

Enhanced Performance of Organic Photovoltaics Using Plasmonic Nanocrescent Structures



Dan Jacobs[†], Mark Swartz[‡], Dr. Jennifer Shumaker-Parry[‡], Dr. Ling Zang^{†*}

[†] Department of Materials Science and Engineering, University of Utah, Salt Lake City, UT 84103

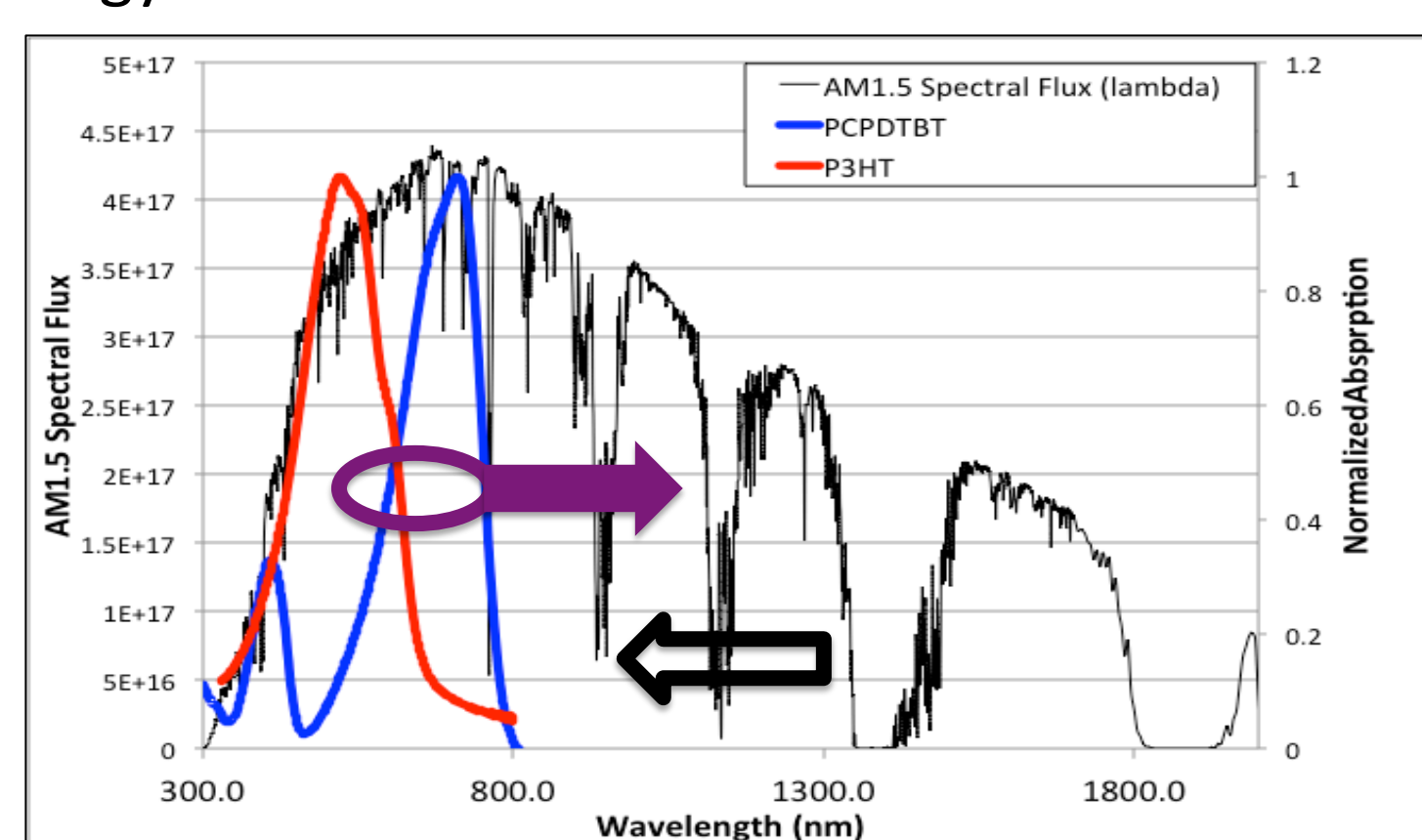
[‡] Department of Chemistry, University of Utah, Salt Lake City, UT 84103



Motivation/Background

Organic photovoltaics (OPV) hold their advantage in their cheap and scalable solution processing, renewable materials and ability to be processed on light flexible substrates. However, their low efficiencies limit their coming to market. A major aspect in the low performance of these devices is poor light interaction stemming from two main points:

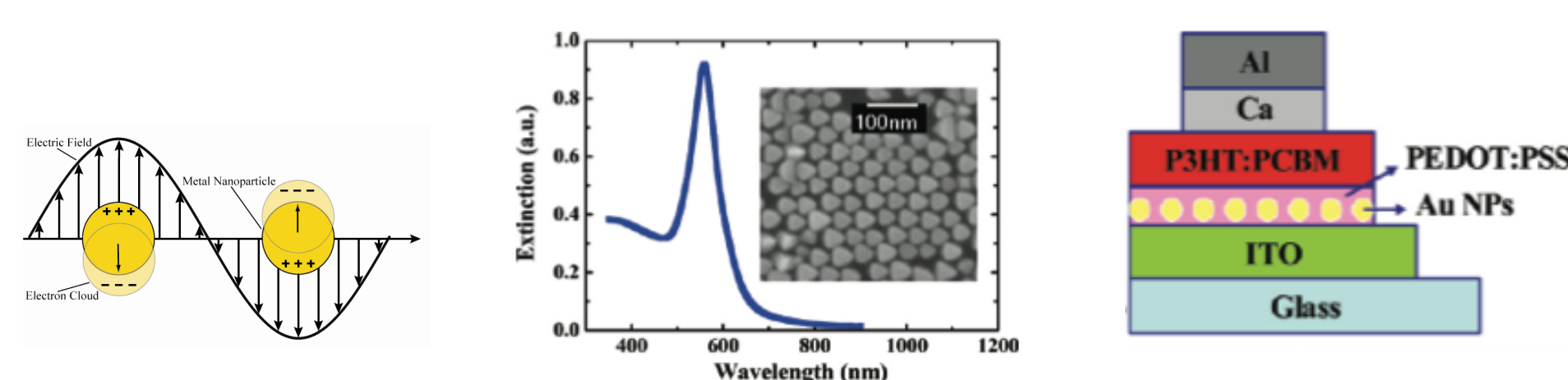
- 1) **Optically thin:** Ultra thin active layers (~100nm) needed for efficient charge separation and collection, are often too thin to absorb all of the light resulting in a semitransparent device.¹
- 2) **Spectral Mismatch:** Organic semiconductors, such as the well studied OPV polymer P3HT (red curve), typically have narrow absorption bands blue-shifted with respect to the solar spectrum limiting the amount light available to be converted into energy.²



Synthesis of new low bandgap polymers such as PCPDTBT (blue curve) better fit the incident solar spectrum, but still suffer from optical thinness. Similarly, optical studies to improve light path length are not broadband or tunable throughout the solar spectrum. This research attempts to address both critical issues together for improved OPV performance.

Plasmonic Photovoltaics

Localized surface plasmons are highly concentrated electromagnetic fields resulting when the electron cloud of metal structures much smaller than the wavelength of light, exhibit a collective resonance at a specific wavelength. In OPV devices, this is used to concentrate specific wavelengths of light into nano-scaled volumes.



For use in OPV devices, much of the research studies spherical nanoparticles, which shows an increase in absorption and device current³. However, these structures are limited by:

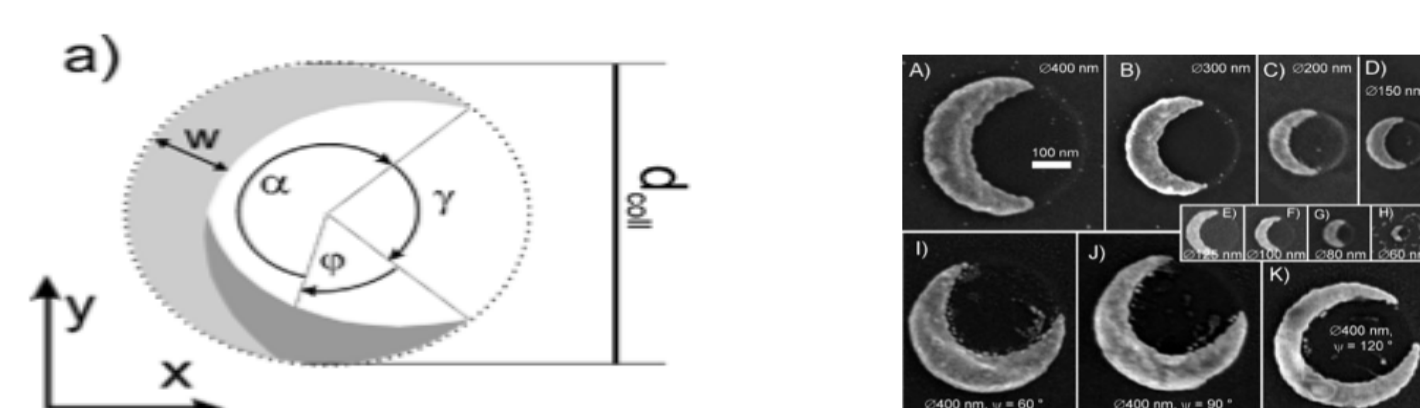
- 1) **Narrow resonance peaks**
- 2) **Limited resonance peak tuning.**

Ideally, plasmonic structures should have wide and tunable resonance peaks to better match the materials absorption properties and cover more of the solar spectrum.

Plasmonic nanocrescents

Nanocrescent (NC) structures have unique plasmonic properties as a result of their anisotropic shape⁴ such as:

- 1) Broad resonance peaks
- 2) Multi peak resonances
- 3) Polarization dependent resonances
- 4) Tunable resonances from visible to infrared wavelengths



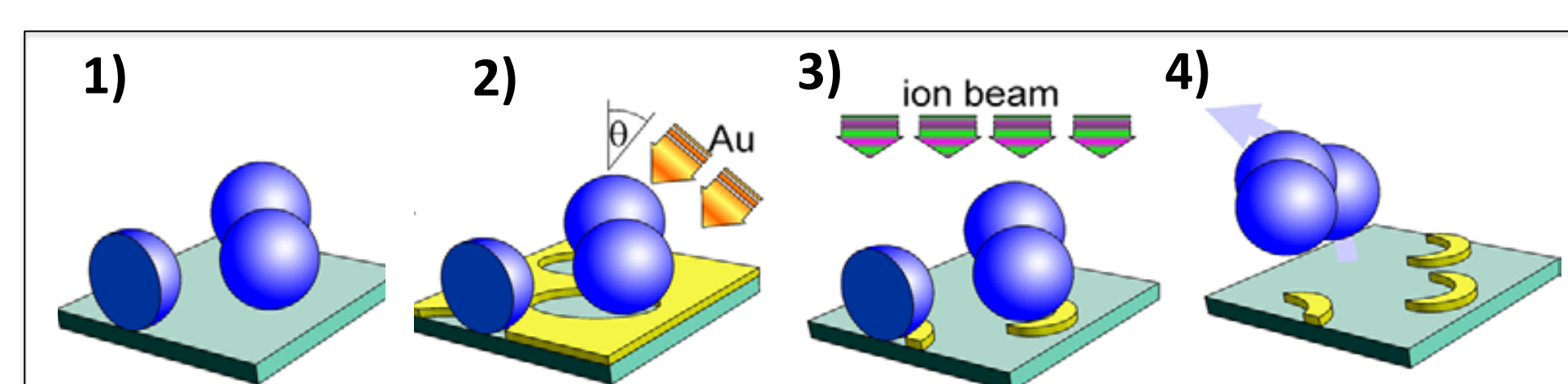
These nanocrescent structures have a ability to enhance OPV performance by harvesting more light that better matches the material as well as has the potential to study plasmonic effects on OPV processes at longer wavelengths, lower energy, not attainable with traditional plasmonic particles.

Nanocrescent Fabrication and Analysis

Nanosphere Template Lithography

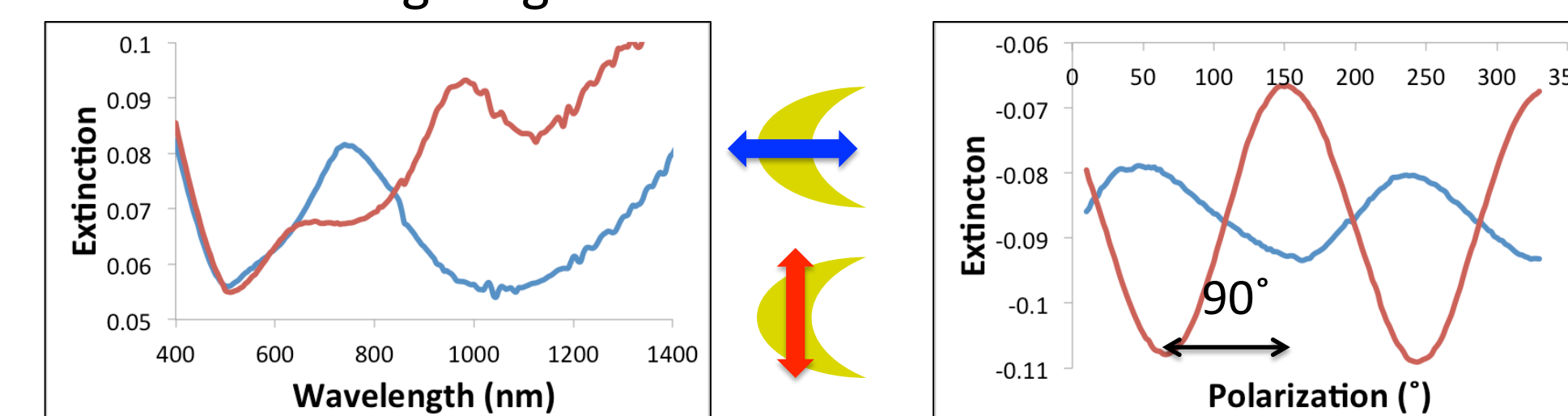
Nanocrescents can be fabricated using the large area, three step process as follows⁴:

- 1) Nanosphere templates are deposited from solution onto a substrate through spin coating.
- 2) A metal (Au, Ag, Al) is deposited at an angle to the substrate normal.
- 3) The metal is etched in a reactive plasmon etch normal to the substrate surface
- 4) Beads are removed to leave the crescent structures



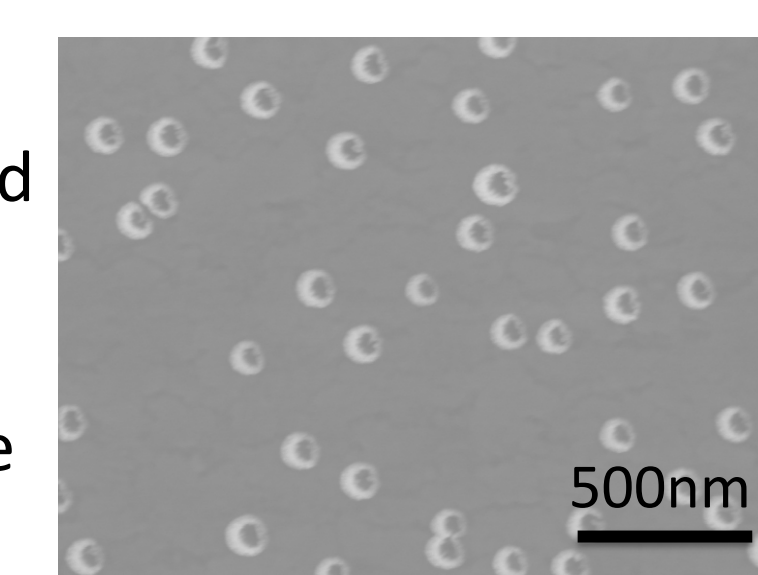
UV-Vis-NIR polarization spectroscopy

Plasmon resonance peaks were identified using UV-Vis-NIR extinction scans. Polarization scans at peak wavelengths show 90° shifts indicating long and short axis resonance excitations



SEM

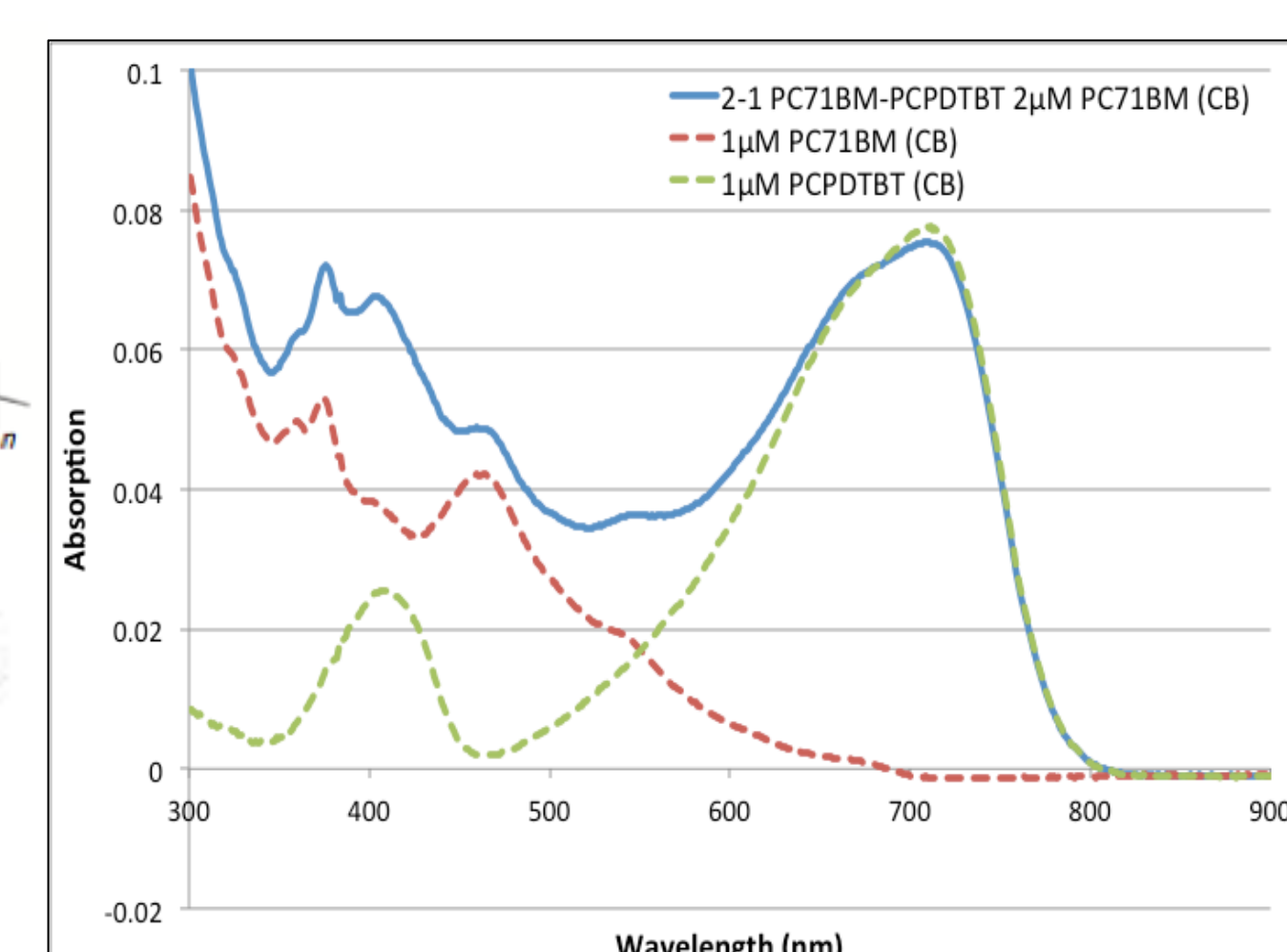
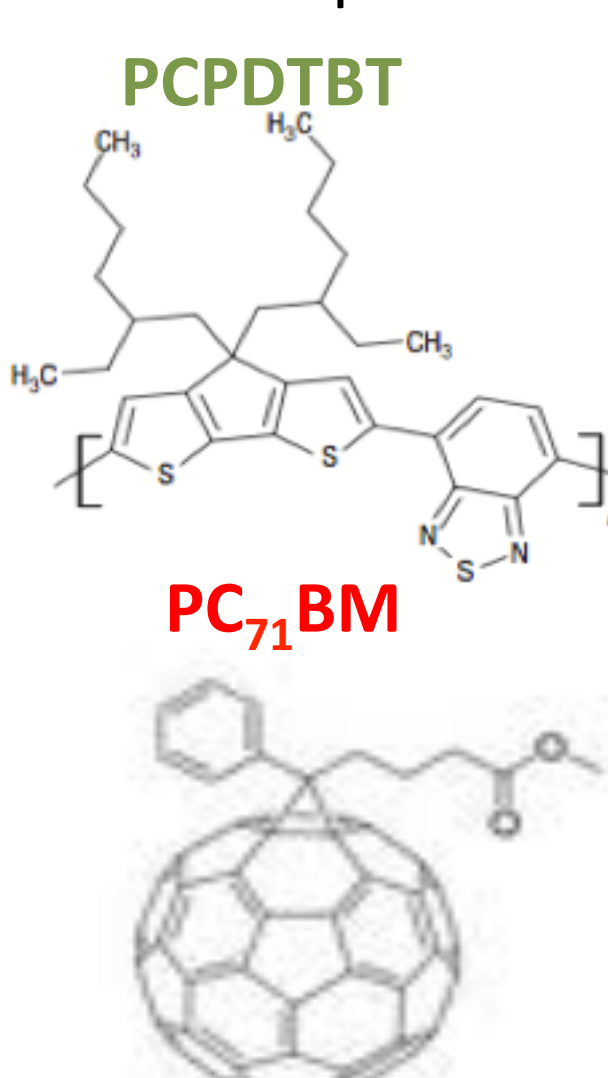
Nanocrescent structures were imaged using high resolution FEI SEM. These images indicated the NCs were well dispersed on ITO substrates and have ~100nm diameters



OPV Device

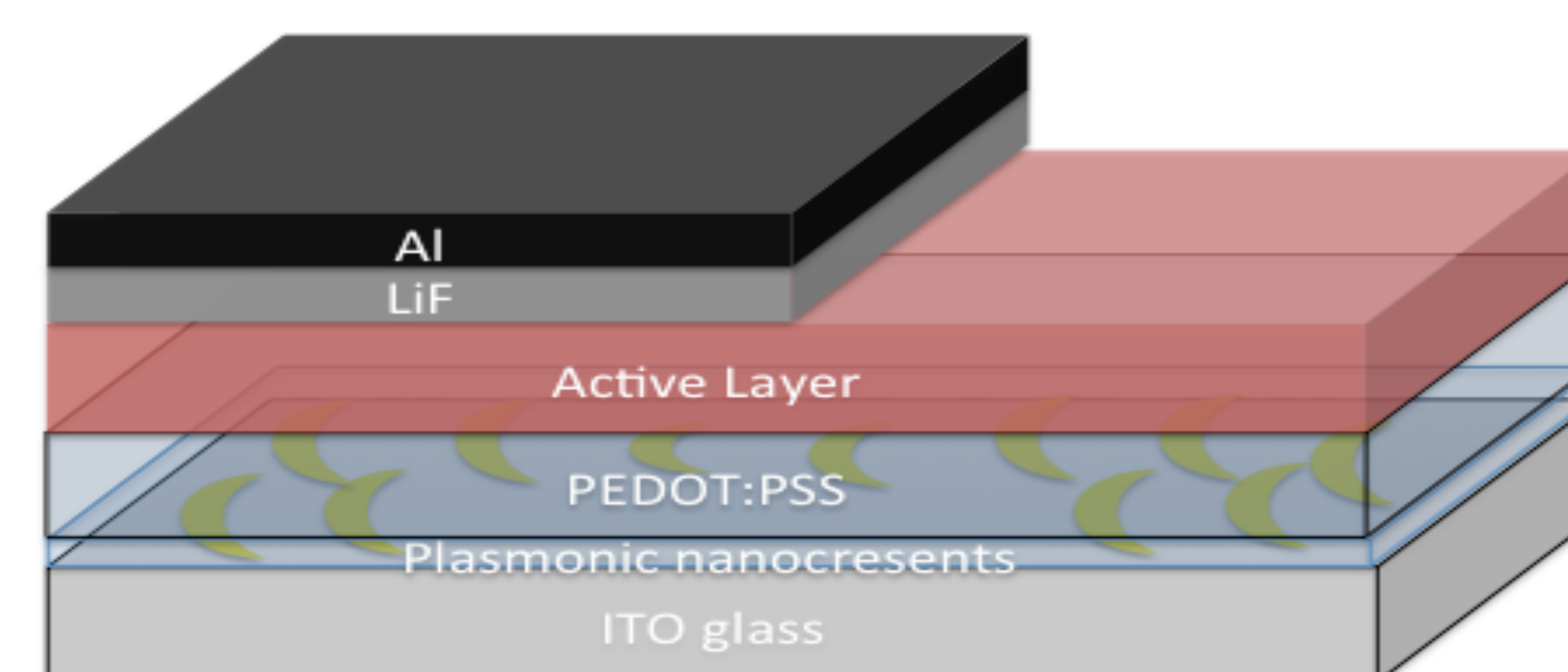
Materials

Low bandgap active layer materials were used because of better spectral matching with the solar spectrum².

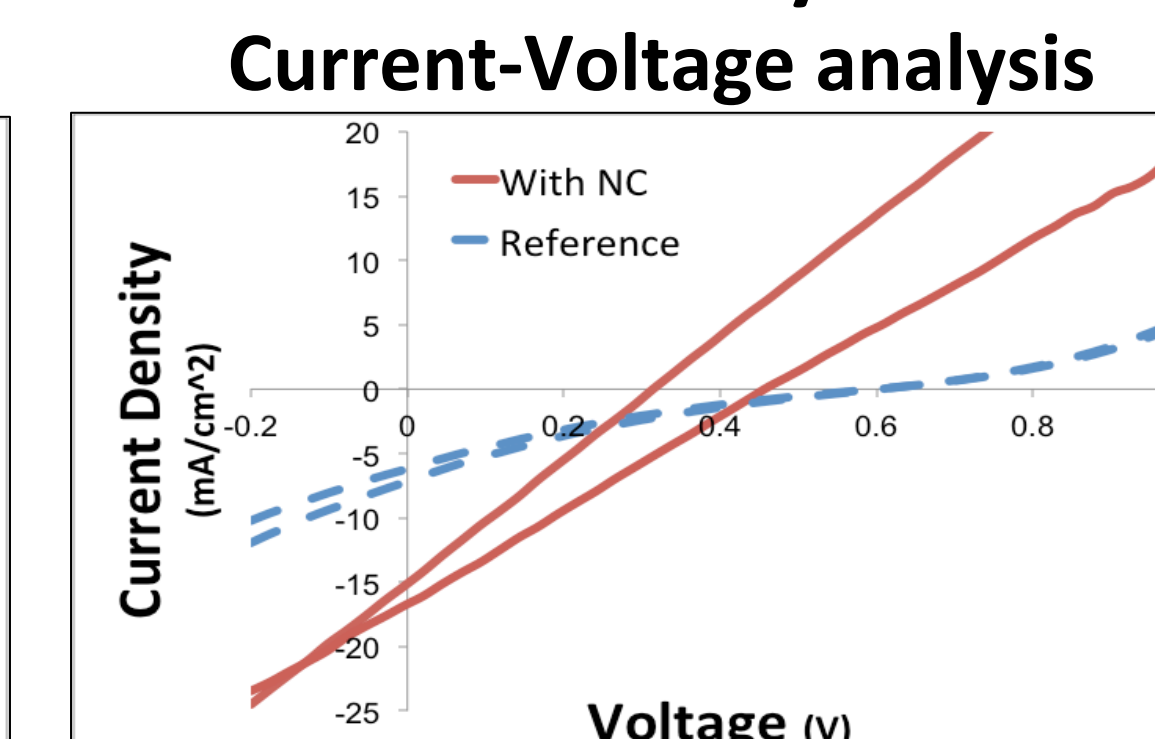
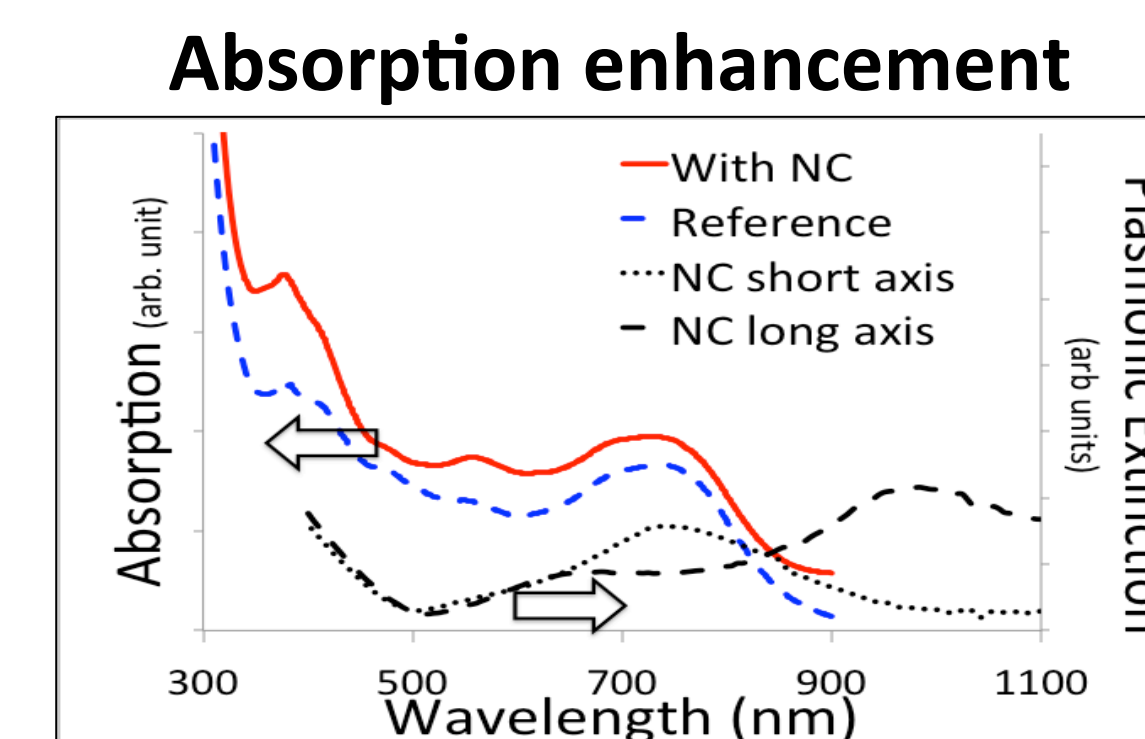


Device Fabrication

The device was fabricated by sequentially spincoating and electron blocking layer (PEDOT:PSS, 50nm) and active layer (1:2 PCPDTBT:PC71BM, 100nm) on the ITO/NC anode. The cathode was fabricated by sequentially evaporating lithium fluoride and aluminum in a thermal evaporator at ~1x10⁻⁵ Torr.



Preliminary Results



Device performance

| | Voc [V] | Jsc [mA/cm²] | Fill Factor | % Efficiency |
|------|---------|--------------|-------------|--------------|
| NC2 | 0.31 | -14.16 | 0.27 | 0.95 |
| NC4 | 0.46 | -16.07 | 0.26 | 1.50 |
| Ref1 | 0.61 | -5.80 | 0.18 | 0.52 |
| Ref3 | 0.61 | -6.41 | 0.18 | 0.57 |

Performance Enhancement with NC structures

- Broadband absorption increase in active layer
- >2x increase of short circuit current (J_{sc})

Using 82nm nanosphere templates, the gold NCs showed short and long axis resonance peaks inside and outside of the absorption profile respectively, although no polarization dependent performance was seen. The increased current is believed to be a result of the increased absorption, although further testing is needed. It is noted that all devices, including references, show non-ideal current-voltage behavior and very low efficiencies. Similarly, devices with NC structures show a decrease in open circuit voltage. These are likely cause by non-optimized fabrication techniques and conditions. Optimization of the entire process is ongoing. Nevertheless, these preliminary results show significant current enhancements with plasmonic NC structures.

Conclusions/Outlook

Metal nanocrescent structures exhibit multipeak, tunable and polarization dependent plasmonic resonances. Preliminary results show these structures can improve the performance of OPV devices by about a factor of 2. However, optimization of the fabrication and testing processes need to be done to realize their full potential.

Once the process is optimized, we will begin to research the effect of below bandgap plasmonic enhancement in OPV devices, which to our knowledge has yet to be studied. Using the polarization dependent resonances we can selectively concentrate specific energies to study:

- Exciton dissociation
 - Charge carrier mobility
 - Direct photocurrent via plasmonic photoemission
- Our goal is to improve light harvesting and optical interactions for better photovoltaic devices.

Acknowledgements/References

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¹ Atwater, H. A. and A. Polman "Plasmonics for improved photovoltaic devices." Nat Mater 9(3): 205-213.
² Bundgaard, E. and F. C. Krebs (2007). "Low band gap polymers for organic photovoltaics." Solar Energy Materials and Solar Cells 91(11): 954-985.
³ Wu, J.-L., F.-C. Chen, et al. "Surface Plasmonic Effects of Metallic Nanoparticles on the Performance of Polymer Bulk Heterojunction Solar Cells." ACS Nano 5(2): 959-967.
⁴ Shumaker-Parry, J. S., H. Rochholz, et al. (2005). "Fabrication of Crescent-Shaped Optical Antennas." Advanced Materials 17(17): 2131-2134.

* To whom correspondence should be addressed. lzang@eng.utah.edu