Addressing the fundamental drawbacks of organic photovoltaics

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Solar Energy In Development

- Renewable
- Potential for High coverage
- Low emission

U.S. Total and Renewable Energy Consumption by Source, 2011

Total = 97.3 Quads

Renewables = 9.1 Quads

- Petroleum 36%
- Natural Gas 26%
- Coal 20%
- Nuclear 8%
- Renewables 9%

- Wind 13%
- Hydroelectric 35%
- Geothermal 2%
- Biomass 48%
- Solar 2%

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Organic Photovoltaics (OPVs)

Solar power offers unique advantages
- no mech. parts – relatively expensive
- flexible & customizable – storage

IIIa generation - Si & Ge cells are efficient but expensive

OPVs are of IIIb type: low to moderate efficiency
- processed at lower T – low efficiency
- versatile manufacturing – inadequate spectral coverage
- distinctive mechanical & optical properties – poor mobility of charges
- tunability
- cheap
Functioning of OPVs

Incident radiation produces e-h pairs (excitons)

Exciton motion length & time scales \( \sim 100 \text{ ps}, 5-20 \text{ nm} \)

Morphology of active material is KEY
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

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

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

P3HT (59.9%)
F8BT (39.9%)
Graphene (~0.2%)
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 N₂
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 ($\eta$)

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

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

Open circuit voltage - $V_{oc}$

Graph showing $V_{oc}$ (V) vs. graphene concentration (mg/ml). The data points indicate a slight decrease in $V_{oc}$ as the graphene concentration increases from 0.00 to 0.10 mg/ml.
Cell Performance

Short circuit current - $J_{sc}$

![Graph showing the relationship between graphene concentration and short circuit current. The x-axis represents graphene concentration (mg/ml) ranging from 0 to 0.2, and the y-axis represents $J_{sc}$ (mA/cm²) ranging from 0 to 0.6. The graph includes error bars indicating variability.]
Cell Performance

Fill factor - FF

Graphene concentration (mg/ml)
Cell Performance

![Graph showing cell performance vs. graphene concentration](image-url)
Cell Performance

External quantum efficiency - EQE

EQE (%) vs Wavelength (nm)

- PF10
- PF10 G0.025
- PF10 G0.05
- PF10 G0.1
- PF10 G0.2
Device physics - recombination

\[ J_{sc} \sim I^\alpha \]

\( \alpha = 1 \) for geminate
\( \alpha = 0.5 \) for bimolecular
graphene dependence of α

$J_{sc} \sim I_\alpha$

(b)

Graphene concentration (mg/ml)
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

![3D plot with concentration dependence]

- [graphene] (mg/ml)
- [P3HT+F8BT] (mg/ml)
- Efficiency (%)
Thickness dependence

- Efficiency (%): 0.03 - 0.18
- Graphene concentration (mg/ml): 0.03 - 0.15
- Film thickness (nm): 30-50, 50-60, 60-70, 70-90

Colors correspond to:
- 0.15 - 0.18
- 0.12 - 0.15
- 0.09 - 0.12
- 0.06 - 0.09
- 0.03 - 0.06
New paradigms in OPV BHJs

- Graphene enhances charge transport - high $J_{sc}$, FF and $\eta$

- 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

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](image1.png)
![PCBM](image2.png)
Future Work

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

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