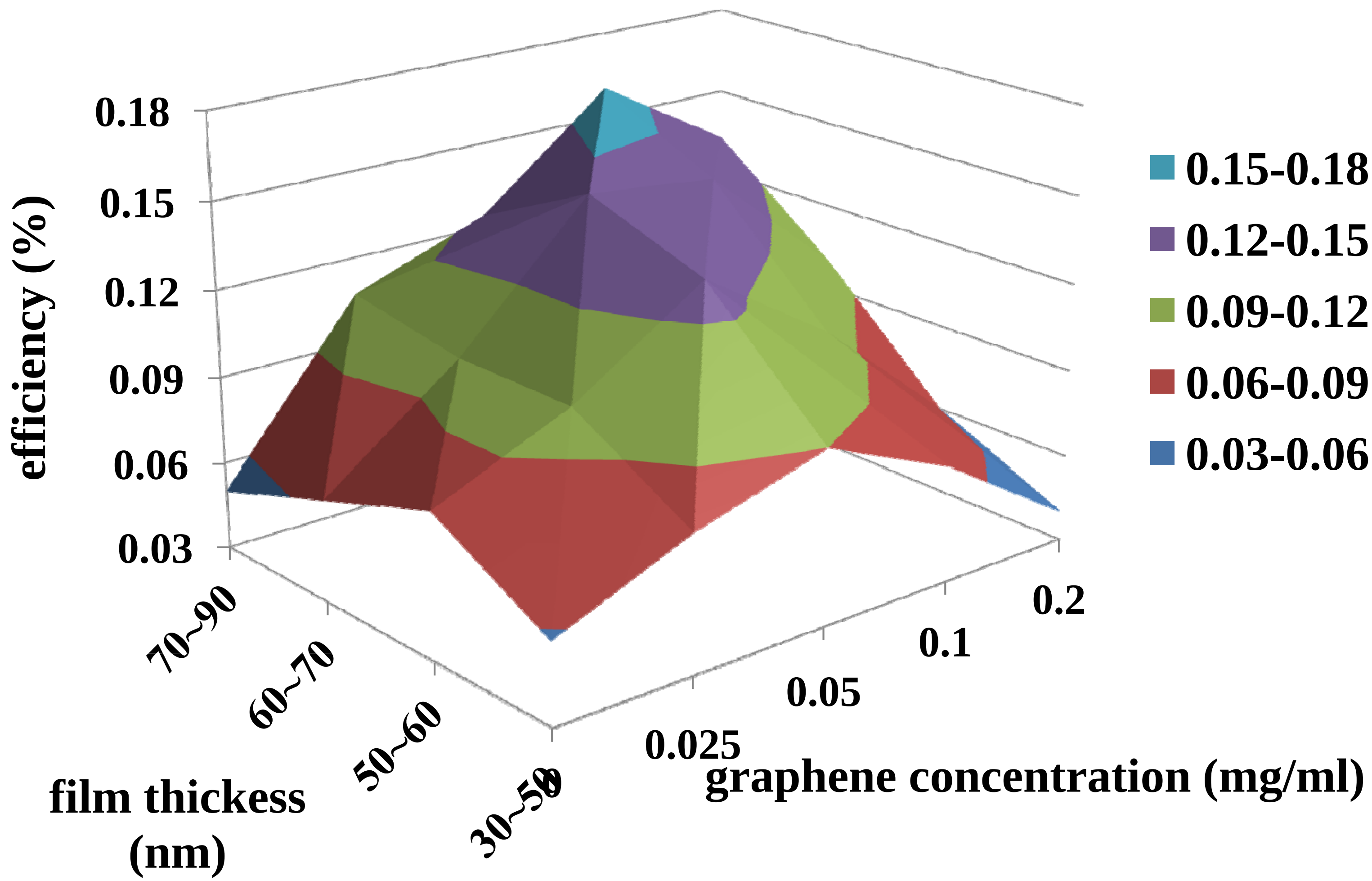
P3HT crystallites

Nucleating agent ?

Concentration dependence



Thickness dependence



New paradigms in OPV BHJs

- Graphene enhances charge transport - high J_{sc} , FF and η
- Cells with majority active layer are now viable
  - Better harnessing of solar energy
  - Improved mobility
- Morphology of blend is altered – enhanced crystallization
- Intrinsic and extrinsic effects are observed
- Complex influence of thickness & concentration
- Synergistic role of high-aspect ratio graphene additives

Jin, Yu and Kuppa, *(manuscript in preparation)*

Factors Affecting BHJ Performance

- **Choice of donor and acceptor materials**: band gap and miscibility
- **Choice of solvent**: polymer chain packing
- **Donor-acceptor ratio**: domain size
- **Annealing conditions**: reorganize polymer chains, crystallization
- **Other post-production treatments**: DC voltage during annealing for ordered structure *

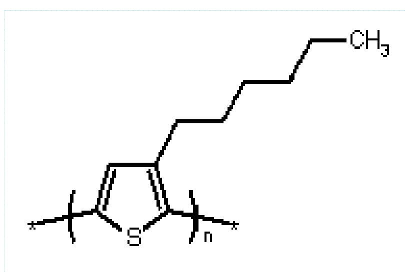
Morphology → Performance

Pictures source: Dennler, Scharber and Brabec, Adv. Mater. 2009, **21**(13): p. 1323-1338.
* Padinger, Rittberger and Sariciftci, Adv. Funct. Mater., 2003. **13**(1): p. 85-88.

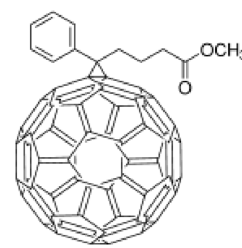
BHJ features

Polymer:Fullerene BHJ device

- High interfacial area for exciton dissociation
- Bicontinuous network for charge transport
- 50:50 w/w P3HT:PCBM for optimum performance
- Increase P3HT ratio to capture more solar energy



P3HT



PCBM

Future Work

- Better dispersed and oriented graphene via morphological control
- Increase FF by reducing interfacial roughness
- Stability and device encapsulation

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Thank you!