Universitat Autònoma de Barcelona
Institut de Ciència de Materials de Barcelona (ICMAB-CSIC)
Nanopto

On Improving the Efficiency of Organic Photovoltaic Devices: Novel Strategies

Martí Gibert Roca

Under the supervision and tutoring of:

Mariano Campoy Quiles

Submitted in part fulfilment of the requirements
for the degree of Doctor of Philosophy in Materials Science
of the Universitat Autònoma de Barcelona, February 2022

Abstract

Recent advances in Organic Photovoltaics have brought this field to the forefront of renewable energy research. Organic photovoltaic devices have gained plenty of attention thanks to their chemical tunability, light weight, flexibility and increasing efficiency. Being roll-to-roll compatible, the manufacturing processes needed to produce such devices are easily scalable, and their low material usage and low embedded energy make for a sustainable commercial technology that can contribute to solve our current energy crisis. This technology, however, still faces several obstacles that prevent its widespread development. On the one hand, low charge mobilities and relatively modest absorption coefficients limit the final solar cell efficiency, while the complex synthetic routes of the best performing materials limit their economic viability. On a device level, the technology faces different issues related to limited thermal stabilities, as well as tandem fabrication difficulties, to name but a few.

This thesis explores three novel strategies focused on improving the overall efficiency of organic photovoltaic devices, specifically designed to increase light absorption, enhance charge carrier mobility and reduce thermalization losses. In order to tackle such an ambitious research program, we first developed a characterization platform that enabled us to measure organic photovoltaic devices in a highly reproducible manner and between 5 and 10 times faster than sequential methods. This platform consists in the combination of hardware and software that enables any user to characterize a photovoltaic device in a fully automated procedure reducing human errors, homogenizing the results amongst all different users, and saving a significant amount of time and effort. This platform is described in Chapter **??**, with further developments also included in other chapters. After this technological chapter, the thesis then details the three approaches to improve efficiency.

Chapter **??** demonstrates the incorporation of photonic structures within photovoltaic devices as means to increase absorption. Specifically, we show that the charge transfer state absorption of organic photovoltaic devices based on P3HT:$PC_{61}BM$ and PBTTT:$PC_{71}BM$, can be enhanced by nanostructuring their active layer in the shape of a 2D photonic crystal. This absorption enhancement results in an increased EQE, which is especially pronounced below the band gap of the blend. While the improvement is modest for solar cells, this technology results in high

performing infrared photodetectors.

Chapter **??** is based on the hypothesis that charge carrier mobility can be increased by raising photoactive material temperature. To evaluate this, we monitor solar cell performance as a function of active layer temperature. We show that the power conversion efficiency (PCE) is enhanced with temperature, and this effect is especially pronounced on thicker active layers, as one may expect if mobility was the limiting performance. We studied the performance of 10 different photoactive blends at different temperatures, noting that only some of those systems exhibit reversible changes with temperature. In order to understand this behaviour, we investigated in more detail devices made of PBDBT:ITIC, showing that this system has a temperature resistant microstructure and greatly improved charge transport at high temperatures, ultimately translated to better PCE. To perform these experiments, we designed and manufactured a custom experimental setup that is able to characterize our devices, while accurately controlling the active layer temperature.

Finally, the last two chapters demonstrate the feasibility of a, seemingly unexplored, tandem solar cell concept based on spectral splitting, which we named RAINBOW solar cell. This architecture combines a wavelength dispersive optical element and a monolithic in plane (c.f. stack in normal tandem) multi-cell layout with a discrete E_g gradient. In Chapter **??** we study this geometry from a theoretical point of view, performing simulations and calculations with ideal and real materials that establish the scaffolding of RAINBOW solar cell theory, as well as guidelines for material selection. While in Chapter **??** we build an experimental setup capable of characterizing and optimizing real RAINBOW solar cells. The calculations and real measurements are in good agreement, with RAINBOW solar cells providing up to 34% higher efficiency than the best performing sub-cell. As a final proof of concept, we developed partial deposition techniques to manufacture a fully functional monolithic horizontal tandem RAINBOW device.

Contents

Chapter 1

Thesis Conclusions and Perspectives

Abstract

This thesis has been devoted to organic solar cell efficiency enhancement, taking notably different approaches, from the development of basic manufacturing and characterization experimental setups, to the exploration of novel strategies focused on improving cell performance in various forms. Firstly, we have developed an entire characterization environment, capable of performing fast, reliable JV and EQE measurements in a highly automated way, as well as processing the generated data with integrated report generation. Secondly, we have explored the effect of active layer nanostructuring on the wavelength dependent response of organic solar cells and photodetectors, which resulted in higher light conversion efficiencies below the band gap of the photoactive material, arising from an increased charge transfer state absorption. Thirdly, we have investigated the effect of active layer temperature on organic solar cell efficiency, designing and building a temperature regulable JV characterization setup. Finally, we have devised a novel horizontal tandem architecture, based on spectral splitting and multi-material monolithic deposition, simulating and fabricating functional devices, as well as developing and building an entirely new experimental setup to characterize them.

1.1 Automation in OPV Characterization

In the first part of this thesis we have developed two experimental setups that accelerate, systematize and automate the characterization of various optoelectronic devices within our group, designed to be easy to assemble, reliable and to have a low cost, to enable implementation on any possible environment. The first is a JV characterization setup, consisting of a custom demultiplexing circuit board with 3D printed accessories, combined with a LabVIEW based orchestrating software that, together with an SMU, coordinates the entire JV characterization process, as well as the data processing and report generation. The second setup is a robotic EQE measurement system that is able to automatically perform multiple cell EQE measurements in a highly reproducible manner. This setup consists of a supercontinuum laser combined with a fully 3D printed XZ stage, and the previously developed demultiplexing board, all together being orchestrated through a powerful piece of LabVIEW software.

Even though during this thesis there has been a continuous process of optimization for both setups, they still have plenty of room for improvement. On one hand the database connectivity of the Pika demultiplexer is not fully implemented, still requiring some polishing with the automatic LabVIEW data input. Parallelly, the "Smart Mode" measuring option needs to be properly benchmarked, to fully make sure the results are as reliable as a normal JV curve sweep. On the other hand, as we can see in every experimental chapter, the EQE measurements performed with our current setup present a significant amount of ringing close to the UV wavelength range, caused by a slight missmatch between the power calibration wavelength and the measurement wavelength (¡1 nm). This can be easily solved by implementing the simultaneous measurement of the power and the cell, with a beam power sampler. Finally, the newest filter flipper version, using faster and stronger servo motors has not yet been implemented, being on the construction phase.

1.2 Enhancing OPV Performance with Nanoimprinted 2D Photonic Structures

In the following chapter we have explored the effects of active layer nanostructuring on both organic solar cells and organic photodetectors, based on different active layer blends. Regarding solar cells, the nanostructuring of P3HT:PC61BM blends resulted in an enhanced J_{sc} combined with lower FF, resulting in similar solar cell efficiencies for both nanostructured and flat devices, whereas for PBDB-T:ITIC the process was unsuccessful because of the additional plasticiser requirements.

On the other hand, we have reported a new organic photodetector architecture based on P3HT:PC61BM and PBTTT:PC71BM, capable of detecting photons with a wavelength significantly below the band gap of either of its active layer components, by enhancing CTS absorption. This CTS absorption enhancement was achieved by integrating photonic nanostructures within the photodetector's active layer via soft nanoimprinting lithography, a highly scalable roll-to-roll compatible technique, which increases the industrial appeal of the final device. Besides, by changing the nanostructure lattice parameter, we can change the CTS absorption wavelength range, allowing us to accurately tune the wavelength response range of our NIR photodetector.

The photodetectors resulting from this novel approach are interesting enough to perform a full exploratory study on the selected fabrication parameters, in order to fully understand their effect and how to optimize them. Additionally, it will be very interesting to apply this strategy to ultra-low band gap materials, to further push the limits of NIR photodetection in organic semiconductors. Besides, we also want to explore the feasibility of hot carrier injection with this configuration, driven by the strong electric fields present around the nanostructured back electrode/active layer interface.

1.3 Organic Solar Cells and Heat

In this chapter we have manufactured a temperature adjustable solar cell characterization setup, used to study the temperature dependence of a variety of organic solar cell materials. These materials exhibited three main behaviours upon thermal cycling: **permanent performance decrease** with increasing temperatures; **reversible performance decrease** with temperature; and **reversible performance increase** with temperature. Within the latter material group, focused on PBDBT:ITIC devices, which exhibited the greatest temperature dependent PCE enhancement.

Thermally cycling PBDBT:ITIC blends results in a PCE enhancement with an irreversible and a reversible component, with both experimental measurements and drift diffusion model simulations confirming that the reversible enhancement contribution can be attributed to an increased charge mobility in the active layer at higher temperatures. The lack of major changes in active layer morphology within the temperature measurement range suggests that irreversible PCE enhancement is related to a small change in the size of ITIC crystalline domains, driven by low temperature phase separation.[1–3] The resulting cells exhibit increased performances at high temperatures for every studied active layer thickness, with a more pronounced enhancement on thicker active layers. These results are relevant for large-scale roll-to-roll solar cell manufacturing, where inconsistent module performance due to thickness variations intrinsic to the manufacturing process, could be minimized by raising module temperature.[4]

This line of research is highly experimental, requiring significantly more profound and thorough exploration, with multiple materials and a higher number of samples to ensure result reproducibility. Besides, fabrication conditions seem to be a critical parameter for active layer temperature dependant performance, which require much more in depth investigations. On a different note, we also want to study the implementation of absorbing structures that raise the active layer temperature upon solar exposure. These include photonic structures, which connect this subject with the previous chapter, and infrared thermal absorbers, which relates this line of research to the beam splitting approaches explored on the following chapter. Additionally, it is necessary to study the effect of substrates with different thermal conductivity and heat capacity, which could help raise and maintain final active layer temperature upon illumination.

1.4 RAINBOW

In the last two chapters we have studied and developed a new solar cell tandem architecture, named RAINBOW solar cell, consisting of a horizontally laid solar cell tandem stack, with multiple graded band gap semiconducting junctions, illuminated with spectrally separated light. The main strength of this architecture is that the incoming light wavelength ranges closely match the band gap of the semiconductor being illuminated, minimizing the amount of unabsorbed photons below the band gap, and reducing thermalization losses associated to high energy photon absorption.

To begin with, we have created a python model that simulates the behaviour of two junction RAINBOW solar cells, providing us with insight on the general rules for material selection. Guided by the simulations, we have manufactured and characterized single junction devices using three suitable active layer blends, PM6:IO-4Cl, PM6:Y6 and PTB7-Th:COTIC-4F. The calculations obtained by feeding the measured EQE and JV curves to the developed algorithm, resulted in two functional RAINBOW combinations with a positive IoBC.

In order to properly characterize RAINBOW solar cells, we have developed an entirely new characterization setup, called SOLS, capable of carving the light spectrum of any light source into a custom spectral shape, by selectively modulating the intensity at each given wavelength. With this setup we have performed RAINBOW measurements by dividing the solar spectrum in two fractions through a precisely controlled dividing wavelength, resulting in partial RAINBOW sub-unit efficiency data that can later be combined to evaluate the RAINBOW tandem performance of a particular RAINBOW combination. Measurements performed with the SOLS setup on single junction devices are in good agreement with previously performed calculations, with similarly good IoBC in both RAINBOW combinations.

Finally, in order to fabricate a proof of concept RAINBOW device, we developed different partial substrate coverage deposition techniques based on blade coating and spin coating, with which we have manufactured two monolithic RAINBOW devices with positive measured IoBC, proving the feasibility of the RAINBOW concept.

These two chapters have opened up so many possibilities that the perspectives on this topic can get too broad. On the side of actual RAINBOW devices, we are already working on lateral deposition of real devices with blade coating, to prove the feasibility of the concept on a larger scale. Besides, there is an ongoing material study with as many combinations as we can manufacture. On the SOLS setup side, we are developing new embodiments that provide better wavelength and power resolution, with a combination of novel strategies. Parallelly, we are undergoing a patentability study to protect the custom spectral shaper, which seems to be a really powerful instrument, useful beyond our current application.

List of Tables

List of Figures

[1] , S. Marina, E. Gutierrez-Fernandez, J. Gutierrez, M. Gobbi, N. Ramos, E. Solano, J. Rech, W. You, L. Hueso, A. Tercjak, H. Ade, and J. Martin. Semi-paracrystallinity in semiconducting polymers. *Materials Horizons*, 9(4):1196–1206, 2022.

[2] , L. Ciammaruchi, O. Zapata-Arteaga, E. Gutiérrez-Fernández, J. Martin, and M. Campoy-Quiles. Structure dependent photostability of ITIC and ITIC-4F. *Materials Advances*, 1(8):2846–2861, 2020.

[3] , L. Yu, D. Qian, S. Marina, F. A. A. Nugroho, A. Sharma, S. Hultmark, A. I. Hofmann, R. Kroon, J. Benduhn, D.-M. Smilgies, K. Vandewal, M. R. Andersson, C. Langhammer, J. Martín, F. Gao, and C. Müller. Diffusion-Limited Crystallization: A Rationale for the Thermal Stability of Non-Fullerene Solar Cells. *ACS Applied Materials & Interfaces*, 11(24):21766–21774, 6 2019.

[4] , F. C. Krebs, T. Tromholt, and M. Jørgensen. Upscaling of polymer solar cell fabrication using full roll-to-roll processing. *Nanoscale*, 2(6):873, 2010.