Final Technical Report

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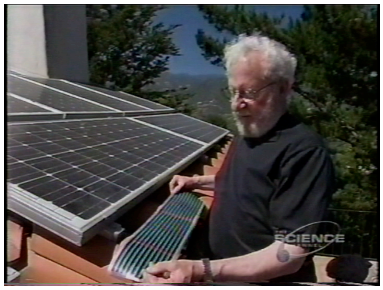
Functional Interfaces in Polymer-based Bulk Heterojunction Solar Cells: Establishment of a Cluster for Interdisciplinary Research and Training

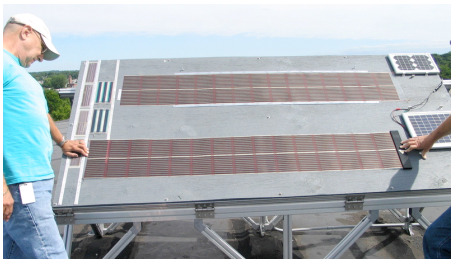
Principal Investigator:
Professor Alan J. Heeger
Department of Physics and Materials Department
University of California, Santa Barbara
Santa Barbara, CA 93103
e-mail: ajhe1@physics.ucsb.edu
Telephone: (805) 570-9053

Co-Principal Investigator:
Professor Thuc-Quyen Nguyen
Department Chemistry
University of California, Santa Barbara
Santa Barbara, CA 93103
e-mail: quyen@chem.ucsb.edu
Telephone: (805) 893-4851

Light Weight Flexible Plastic Solar Cells



The "colored liquids" above are examples of semiconducting polymers in solution (different molecular structures) --- these semiconducting polymers can be formulated as "electronic inks". Because semiconducting polymers can be dissolved in common solvents, "plastic" solar cells can be printed/coated on flexible substrates with roll-to-roll processing, thereby enabling light weight, flexible solar cells and solar modules.



Konarka Technologies Inc., co-founded by PI Alan Heeger, has demonstrated outdoor exposure exceeding one year *without* performance loss using module scale "plastic" solar cells; see photo on the right above. In parallel studies, plastic solar modules were demonstrated to meet the high temperature, high humidity (in full sun) specifications of the solar cell industry; e.g. 10^3 hrs at 65ºC under AM1.5 irradiation, 10^3 hrs at 65ºC and 85% humidity.

- ***Light weight flexible solar cells are a reality!***

Improving Efficiency: Recent Progress at UCSB by the PI Alan Heeger, inventor of the bulk heterojuction (BHJ) polymer: fullerene "plastic" solar cell, and collaborators Guilermo C. Bazan and Thuc-Quyen Nguyen include the following:

- Device efficiencies have steadily improved from 1% to 6.5%. Briefly, in a BHJ solar cell, an excited electron-hole pair generated from light absorbed in the polymer must travel only ~10nm before ultrafast (~10^{-13} s) electron transfer to a fullerene at a polymer:fullerene interface. The separated electron and hole travel along phase separated fullerene and polymer networks, respectively, guided by the internal built-in electric field from electrodes with different work functions.
- Inclusion of low-temperature amorphous titanium sub-oxide, TiO_x, films into the multilayer cell architecture provides numerous benefits to device performance including higher efficiency and increased lifetime by a factor of > 100 for unpackaged devices. Moreover, the TiO_x layer provides the technology required to create multi-junction devices, opening up new opportunities for creating Tandem Cells with still higher efficiency.
- Discovery of Processing Additives that enable greater control of the nano-morphology without the need for post-production annealing.

Technical Progress

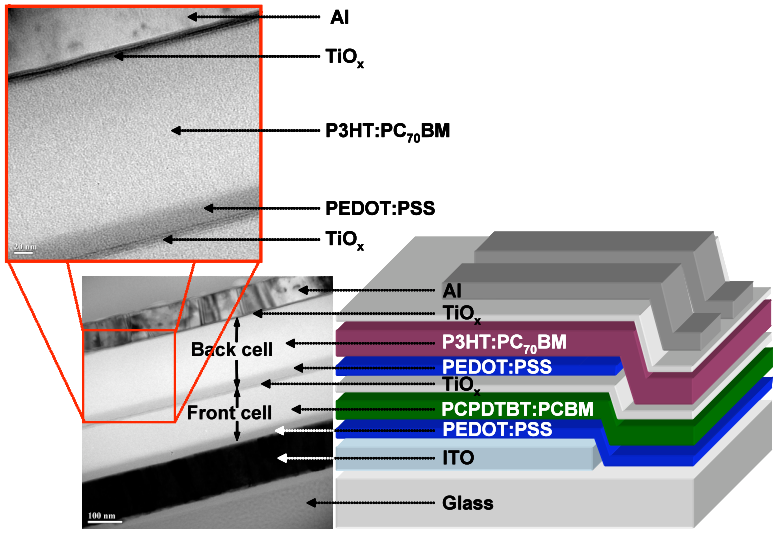
Recent accomplishments from our effort at UC Santa Barbara include the discovery and creation of hybrid solar cells in which a sol-gel processed TiO_x layer serves multiple functions:

1. Deposited between the charge separation layer (BHJ phase separated mixture) and the Al cathode, the TiO_x functions as an optical spacer that redistributes the light intensity to optimize the efficiency.
2. By introducing a TiO_x layer between the charge separating layer and the Al cathode, excellent air stability has been demonstrated. The TiO_x layer improves the lifetime of unpackaged devices by nearly two orders of magnitude.
3. The TiO_x functions as an electron transport layer and a hole blocking layer and thereby enhances carrier collection at the electrodes.
4. The TiO_x layer enables the fabrication of tandem cells. The transparent TiO_x layer is used to separate and connect the front cell and the back cell. The TiO_x layer serves as an electron transport and collecting layer for the first cell and as a stable foundation that enables the fabrication of the second cell to complete the tandem cell architecture.
5. TEM studies of the interfaces show nearly "ideal" structures despite the fact that hydrophobic and hydrophilic layers are included in the multi-layer stack (see Summary Progress on the Tandem Cell below)

Tandem cells have been demonstrated with power conversion efficiencies of 6.5%. Recent progress using dithiols as a processing additive resulted in an increase in the efficiency of the smaller bandgap polymer in the Tandem Cell by nearly a factor of two.

Tandem solar cells with a power conversion efficiency of 6.5%, with each layer processed from solution, were fabricated using bulk heterojunction materials comprising semiconducting polymers and fullerene derivatives. A transparent titanium oxide (TiO_x) layer is used to separate and connect the front cell and the back cell. The TiO_x layer serves as an electron transport and collecting layer for the first cell and as a stable foundation that enables the fabrication of the second cell to complete the tandem cell architecture. We use an inverted structure with the low band-gap polymer/fullerene composite as the charge separating layer in the front cell and the high band-gap polymer composite as the charge separating layer in the back cell.

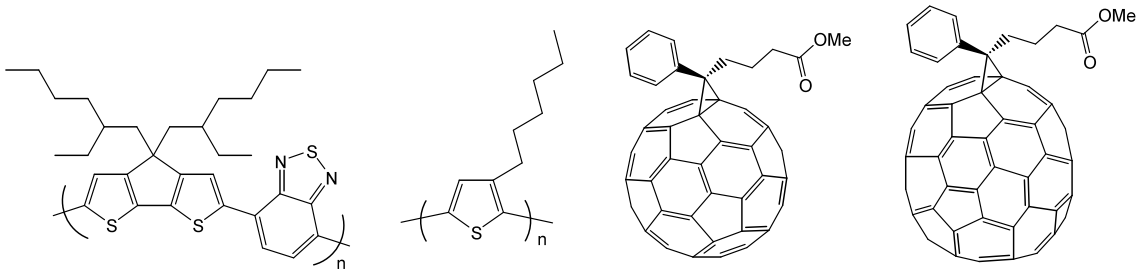
The multi-layer structure --- each layer processed from solution and therefore "printable" --- is shown below:



The device structure (right) and TEM cross section image (left) of the polymer tandem solar cell. The scale bar is 100 nm in the lower image and 20 nm in the upper image. The cross-sectional TEM images were obtained using the novel technique developed by Prof. Nguyen. To prepare the solar cell cross sections, ca. 200 nm-thick SiO_2 layer was deposited on top of the device using electron beam evaporator (BOC Edwards Temescal) to prevent sample damage. Next, a focused ion beam (FEI Strata) was used to cut a thin slide (~ 130 nm thick) of the sample (4 μm × 15 μm) and this slide was transferred onto a TEM grid for imaging using a micromanipulator with a glass needle. The TEM images were collected in bright-field mode (FEI Tecnai G2 Sphera Microscope).

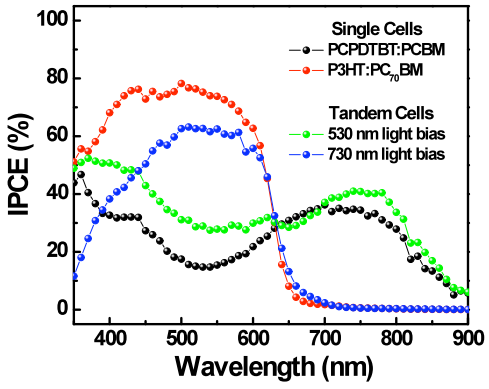
Note the clean interfaces; the various interfaces are remarkably sharp; there is no inter-layer mixing. Remarkable since these layers were processed from solution --- not by molecular beam epitaxy!

The specific materials used in the BHJ charge separating layers of the two cells in tandem as shown below:



PCPDTBT **P3HT** **PCBM** **$PC_{70}BM$**

IPCE spectra of single cells and a tandem cell are shown below. Note that the Tandem Cell is capable of light harvesting over a broad range of the solar spectrum --- from the UV, across the visible and out into the IR to approx. 900 nm.



IPCE spectra of single cells and of a tandem cell

The current-voltage (*J-V*) characteristics of single cells and a tandem cell using PCPDTBT:PCBM and P3HT:$PC_{70}BM$ composites under AM1.5G illumination from a calibrated solar simulator with irradiation intensity of 100 mW/cm^2 are shown below. The power conversion

efficiency (η_e) of a solar cell is given as $\eta_e = (J_{sc} \cdot V_{oc} \cdot FF) \cdot 100 / P_{inc}$, where P_{inc} is the intensity of incident light. The device performance is summarized as follows:

- PCPDTBT:PCBM single cell shows J_{sc} = 9.2 mA/cm^2, V_{oc} = 0.66 V, FF = 0.50, and η_e = 3.0%,
- P3HT:$PC_{70}BM$ single cell shows J_{sc} = 10.8 mA/cm^2, V_{oc} = 0.63 V, FF = 0.69, and η_e = 4.7%,
- Tandem cell shows J_{sc} = 7.8 mA/cm^2, V_{oc} = 1.24 V, FF = 0.67 and $\eta_e = 6.5\%$.

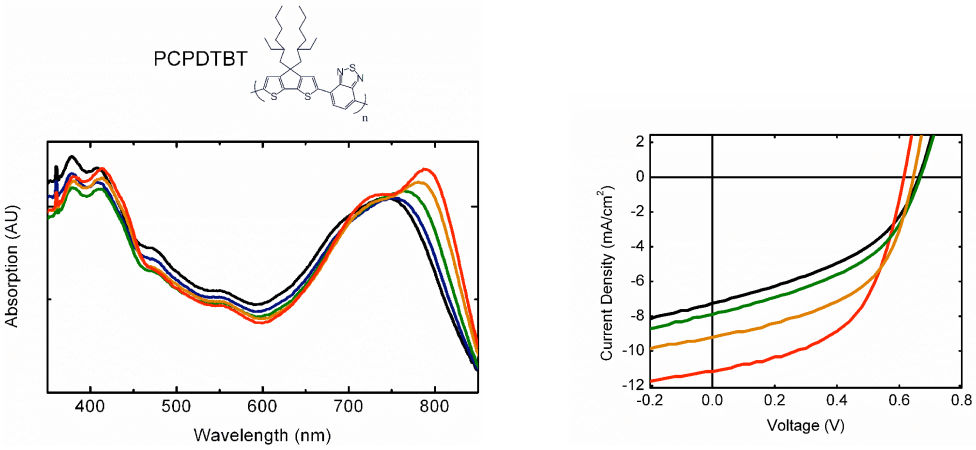
Over 200 individual tandem cells were made in order to optimize the fabrication procedure and device architecture. Using the inverted structure shown in first Figure above, more than 20 tandem cells were fabricated with efficiencies above 6.2%.

The achievement of polymer tandem cell in which each of the individual layers is processed from solution without significant interlayer mixing is a major step toward the achievement of high efficiency solar cells that can be fabricated in large areas using low cost printing and coating technologies. We anticipate that polymer tandem cells utilizing both new materials with fine-tuned absorption spectra and high mobility, and the opportunity to increase the multilayer stack to create three cells in tandem will yield results approaching or even exceeding 10% efficiency. The use of TiO_x as the separator, charge transport layer, hole blocking layer, symmetry breaking layer, and optical spacer in fully solution processible polymer tandem solar cells is an important development step toward large scale commercialization. The Tandem Cell results were published in *Science* **317**, 222-225 (2007).

Use of dithiols as processing additives: Increase in the efficiency by a factor of two.

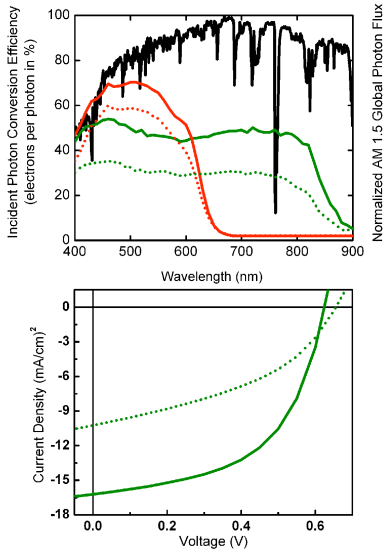
Attempts to control the donor/acceptor morphology in BHJ materials as required for achieving high power conversion efficiency have met with limited success. By incorporating a few volume percent of alkanedithiols in the solution used to spin cast films comprising a low bandgap polymer and a fullerene derivative, the power conversion efficiency of photovoltaic cells (AM 1.5G conditions) is increased from 2.8% to 5.5% through altering the bulk heterojunction morphology.

The Figure below (left) shows the shift in the film absorption caused by adding different alkanedithiols to the PCPDTBT:C_{71}-PCBM solution in chlorobenzene (CB) prior to spin casting. One observes the largest change with the addition of 2.4 mg/mL of 1,8-octanedithiol into the CB; the film absorption peak red-shifts 41 nm to 800 nm. Such a shift to lower energies and the emergence of structure on the absorption peak associated with the π-π* transition when films are processed with alkanedithiols indicates that the PCPDTBT chains interact more strongly and that there is improved local structural order compared with films processed from pure CB. The Figure below (right) shows clearly the increase in I_{sc} and the increase in FF.



As demonstrated in the Figure below, by processing the BHJ film using 1,8-octanedithiol as a processing additive, the solar conversion efficiency can be increased by a factor of two.

Device optimization involved over 1000 devices made from over 250 independently prepared PCPDTBT:C_{71}-PCBM films; optimum photovoltaic efficiencies between 5.2% and 5.8% were obtained.



Top: IPCE spectra of polymer bulk heterojunction solar cells composed of P3HT:C61-PCBM before (dotted red) and after (solid red) annealing, and PCPDTBT:C71-PCBM with (solid green) and without (dotted green) the use of 1,8-octanedithiol. The AM 1.5 global reference spectrum is shown for reference (black).

Bottom: Current voltage characteristics of the same PCPDTBT devices used for the IPCE measurements, processed with (solid) and without (dotted line) 1,8-octanedithiol under 100 mW/cm2 AM 1.5G illumination; Isc = 16.2 mA/cm2, FF = 0.55, and Voc = 0.62 V.

The results shown in the lower panel indicate a power conversion efficiency of 5.5 %, an increase by a factor of two over that obtained from the same polymer but without the use of the 1,8-octanedithiol. This represents the highest efficiency yet reported for a single cell (our Tandem Cell architecture has yielded 6.5% --- see above). The approach described here provides an operationally simple and versatile tool available for the tailoring of the heterojunction solar cell morphology in systems where thermal annealing is not effective. Note that this new approach works even on a system in which polymer crystallinity is not observed. Based on calculations by Brabec et. al. on photovoltaic cells fabricated from PCPDTBT:C_{71}-PCBM, further optimization of morphology and equalization of bipolar transport could lead to power conversion efficiencies as high as 7%. This expectation is fully consistent with the ICPE data shown above; there is a clear opportunity to increase the IPCE. The paper which describes the results obtained using the dithiol processing additive was published in *Nature Materials* **6**, 497-500 (2007).

Conclusion: Remarkable scientific progress has been demonstrated toward the creation of a low cost ("printable") solar cell technology by the interdisciplinary group at UC Santa Barbara. Multi-layer architectures were implemented with clean interfaces were demonstrated; the various interfaces are sharp; there is no evidence of inter-layer mixing. This is indeed remarkable since each of these layers was processed from solution. The use of "Processing Additives" such as the alkanedithiols was demonstrated to increase the power conversion efficiency of BHJ solar cells by a factor of two. Equally important, the mechanism by which these Processing Additives function has been identified.