In this chapter we will explore how the structural morphology of organic solar cells and organic photodetectors, more specifically their active layer and back electrode nanostructure, can modify their spectral response as well as their overall performance. We will mainly focus on nanostructured near infrared organic photodetectors.

Organic solar cells and photodetectors exhibit rather poor carrier mobilities, with short diffusion lengths, which often lead to poor charge separation on the active layer. This phenomenon forces the active layers of such devices to be thinner than other photovoltaic technologies to ensure proper charge extraction. However, thinner layers compromise the ability of the active layer to absorb light further hindering the device performance. This thickness trade-off has been one of the major Achilles heels for OPV since the origins of the field.

This problem has been addressed from several perspectives from enhanced charge extraction layers and higher charge mobility active materials to ferroelectric polarization of the active layer to further drive charges to their corresponding electrodes. However, one of the most attractive approaches is to utilize some form of light trapping to enhance the active layer absorption with an optical approach.

In this work we decided to follow this route to breach the gap between absorption and thickness by harvesting the power of photonics and light coupling. The main hypothesis is that, if we can in couple the light into the active layer the light path through the active layer will become much longer, endowing the device with a much higher effective absorption. All that without having to sacrifice on electrical performance due to a thicker active layer.

4.1 Photonics in Photovoltaics; State of the Art

When we talk about photonics in photovoltaics there are generally two main schools of thought or approaches typically exploited. The first one is focused on increasing overall performance and absorption. This approach tends to be more of a broadband approach, less wavelength dependant and more cantered on the overall absorption of light. This approach would include anti reflection coatings, (FICAR MES COSES QUE VAGIN A AQUEST APPROACH). This approach is much more widely seen in organic solar cells, even though it is also somewhat present in organic photodetectors.

On the other hand, we have the wavelength selective approach. This approach is more focused on finely selecting the spectral response, with a narrower bandwidth and less centered in overall performance. This approach includes fabri perot resonators, color filters, periodic nanostructure (POSAR MES COSES QUE VAGIN A AQUEST APPROACH). This approach is much more widely seen in organic photodetectors.

* 1. Nanostructured Solar Cells

Lots of different approaches that rely on various light trapping mechanisms induced by nanostructures in OPVs have been reported in the past years. Arguably, the most straight forward and less invasive approach, is to introduce an out- of-cell antireflective microstructure on the front side of the substrate or transparent electrode. This has proven to be a direct method to enhance light harvesting via reduction of reflective losses. On the other hand, more complex in-cell nanostructures as well as nanomaterials have also been studied as a strategy to further concentrate and amplify light absorption within the photoactive layer. These include metal nanostructures or nanomaterial-induced plasmonic scattering, surface plasmon polariton effects and localized surface plasmon resonance effects. Another approach is to construct OPV devices with microcavities, optical spacers and distributed Bragg reflectors, to optimize the optical field distribution and improve the efficiency of OPVs.

In this work we have attempted to modify the active layer and the back electrode of an organic solar cell into a photonic crystal as a light trapping mechanism. This 2D photonic nanostructure consists of a periodic structure that in couples the incoming light into the active layer, enhancing the optical path thus rendering higher absorption efficiencies.

4.3 Nanostructured NIR Photodetectors

Currently, NIR photodetector technologies are based on the combination of regular silicon or, to a lesser extent, III–V (InGaAs) photodetectors with colour filters or gratings. However functional and reliable, such wafer-based approaches, fail to satisfy the new demands for wearable, cheap and flexible devices. That is why, appealing alternatives are emerging such as organic photodetectors (OPDs), which are flexible, have low embedded energy processing and are highly compatible with available and easily scalable techniques such as roll to roll processing. On top of that, the composition of organic polymers and/or small organic molecules, can be chemically tuned to provide a variety of absorption ranges, further increasing the appeal of organic photodetectors.

Chemical tailoring of organic molecules has worked well within the visible range, however extending OPD wavelength response towards the NIR range while maintaining device performance still remains quite a challenge. A variety of polymers and small molecules with a smaller bandgap that goes deeper into the infrared region are being synthesized. Nevertheless, manufacturing these exotic materials is a resource intensive process, taking a lot of effort and costing a lot of money, further reducing their potential to be used in real devices. On top of that, each new molecule is developed for a specific wavelength range, which means that a lot of new molecules have to be synthesized to cover the entire spectrum.

Parallelly, a branch of research has been trying to extend and increase OPD response on the NIR region by using inexpensive, readily available materials. Instead of focusing on tuning the intrinsic absorption of the material itself, this research has focused on alternative strategies to increase OPD response within the NIR region. One simple yet powerful approach consists in taking advantage of the filtering effect in thick polymer layers, also known as charge collection narrowing. With this effect we can obtain narrow peaks with high external quantum efficiencies in the NIR region. There is, however, a downside to this approach, which is that it relies on the intrinsic absorption of the active layer materials so it still requires low bandgap molecules to go deeper into the NIR. Another elegant alternative consists in taking advantage of the direct intermolecular charge transfer state (CTS) absorption, to extend the OPD wavelength response far into the NIR region without the need of any low bandgap material. The CTS is the state that results from the interaction between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor. This state is only present at the donor–acceptor interface, where the electronic orbitals with different energies come together to form a new, intermediate state. This newly created state usually exhibits a lower transition energy than its composing states for a type II heterojunction, such as typical donor/acceptor blends. To put it simply, the energy levels form a step like shape as can be seen in figure x. The CTS lower transition energy endows the blend with the possibility of absorb light with longer wavelengths than each of its separate components.

Because it is mainly localized within the donor acceptor interface CTS absorption strength is strongly dependant on molecular intermixing. Unfortunately, the latter is around two orders of magnitude lower than singlet absorption strength due to the fact that it is an intermolecular state. This intrinsically low oscillator strength often demands for the use of very thick active layers at high reverse voltages in order to guarantee light absorption and extract the generated charges. For traditional device architectures, in order to increase the absorption of the CTS, active layer thicknesses must be increased enormously (up to tenths of microns). This requires applying biases of up to hundreds of volts to extract charges efficiently. Aiming to avoid such high voltages and thick layers, research has focused on light trapping schemes in search for an interesting alternative to greatly enhance CTS absorption.

A recent development in the field of CTS absorption enhancement is the use of metal cavities, which has led to impressive OPD photoresponse. These have pushed OPD response far beyond the bandgaps of the composing materials with significant EQE responses of around 20-40%. Not only do they achieve high EQE values significantly below the band gap of the composing materials, but by accurately controlling the cavity dimensions, basically by modifying the thickness of the electrodes and the active layer, the detection wavelength can be finely tuned. Even though optical microcavity based devices show remarkable performances, the nature of the cavity device makes the resonant frequency critically dependant on film thickness. That is why these devices will, most likely, not be compatible with techniques such as roll to roll, in which thickness usually fluctuates within a certain tolerance.

In this work, inspired by the micro-cavity devices, we have explored a device configuration that enhances CTS absorption by Nanostructuring the active layer and the back electrode with the shape of a photonic crystal. Photonic crystals are not an entirely new concept within photovoltaics, as some major accomplishments have been achieved already by nanostructuring photovoltaic devices. More specifically, 2D photonic crystal periodic structures have been used to diffract incident light and enhance the optical path within the active layer and increasing overall efficiencies. In this thesis we developed a photodetector with a nanostructured active layer and a back-electrode. This nanostructure consists of a 2D photonic crystal periodic structure, engineered to couple incident light to photonic modes with enhanced electric field concentration in the photoactive medium within the wavelength range of the CTS absorption of our materials. In order to fulfil real application requirements, our devices have been mainly fabricated with low cost active layer materials, using inexpensive and scalable techniques such as blade coating for the photodetector manufacturing and nanoimprinting soft lithography for active layer nanostructuration. Our devices are based on a bulk heterojunction (BHJ) architecture, consisting of an electron donor PBTTT or P3HT and an electron acceptor PC71BM or PC61BM. We have been able to easily and seamlessly nanostructure these active layers via soft nanoimprinting lithography, leading to an increased EQE response from 750 to 1000 nm and from 775 to 1075 nm, for P3HT:PC61BM and PBTTT:PC71BM, respectively. This photoresponse increase can be attributed to the absorption of the CTS, since it is significantly beyond the band gap of the active layer. We also used different nanostructure lattice parameters to select the wavelengths where the absorption would be enhanced, providing us with wavelength response tunability on the NIR region.

Finally, we demonstrated that, in our devices, enhanced photodetection wavelengths are thickness independent within a certain range. This means that processing tolerances can be higher, making this device attractive for further development and commercialization. In summary, the designed light trapping configuration implemented enables us to use inexpensive organic materials for photodetection into the NIR with minimal disruption of the fabrication process and where the nanostructuring step does not negatively affect the electrical performance of the photodetector.

* + 1. Materials

The OPD active layer was composed of either P3HT:PC61BM or PBTTT:PC71BM BHJ blends. These materials were chosen because of several reasons: first, they are really affordable and widely available materials, which makes them appealing for further development and upscaling; second, these specific combinations show a significant CTS absorption tail that extends into the NIR region, which means that we can enhance this absorption, and extend the response of the devices beyond their individual band gaps; and third, their high carrier mobilities allow us to deposit thicker active layers, which is an essential aspect to make the most out of the CTS low absorption coefficient.

First, we deposited the electron transport layer (ETL) from a ZnO nanoparticle solution on an ITO covered glass substrate by blade coating, a technique often used as a pre-upscaling method as we have discussed on chapter (). After annealing the ZnO film to remove the solvent and settle the structure, we deposited a thick layer of active material with the same technique. After the active layer had dried, we nanostructured it via soft nanoimprinting lithography. With this reliable technique we did not require the usage of a cleanroom, yet we could produce extensive nanostructured areas with high fidelity and reproducibility as discussed in chapter ().

The nanostructure is composed of an array of cylindrical pillars that collectively act as a diffraction grating, in coupling light into propagating modes within the active layer. With Finite-Differences Time-Domain method (FDTD) we were able to engineer the optimal photonic structures for our photoactive materials while we got useful insights about light propagation within the device. As a result of our simulations we decided that array lattice parameters (L) of 400, 500 and 600 nm (from now on also referred to as L = 400, L = 500 and L = 600) were the most interesting ones to study. That is because their first order of diffraction is inside the range of absorption of the CTS of our active materials. This in coupling phenomenon provides efficient light trapping within a specific range of NIR frequencies below the band gap of the active layer materials, by selectively enhancing CTS absorption.

On top of the nanostructured active layer a 10 nm thick MoO3 layer was deposited by thermal evaporation. The thickness was set so that it was enough to have a uniform film, without any pinholes and good charge blocking characteristics while maintaining the diffractive behaviour of the photonic crystal. As the last layer, we deposited a thick 200 nm Ag back electrode contact also by thermal evaporation and we performed a thermal annealing to increase the active layer crystallinity. The back electrode, being deposited onto the nanostructured active layer, adopted the shape of the nanostructure which provided the sample with a strong optical response.

* + 1. Nanostructure Optimization

The first problem we encountered with nanostructured photodetectors were that they exhibited really high dark currents when we applied a reverse voltage bias. These were orders of magnitude higher than their flat, non-nanostructured, equivalent photodetectors. These posed a serious problem because photodetector performance is highly dependant on dark currents. Higher dark currents lead to higher noise levels which lead to lower signal to noise ratio and an overall reduced photodetector sensitivity.

We believe that this dark current increase on the nanostructured devices was mainly due to the introduction of pinholes in the hole transport layer. These pinholes would arise from the non-isotropic nature of the thermal evaporation process. As we have discussed on chapter () thermal evaporation is a highly anisotropic process, where there is a clear preferential deposition direction. This means that the deposited thickness at any given point will depend on the angle between the sample and the evaporation source. For a flat sample, if placed far enough from the evaporation source, the angle between the sample and the evaporation source will be 0. This leads to a uniform thickness over the entire sample. However, if the sample is nanostructured with pillars, the pillar sides will be at almost 90º with respect to the evaporation source, greatly hindering the deposition capabilities on those areas. Furthermore, if the pillars are significantly taller than the deposited thickness, and nothing else is changed, a non-conformal coating is almost guaranteed. When we combine this non-conformal coating with the subsequent deposition of a thick back electrode metal deposition that is thick enough to completely cover everything, we end up with a situation where the back electrode is in direct contact with the active layer through the pillar sidewalls leading to extremely high dark currents.

In order to reduce the dark currents caused by the nanostructuring process we followed several approaches. The first, and easiest one was to study the thickness of the hole transport layer. In theory a thicker transport layer should be able to more conformally cover the nanostructured active layer surface, since a thicker layer has higher chances of completely covering the pillar walls. And as we see in figure X the dark currents become significantly lower with thicker HTL. However, the big drawback of this approach is that we hinder both the electrical and optical performance of the device. First the electrical response is hindered because we are adding a thick poorly conducting layer on our device. Granted it is selecting the charges, but the low electrical conductivity is also lowering the chance of charge extraction. On the other hand, it is also hindering optical performance due to the fact that depositing a thick HTL leaves a smoother surface for the back electrode. This smoother surface leads to a shallower nanostructure on the back electrode, which is directly related to a lower overall optical response.

Another approach that we briefly tried to explore was to use a fully metallic HTL trying to make a Schottky barrier. When a metal is placed in electrical contact with a semiconductor the fermi level of the semiconductor and the work function of the metal will align. If the metal work function is low enough, the semiconductor bands will bend upwards creating an electron barrier where the holes will be the major contributors to overall device current. We decided to use gold, as it has one of the lowest work functions of all metals and it can be easily deposited by thermal evaporation. In terms of external quantum efficiency, the device performance was quite good, but again the dark currents were still too high because the Schottky barrier was not efficient enough at selecting the charges. We could see this because dark currents were really high for both flat and nanostructured photodetectors.

The final approach, and the one that gave the most desirable results, was to lower the nanostructure depth. By using RIE on our existing soft lithography stamps, as described in chapter 2.2.3.1 we were able to manufacture a couple of nanostructured stamps with shallower features. With these shallower stamps we performed a study to check the dark currents at different nanostructure feature depth and we saw that for shallow nanostructures, the optical response was more or less maintained, while the dark current was dramatically decreased down to the same dark current levels as the flat equivalent photodetectors. We decided to keep using the shallower nanostructure to further develop our photodetectors, since it provided good electrical and optical properties.

* + 1. Simulations

In order to calculate the potential enhancement of the CTS absorption we decided to perform some optical simulations for our photodetector device. These simulations were performed using Finite-Differences Time-Domain method (FDTD) by my fellow colleague, Dr. Molet.

The simulations consist of two full device layer stacks, one with a shallow 60 nm nanostructure and the other without any nanostructure at all. The lattice parameter we chose for the simulations was L500 because it was located in the middle of our range and the expected enhancement fell not too far nor too close from the absorption tail of our materials.

We can see in the simulations that the calculated absorption spectrum of the L = 500 nm PBTTT:PC71BM will show a series of peaks around 900 nm that correspond to the resonance modes seen in figure x. These peaks are in good agreement with the measured external quantum efficiency that we will see in the following chapter, confirming the effect of the photonic architecture within our device. We also examined the spatial distribution of the electric fields at the wavelengths of maximum response, which correspond to resonant modes. The electric field distribution at 862 nm and 907 nm is represented for both the nanostructured and the flat devices. In the planar device, the electric field presents a standard plane wave distribution, while in the nanostructured devices a diffraction pattern appears inside the active layer with field enhancements of around 6 times the incident power. This leads to the conclusion that the enhanced optical path in the active layer, caused by the diffraction modes of the nanostructure, provides a higher CTS absorption at the selected wavelengths.

* + 1. Active layer Thickness

Another important aspect to be studied is the active layer thickness of our photodetectors. This thickness will affect both electrical and optical performance of our devices, so we decided to perform a simple study on both systems to determine a more or less optimal thickness.

In order to perform correctly within the NIR region we need to be able to absorb light in that region. However as stated before, the absorption strength of the CTS is really low when compared to the singlet absorption strength. This means that, in order to efficiently absorb light in the NIR region we will most likely need active layers that are thicker than in regular organic photodetectors. However, since charge mobility of organic semiconductors is not really high, we can not make extremely thick active layers without sacrificing on electrical performance. In this work we compared a variety of active layer thicknesses to compare both their optical and electrical performance in order to select a, more or less optimized thickness range to work with. This is by no means a full optimization process but rather an exploratory study.

The active layer thickness is also strongly correlated with the dark current since thicker layers will provide a better charge separation.

In thicker layers, the majority of visible light is absorbed within the top surface of the active layer, hence most charge generation occurs there. However, since all those generated charges are far away from the back electrode, most just recombine and do not contribute to the overall current. For NIR light however, since the absorption is much lower, the light is more evenly distributed throughout the active layer, which leads to more homogeneous charge generation. These charges are more effectively extracted since they are not highly localized. This is the phenomenon known as charge collection narrowing, further described by (FICAR AUTOR)

We see that the optimal thickness is not the same for different materials, mainly due to differences in charge mobility and index of refraction. Materials with higher charge mobilities will benefit from thicker active layers to absorb more light, while materials with higher refractive indices will be able to in couple the light more effectively. We define as “optimal thickness” the thickness at which the NIR range EQE enhancement is maximized. At lower active layer thicknesses, light does not travel long enough through the active layer to get absorbed, while at higher thicknesses the overall lowering of the electrical response hinders device performance completely erasing any enhancement provided by the 2D photonic crystal. With this we find a sweet spot around xnm for the P3HT:PC61BM and ynm for the PBTTT:PC71BM where device performance is maximized in the NIR region.

A very interesting result from this experiment is the fact that the enhancement peak position is not significantly affected by active layer thickness. This is more important than it might seem, since it means that these devices are really robust against thickness variations, making them really appealing for the industry, where higher manufacturing tolerances lead to overall cost and effort reduction. This is in opposition to the cavity devices on which our devices are inspired where thickness tolerances are extremely tight and few nanometres completely change the peak wavelength.

* + 1. Annealing

To obtain the highest performing organic photodetectors we performed a very brief study to asses the effects of different annealing temperatures on our device performance. While all ETL were annealed as a part of the optimized deposition procedure, the active layers annealing conditions had not been previously optimized, especially for such high thicknesses where mobility plays a more important role. Sample annealing is usually performed to improve device performance or stability through selective recrystallization. This can be done in several ways but the most typical are solvent annealing, where the material is partially redisolved in a solvent vapour to redistribute its components, or thermal annealing where the same redistribution is achieved by thermal agitation. In both cases what we achieve is a change in the crystalline phases of the material, that, if done right, improves some aspect of our final device.

In this work we mainly worked with thermal annealing since it is really simple and can be applied to encapsulated samples. As we can see in figure x the performance is significantly affected upon sample annealing. However, hotter is not always better, as represented in the plot, higher temperatures ultimately cause device performance to drastically drop indicating an unfavourable recrystallization. This is because in a BHJ a certain degree of amorphous well intermixed phases is desirable to ensure charge separation.

We decided to anneal our devices for x minutes at xºC, parameters which provided satisfactory performances for our devices. I want to stress, however, that this was not at all an extensive study and further optimization is not only possible but desirable.

4.4 Optical and Structural Characterization

In order to assess the optical performance of our devices as well as the reliability of our nanoimprinting method we decided to use mainly two characterization techniques that provided some insight on device optical and topographical characteristics. The first one is FTIR spectroscopy, which is a really powerful technique that is used to measure transmission and reflection spectra, further described in chapter 2.3.2.1. The other one is SEM characterization, which provides very detailed topographical information about the sample and its different layers. This technique is further described in chapter 2.3.3.1.

4.4.1 FTIR Spectra

The spectra obtained from the different flat and nanostructured devices clearly indicates that the optical properties are significantly different. Even though this difference is apparent already with the naked eye (see figure x), it only becomes more pronounced when we observe the absorption spectra for the different lattice parameters. As we can see in figure x, the difference between flat and nanostructured devices is abysmal, especially on the NIR region where we engineered our photonic crystals to absorb.

Not only do we have impressive absorption peaks, but they also behave as expected, where the largest layer parameter (L600) absorption peak is further into the infrared, while L400 is much closer to the visible. We can also see the second absorption order for L600 starting to appear close to the visible.

4.4.2 SEM Images

The topology pictures obtained with the SEM confirmed that the nanoimprinting lithography was reliable and reproducible. As we can see, the nanostructure is practically perfectly reproduced on both the active layer and the back electrode. These structures exhibit a continuous cylinder pattern with virtually no imperfections.

SEM cross-section images provide a lot of insight into the layer composition and thickness. As we can see in figure x the layers are not only clearly defined, but the nanostructure is really visible and easily identifiable on both the active layer, and the back electrode, with the thin HTL being sandwiched in the middle. Wit these cross-section images we could also examine the effect of different nanostructure depths, providing a lot of information about pinhole formation on the HTL as we discussed in chapter 4.3.

* 1. Electrical Characterization

A wide variety of experimental setups have been used to fully characterize our photodetectors, within the possibilities of our facilities. In this chapter we explore a variety of techniques focused on, but not strictly specific to, photodetector electrical characterization. With these techniques we can assess our device performance in a variety of measurables that, when combined, determine the quality of our devices. The techniques mainly revolve around light to electron conversion, where we shine our photodetector with a source of light and measure the outcome. As we will see, techniques differ on the illumination wavelength range, intensity, measurement area and some more parameters that can be varied to obtain all the possible information from our photodetector.

4.5.1 EQE Curves