The effects of solvents on the morphology of P3HT:PCBM solar cells

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Efficiency Scoreboard

Best Research-Cell Efficiencies

- Multijunction Concentrators
  - Three-junction (2-terminal, monolithic)
  - Two-junction (2-terminal, monolithic)
- Single-Junction GaAs
  - Single crystal
  - Concentrator
  - Thin film
- Crystalline Si Cells
  - Single crystal
  - Multicrystalline
  - Thick Si film
  - Silicon Heterostructures (HIT)
- Thin-Film Technologies
  - Cu(In,Ga)Se₂
  - CdTe
  - Amorphous Si:H (stabilized)
  - Nano-, micro-, poly-Si
  - Multijunction polycrystalline

Emerging PV
- Dye-sensitized cells
- Organic cells (various technologies)
- Inorganic cells

Inorganic cells

Efficiency (%) vs. Year

Inorganic cells

Efficiency (%) vs. Year

Inorganic cells

Efficiency (%) vs. Year

Inorganic cells
Materials are cheaper and less toxic
Lower purity requirements
Lower temperature processing
Solvent based printing
Flexible plastic substrates
Roll-to-roll production

http://www.konarka.com/
The Cost!!!

How does it work?

Al Electrode

P3HT:PCBM Mixture

PEDOT:PSS

Glass ITO Substrate

D*  A
δ+δ  Exciton

D+  A−
Geminate Pair

D+  A−
Free Charges

D  A
Recombination

D+  A−
Photocurrent

P3HT

PCBM
How does solvent effect morphology?

ODCB bp = 182 °C is harder to remove from the bulk-heterojunction layer than CB bp = 131 °C

Data shows increased size of PCBM crystal growth for ODCB longer heating times.

Conclusion – ODCB remains in layer and increases PCBM diffusion rate upon heating
Proof with GCMS

1) spin coat with solvent
2) heat treat (HT) at 150 °C for various times
3) dissolve layer in CHCl₃ and run in GCMS

I don't get it.
Why doesn’t the solvent leave the bulk-heterojunction layer?
Glove box vs. fume hood

Saturated Vapor Pressures

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Pressure</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIB</td>
<td>11.8 Torr</td>
<td>25°C</td>
</tr>
<tr>
<td>ODCB</td>
<td>1.2 Torr</td>
<td>20°C</td>
</tr>
<tr>
<td>NtB</td>
<td>0.15 Torr</td>
<td>20°C</td>
</tr>
</tbody>
</table>

Conclusion: solvent is removed in fume hood but not in a glove box.
Cartoon Break

Solvent Induced Diffusion

Conclusion: moving air is necessary for solvent removal

Microscopy and LBIC together

Conclusion: Large PCBM domains are bad for device function

Effect of polar co-solvent

Conclusions: the presence of NB increases the $T_g$ of P3HT side chains and the melting temperature of PCBM and the onset of melting for P3HT backbone.
Longevity Data 2 – Dark heat at 80 C
Conclusions/Recommendations

• Use low bp solvents
• Remove solvents using heat and air flow
• Solvent additives can change the $T_g$ and $T_m$ of both the polymer and fullerene
• “Good solvents” decrease $T_g$ and $T_m$
• “Bad solvents” increase $T_g$ and $T_m$
• Solvent additives that are bad for polymer seem to reduce occurrence of sudden death syndrome for OPV
So, if PCBM is mobile (diffuses) in P3HT, will it always phase separate to form large domains?
• Results contrary to what is expected from bilayers.
• Over a 95% quenching of 80 nm P3HT fluorescence.
• Increased current density with increased P3HT Thickness.
Conclusion: PCBM Penetrates the P3HT Layer. The PCBM can Removed selectively.
P3HT/PCBM Bilayers

Spincoat PCBM onto P3HT film

Wash off PCBM with CH₂Cl₂

PCBM solution in CH₂Cl₂

CH₂Cl₂
How Much PCBM?

- 28 wt% PCBM in P3HT of bilayer

Conclusion: PL + a calibration curve can be used to determine PCBM content in BHJ layer
BHJ Wash

- Spin coat a mixed film of P3HT:PCBM (7:3 by wt.)
- Wash film with CH₂Cl₂

Conclusion: PCBM can be selectively removed from BHJ layer
Neutron reflectometry

Bi-layer cast

Bulk Heterojunction
Vertical Concentration Profile

Bi-layer Cast

Bulk Heterojunction
Conclusions

- P3HT has ~30% expansion volume from “poor” solvent that can be filled with PCBM
- PCBM can be removed from BHJ layer no matter how it was formed
- Heating induced morphology change is driven by BHJ interfaces but the initial condition still changes VCP and device function
Thank you for your attention