Nanoscale Light Manipulation for Improved Organic Solar Cells

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Declaration

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“Nothing in the world is worth having or worth doing unless it means effort, pain, difficulty… I have never in my life envied a human being who led an easy life. I have envied a great many people who led difficult lives and led them well.”

Theodore Roosevelt
Abstract

Organic Solar Cells can be made to be flexible, semi-transparent, and low-cost making them ideal for novel energy harvesting applications such as in greenhouses. However, the main disadvantage of this technology is its low energy conversion efficiency (<15%); mostly due to high recombination rates, compared with other higher performing technologies, such as thin-film GaAs (>30% Efficiency), and Si-based (>20% Efficiency), solar cells, where recombination within these technologies is much less than Organic Solar Cells. There are still many challenges to overcome to improve the efficiency of Organic Solar Cells. Some of these challenges include: Maximising the absorption of the solar spectrum; improving the charge dynamics; and increasing the lifetime of the devices.

One method to address some of these challenges is to include plasmonic nanoparticles into the devices, which has been shown to increase the absorption through scattering, and improve the charge dynamic through localised surface plasmon resonance effects. However, including nanoparticles into Organic Solar Cells has shown to adversely affect the performance of the devices in other ways, such as increasing the recombination of excitons. To address this, an additional (insulating) coating around the nanoparticles supresses this increase, and has shown to be able to increase the performance of the solar cells.

In this work, we demonstrate the use of our all-inclusive optical model in the design and optimisation of bespoke colour-specific windows (i.e. Red, Green, and Blue), where the solar cells can be made to have a specific transparency and colour, whilst maximizing their efficiency. For example, we could specify that we wish the colour to be red, with 50% transmissivity; the model will then maximise the Power Conversion Efficiency. We also demonstrate how our extension to Mie theory can simulate nanoparticle systems and can be used to tune the plasmon resonance utilising different coatings, and configurations thereof.
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A very close friend of mine said to me in the first year: "What are you doing to yourself, don’t do it, quit while you can!". This just motivated me further, and he has been there every step of the way since, so thank you Nasser Haddad.

I have constantly been mocked in the past about my so-called ‘un-realistic’ dreams and goals. Some of these people have also attempted to purposefully sabotage my progression. There have been several times during my journey where I have doubted myself based on these people’s opinions. However, there have also been many who have believed in me, and supported and encouraged me and my decisions. Therefore, I would like to thank Dave Smith, Nasser Haddad, Louis Christodoulou, Mark Langdrige, Dimitar Kutsarov, and more recently Martin Joseph. Furthermore, Raymond and Stella Fisher, my grandparents, have been the most consistent, strong, and stable part of my life, supporting and guiding me through many difficult times, every step of the way.

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permission from Bastús et al.[174]. Copyright 2015 American Chemical Society. (bottom) Au
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permission from Bastús et al. [130]. Copyright 2011 American Chemical Society. .......... 103

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<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>Absorption</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>AM*</td>
<td>Air Mas (* is a number for the standard)</td>
</tr>
<tr>
<td>BE</td>
<td>Back Electrode</td>
</tr>
<tr>
<td>BHJ</td>
<td>Bulk Hetero-Junction</td>
</tr>
<tr>
<td>CIE</td>
<td>International Commission on Illumination</td>
</tr>
<tr>
<td>DSSC</td>
<td>Dye-Sensitised Solar Cells</td>
</tr>
<tr>
<td>EQE</td>
<td>External Quantum Efficiency</td>
</tr>
<tr>
<td>ETL</td>
<td>Electron Transport Layer</td>
</tr>
<tr>
<td>FDTD</td>
<td>Finite-Difference Time-Domain</td>
</tr>
<tr>
<td>FEM</td>
<td>Finite Element Modelling</td>
</tr>
<tr>
<td>FF</td>
<td>Fill Factor</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>HR-TEM</td>
<td>High Resolution – Transmission Electron Microscopy</td>
</tr>
<tr>
<td>HTL</td>
<td>Hole Transport Layer</td>
</tr>
<tr>
<td>ICC</td>
<td>International Colour Consortium</td>
</tr>
<tr>
<td>IQE</td>
<td>Internal Quantum Efficiency</td>
</tr>
<tr>
<td>LSOPR</td>
<td>Localised Surface Plasmon Resonance</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>MRI</td>
<td>Magnetic Resonance Imaging</td>
</tr>
<tr>
<td>NIR</td>
<td>Near Infra-Red</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticle</td>
</tr>
<tr>
<td>NREL</td>
<td>National Renewable Energy Laboratory</td>
</tr>
<tr>
<td>NW</td>
<td>Nanowire</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic Light Emitting Diode</td>
</tr>
<tr>
<td>OSC</td>
<td>Organic Solar Cell</td>
</tr>
<tr>
<td>Symbol</td>
<td>Brief Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------------------</td>
</tr>
<tr>
<td>$E_i, E_r, E_t$</td>
<td>Incident, Reflected, and Transmitted energy.</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Band Gap Energy</td>
</tr>
<tr>
<td>$V_{OC}$</td>
<td>Open Circuit Voltage</td>
</tr>
<tr>
<td>$J_{SC}$</td>
<td>Short Circuit Current Density</td>
</tr>
<tr>
<td>$G_{opt}$</td>
<td>Exciton Generation Rate</td>
</tr>
<tr>
<td>$J_m$</td>
<td>Current Density at the Maximum Power Point</td>
</tr>
<tr>
<td>$V_m$</td>
<td>Voltage at the Maximum Power Point</td>
</tr>
<tr>
<td>$P_{tot}$</td>
<td>Total Spectral Irradiance (Integral)</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>$P_{AM1.5}$</td>
<td>Solar Spectrum Irradiance</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Efficiency</td>
</tr>
<tr>
<td>$I_{AM1.5}$</td>
<td>Intensity of the Solar Spectrum</td>
</tr>
<tr>
<td>$\varepsilon_m$</td>
<td>The complex permittivity of a metal.</td>
</tr>
<tr>
<td>$\varepsilon_d$</td>
<td>The complex permittivity of a dielectric material.</td>
</tr>
<tr>
<td>$\theta_0$</td>
<td>Incident angle from an incident source.</td>
</tr>
<tr>
<td>$d$</td>
<td>A distance or spacing.</td>
</tr>
<tr>
<td>$\beta_{spp}$</td>
<td>Surface Plasmon Polariton Propagation Constant</td>
</tr>
<tr>
<td>$k_x$</td>
<td>Wave-vector travelling in the $x$ direction.</td>
</tr>
<tr>
<td>$k_0$</td>
<td>Incident wave-vector traveling at an incident angle.</td>
</tr>
<tr>
<td>$r$</td>
<td>Radius</td>
</tr>
<tr>
<td>$\alpha_p$</td>
<td>Polarizability of a sphere.</td>
</tr>
<tr>
<td>$E_{sca}, E_{abs}, E_{inc}$</td>
<td>Scattering, Absorption, and Incident Electric Field Vectors</td>
</tr>
<tr>
<td>$H_{sca}, H_{abs}, H_{inc}$</td>
<td>Scattering, Absorption, and Incident Magnetic Field Vectors</td>
</tr>
<tr>
<td>$S$</td>
<td>Poynting Vector ($E \times H$)</td>
</tr>
<tr>
<td>$C_{sca}, C_{abs}, C_{ext}$</td>
<td>Scattering, Absorption and Extinction Cross Sections</td>
</tr>
<tr>
<td>$x, y$</td>
<td>(Mie) Size Parameters (ratio)</td>
</tr>
<tr>
<td>$Q_{sca}, Q_{abs}, Q_{ext}$</td>
<td>Scattering, Absorption, and Extinction Efficiencies</td>
</tr>
<tr>
<td>$W_{sca}, W_{abs}, W_{ext}$</td>
<td>Scattering, Absorption, and Extinction Energy Rates</td>
</tr>
<tr>
<td>$J_v(z)$</td>
<td>Bessel function of the first kind</td>
</tr>
<tr>
<td>$\theta_i, \theta_r, \theta_t$</td>
<td>Incident, Reflected and Transmitted Angle</td>
</tr>
<tr>
<td>$I_{jk}$</td>
<td>(TMM) Interface Matrix for an interface between layer $j$ and $k$.</td>
</tr>
<tr>
<td>$\tilde{n}_k$</td>
<td>Complex refractive Index of material $k$.</td>
</tr>
<tr>
<td>$n$</td>
<td>Real part of complex refractive index.</td>
</tr>
<tr>
<td>$k$</td>
<td>Imaginary part of complex refractive index.</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Permeability (mathematical), or mean (statistical).</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$r_{jk}$</td>
<td>Fresnel reflection coefficient at an interface between layers $j$ and $k$.</td>
</tr>
<tr>
<td>$t_{jk}$</td>
<td>Fresnel transmission coefficient at an interface between layers $j$ and $k$.</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Refractive index of non-absorbing material (no imaginary part).</td>
</tr>
<tr>
<td>$\theta_c$</td>
<td>Critical angle.</td>
</tr>
<tr>
<td>$S$</td>
<td>Scattering Matrix</td>
</tr>
<tr>
<td>$E^+_{jR}$</td>
<td>Electric field in the right (R) side of the layer $j$ travelling in the forward (+) direction.</td>
</tr>
<tr>
<td>$L_j$</td>
<td>(TMM) Layer Matrix.</td>
</tr>
<tr>
<td>$d_j$</td>
<td>Thickness of the $j$th layer.</td>
</tr>
<tr>
<td>$\beta_j$</td>
<td>The Phase within the $j$th layer.</td>
</tr>
<tr>
<td>$S'_j$</td>
<td>Sub-scattering matrix to the left (') of layer $j$.</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>(TMM) Correction factor for incoherent glass. (Mie) Correction factor for absorbing surrounding medium.</td>
</tr>
<tr>
<td>$\bar{S}, \bar{I}, \bar{L}$</td>
<td>Intensity form of scattering, interface and layer matrices.</td>
</tr>
<tr>
<td>$U^+_{kl}$</td>
<td>Intensity of the electric field at the left ($L$) of the $k$th layer travelling in the backwards direction ($-$)</td>
</tr>
<tr>
<td>$s_t, s_r$</td>
<td>Fresnel scattering coefficients for a surface ($t$) and interface ($r$).</td>
</tr>
<tr>
<td>$\sigma_{RMS}$</td>
<td>Root Mean Squared surface roughness.</td>
</tr>
<tr>
<td>$\phi_{rand}$</td>
<td>Random number from a normal distribution.</td>
</tr>
<tr>
<td>$H^+_{jR}$</td>
<td>Magnetic field in the right (R) side of the layer $j$ travelling in the forward (+) direction.</td>
</tr>
<tr>
<td>$Q$</td>
<td>(TMM) Time averaged energy dissipation</td>
</tr>
<tr>
<td>$P$</td>
<td>(TMM) Power Dissipation</td>
</tr>
<tr>
<td>$\hat{f}$</td>
<td>Directional unit vector.</td>
</tr>
<tr>
<td>$a_n, b_n$</td>
<td>(Mie) Amplitude coefficients.</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------------------</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Absorption Coefficient</td>
</tr>
<tr>
<td>$N_d$</td>
<td>Number density</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Standard Deviation (statistics)</td>
</tr>
<tr>
<td>$\delta r$</td>
<td>Change in radius</td>
</tr>
<tr>
<td>$X_n, Y_n$</td>
<td>(Mie) Logarithmic derivatives of the Ricatti-Bessel functions.</td>
</tr>
<tr>
<td>$\zeta_n, \psi_n$</td>
<td>(Mie) Ricatti-Bessel functions.</td>
</tr>
<tr>
<td>$N$</td>
<td>Number of elements.</td>
</tr>
<tr>
<td>$\pi_n, \tau_n$</td>
<td>(Mie) Radial functions.</td>
</tr>
<tr>
<td>$P_n^1(\theta)$</td>
<td>(Mie) Legendre Polynomial of the first degree.</td>
</tr>
<tr>
<td>$i_n(\theta)$</td>
<td>(Mie) Angular intensities.</td>
</tr>
<tr>
<td>$S_n(\theta)$</td>
<td>(Mie) Scattering functions.</td>
</tr>
<tr>
<td>$r_{eq}$</td>
<td>Equivalent radius of an arbitrary particle.</td>
</tr>
</tbody>
</table>

**List of Constants**

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plank’s Constant</td>
<td>$h = 6.62607004 \times 10^{-34}$</td>
<td>J/s</td>
</tr>
<tr>
<td>Reduces Plank’s Constant</td>
<td>$h = 1.0545718 \times 10^{-34}$</td>
<td>J/s</td>
</tr>
<tr>
<td>Speed of Light</td>
<td>$c = 2.99792458 \times 10^8$</td>
<td>m/s</td>
</tr>
<tr>
<td>Permittivity of Free Space</td>
<td>$\varepsilon_0 = 8.5418782\times10^{-12}$</td>
<td>F/m</td>
</tr>
</tbody>
</table>
Chapter 1

1. Introduction

1.1. Organic Solar Cells

Organic Solar Cells (OSCs) are an emerging photovoltaic (PV) technology, with some niche application areas. They can be made to be flexible, semi-transparent, low-cost, and lightweight, making them suitable for applications in windows [1], [2]. They also have a low environmental impact and the fabrication techniques can be scaled, such as roll-to-roll techniques [3]. However, their efficiencies are generally much lower than other types of PV technology, with reported efficiencies reaching up-to 13.2% for a triple-junction cell [4]. One such niche application is in greenhouses [5], where semi-transparent OSCs can be utilised to harvest a portion of the incident energy, whilst still allowing crops to grow. Another niche application would be energy harvesting from windows in office buildings, where modern buildings have large glass coverage [6]. If the efficiencies of OSCs are improved, and the cost of production driven down, then the technology could compete with other technologies on a cost/unit energy scale. We discuss some of these applications in more depth in Chapter 4.

Error! Reference source not found. demonstrates the progress of different PV technologies over time as of 2017, which have been confirmed under the AM1.5 standard measurements (explained further in Chapter 2). The highest performing confirmed OSC efficiency, as reported by NREL [7], is currently 11.5% (11.7% [8]), which was the result of the design of a novel low band-gap donor material and the use of improved processing techniques. Green et al. [9] have reported that the current highest performing single-junction device is by Toshiba at 11.2% (11.5% [10]). This was due to the design of a novel low-bandgap donor material and the use of band matching hole transport material, which they have not disclosed.
Figure 1.1: Solar cell efficiency table showing all types of photovoltaic devices. The emerging technology, such as DSSC and OPVs, are given by a red colour (circled) in the bottom right of the graph. The highest OPV is 11.5% held by Hong Kong UST [7].
Beyond the confirmed power conversion efficiencies, Heliatek have demonstrated a 13.2% OSC, based on a triple-junction [4]. This is constructed of 3 active layers, which absorb different parts of the solar spectrum. Tandem and Ternary cells are one way to increase the efficiency of the devices, however it also increases the cost and complexity of fabrication.

The highest efficiency for mini-modules is currently held by Toshiba (9.7% [10]), where they demonstrate a novel structure that improves the overall fill factor of the module. The development of novel materials and techniques are paramount for achieving more efficient OSCs.

### 1.2. Limitations and Challenges

Unlike some other types of PVs, OSCs suffer from high recombination rates, and hence their maximum theoretical efficiencies (~23% [11]) are much lower than common PV technologies (~33% for single-junction cells). This is mostly due to the difference in the actual open-circuit voltage (Section 2.1.2) to that of the theoretical maximum [12]. In this section, we briefly discuss the limitations and challenges that need to be overcome to realise high efficiency OSCs. A more in-depth description of the processes involved, and where losses occur in OSCs is given in Chapter 2.

To achieve a high efficiency in any PV device, the device should absorb most of the incident solar spectrum (AM1.5, explained further in Chapter 2). The materials used for the photoactive blend in OSCs have a typical band-gap of >1.4 eV [13]. When considering the maximum theoretical efficiency (Shockley-Queisser limit [12]), the optimal band-gap is said to be ~1.1 eV [14]. When designing materials for OSC applications, the band-gap, charge transport properties, energy levels (HOMO/LUMO), and the resulting morphology are some of the considerations [13].

The morphology of the devices plays an important role, where the phase difference between the materials creates a strong localised electric field at the interface. Excitons generated from incident photons require a driving force to separate the charges, hence, they will diffuse towards an interface to be dissociated (Chapter 2). The dissociated charges then need to be transported to their corresponding contacts. At the same time, exciton quenching and charge recombination are detrimental effects that reduce the efficiency of the cell. The blend (Figure 1.2 (a)) then should have domains small enough to dissociate most of the excitons, and be bi-continuous to efficiently transport the charges to the contacts [15]. The ratio of the materials (donor and acceptor) used, the selected solvent or other additives, and fabrication methods, all have an impact on the morphology of the bulk heterojunction (Figure 1.2) [13], [16].
Figure 1.2 (a) illustration of a bi-continuous polymer blend of two materials (red and green), the bi-continuous blend reaches from one contact to the other, and is interpenetrating. (b) a standard device configuration, consisting of a substrate (glass), a transparent conducting electrode (TCE), a hole transport layer (HTL), a bulk-heterojunction, such as that shown in (a), an electron transport layer (ETL), and a back electrode (BE) commonly not transparent. The device in (b) would be illuminated from the glass substrate side.

The thickness of the layers is another limitation, if the active layer is too thick, the probability that dissociated charges will reach the contacts is reduced due to the introduction of trap centres, where the blend is no longer bi-continuous (Figure 1.2 (a)). The thickness of the photoactive blend also determines the amount of the incident photons that can be absorbed. Active layer thicknesses of ~100 nm are generally utilised, which allows for any remaining incident light to be reflected from the contact back into the active layer and absorbed on the second pass (effective thickness of ~200 nm, which is smaller than the wavelength of visible light: ~400 – 750 nm), so a balance between light absorption and charge extraction must be struck.

Due to the thickness of the layers used within OSCs, optical interference effects play an important role. Incident light within the cell will constructively and destructively interfere with reflections from interfaces [17]. This is another factor that can affect the efficiency of the device, and one which we have explored in-depth in Chapter 4. Optimising the device structure to maximise the optical absorption within the active layer has been the focus of many studies [18], [19]. This is one of the motivations behind the development of a model capable of optimising multi-layered structures such as OSCs (Chapter 3), and we demonstrate how the model can be used to optimise various OSC configurations, including semi-transparent solar cells, which comes with its own set of challenges (Chapter 4).
1.3. Plasmonics for Improved OSCs

In Section 1.2, we discussed some of the limitations and challenges associated with OSCs. This included maximizing the optical absorption within the active layer of the OSCs, and improving the charge transport properties. One direction that people have taken is to include plasmonic nanoparticles into the devices [20]–[22], which has shown to increase the absorption and increase the short-circuit current (\(J_{SC}\), discussed in Chapter 2) of the devices.

Localized surface plasmon resonance (LSPR) effects can be excited by visible light under certain conditions; where noble metals (e.g. Au, Ag) tend to have a plasmon resonance peak that falls within the visible region; as they are highly conductive. LSPR is the collective oscillation of free electrons in nano-sized structures in highly conductive metals, which are non-propagating (localized to the surface) [23], unlike surface plasmon polaritons (SPPs) that propagate across the surface.

When a nanoparticle exhibits LSPR effects, two things happen: The incident light is either scattered by the nanoparticle at wider angles (this includes backscattering effects, which can lead to shadowing effects within the device [24]) or the energy is absorbed and converted into a strong localized electric field around the surface of the nanoparticle. This localized electric field can lead to better exciton generation, charge transport, and charge extraction. These effects can have beneficial consequences to the performance of OSCs.

The scattered fields from the nanoparticles can be used to increase the amount of light absorbed within the active layer, through wide angle scattering, which would otherwise be reflected back out of the device, or absorbed elsewhere [22]. It can also be used to scatter the incident light at wider angles into the active layer, allowing it to absorb more of the incident light [21]. Some of the drawbacks of including nanoparticles in OSCs are that they could backscatter the light, leading to more reflection, and/or act as recombination centers for excitons (exciton quenching).

The near electric field created when the incident light is absorbed can increase the dissociation probability of the generated excitons (Chapter 2), and can also improve the charge transport within the device. It has also been found that larger nanoparticles included into the active layer of the devices can have a negative effect on the morphology [25]. For example, the inclusion of nanoparticles into a layer can: act as a trap center for the generated excitons (causing recombination); increase the overall roughness of the device; and allow the polymer blend to form dis-continuously (not bi-continuous).
Chapter 1 - Introduction

The inclusion of nanoparticles in OSCs has also been shown to improve the lifetime of the devices [26]. The challenges and limitations that arise from the inclusion of nanoparticles into OPVs is discussed in Chapter 2.

Part of this work is dedicated to investigating the optical effects from nanoparticles under different conditions, where we have developed an all-inclusive model (Chapter 5), which can simulate a particle size distribution, with multiple coatings, in an absorbing surrounding medium. These additions are required in-order to accurately simulate the nanoparticles in a realistic environment, such as in OSCs. The applications for the model extend beyond the area of OSCs, where similar nanoparticle systems are employed in drug delivery systems [27] and biosensors [28], as well as OSCs. More applications and examples are given in Chapter 5, and an investigation into the treatment of coating configurations is given in Chapter 6.

1.4. Layout and Aims

In this chapter, we have introduced OSCs and their main advantages: they are a cheap alternative to other types of solar cell, and they can also be light-weight, flexible, and semi-transparent. Section 1.2 discussed the limitations and challenges associated with OSCs. The challenge of maximising the optical absorption in OSCs will be part of the focus of this work, through optical modelling and optimisation. A model, capable of optically simulating N-layered thin-film devices was developed. This model is presented in Chapter 3, where the model was created as a basis for simulating the inclusion of nanoparticles into an OSC.

As stated by the International Renewable Energy Agency: ‘[OSC]s are inexpensive, but not very efficient’ [29]. They also stated that they are emerging as a niche technology, and one of these niches could be energy harvesting from windows [5]. Using the model that we present in Chapter 3, we can simulate semi-transparent OSCs, and have developed a design tool capable of optimising the power conversion efficiencies for specific window transparencies and colours. Optimisation studies for both standard and semi-transparent OSCs are presented in Chapter 4, where we demonstrate a semi-transparent (20% transmissivity) device with a 4.5% PCE, and discuss how we can work towards realising high-efficiency semi-transparent OSCs.

Section 1.3 explained how nanoparticles may be used to manipulate light on the nanoscale to maximise device efficiencies. The improvements in the device efficiencies have been shown to be due to increased absorption through light trapping techniques, and improved charge dynamics within the cell. We have focused on the former, and created an all-inclusive optical model capable of considering a particles size distribution, an absorbing surrounding medium, and multiple and graded coatings. An in-depth description of the model is given in Chapter 5,
where we also show how we can reproduce results from the literature concerning multiple-coatings (Section 5.4.2), and particle size distributions (Section 5.4.1).

The model presented in Chapter 5 is the most inclusive Mie-based model to date, allowing us to simulate realistic complex nanoparticle systems, such as mixed media coatings (e.g. SiO$_2$:TiO$_2$) [30]. During our investigations using the model, we found that under specific conditions, a blue-shift in the plasmon resonance can result with an increase in the nanoparticle size. This blue-shift has also previously been seen in smaller particles [31]; we present our study on this in Chapter 6, where we also demonstrate how we can tune the plasmon resonance by $\sim$200 nm (370 – 580 nm) in a double-layered configuration. The ability to tune the plasmon resonance has applications in biomedical imaging, and photothermal cancer treatments, and lithography processes to name a few [32]–[34], where control over the plasmon resonance peak can be used to target these specific applications.

Our observations, conclusions and suggested future work are given in Chapter 7. Chapter 2 focuses on the literature and basic theory related to the work that we have presented within this thesis; including a comprehensive overview of the field of plasmonics in OSCs (Section 2.2.4). In addition to the work presented within the chapters, we have also provided appendices containing:

A) List of plasmonic OSC device efficiencies and references – A complete list of the data used in Chapter 2 regarding Organic Solar Cell and Dye-Sensitised Solar Cell device efficiencies, with additional information and references.

B) Logarithmic derivatives and Matlab – This gives a breakdown of the logarithmic derivatives that have been designed to be more efficient in Matlab. This is used in this work as an example of code optimisation that has been used.

C) Alteration to refraction parameter presented in the paper by Pettersson et al. [19].

D) Correction to E-Field formula presented in the paper by Jung et al. [35].

E) Library of refractive indices provided with the optical model, and used throughout this work – Contains a library of materials that have been included with the Matlab model created. These include all the optical properties for the materials used throughout this work.

F) Additional convergence information from the recursive Mie model – contains information from the verification of the model in terms of performance and accuracy.


H) Additional results from optical spacer investigation – An additional investigation using a different material system, explained in more depth in Chapter 4.
Chapter 2

2. Basic Theory and Literature

In the Introduction (Chapter 1) we discussed some of the limitations and challenges associated with Organic Solar Cells (OSCs). In this chapter, we provide the basic theory and literature related to these challenges; particularly focusing on maximising the optical absorption of the solar cells through the addition of plasmonic nanoparticles into the OSCs.

This chapter is broken down into three sections, the first being focused on the fundamentals of OSCs: How they work (Section 2.1.1); Metrics and Parameters that have been used throughout this work (Section 2.1.2); and different device configurations and some of the common materials that have been used within the literature (Section 2.1.3).

The second part of this chapter is focused on Plasmonics in OSCs (Section 2.2): Descriptions of the different plasmonic modes are given in Section 2.2.1, whereas description of the quasi-static approximation and the limitations associated with this (Section 2.2.2) are given. A comprehensive overview of plasmons in OSCs, and Dye Sensitised Solar Cells (DSSCs) for comparison, is given in Section 2.2.4, which includes results from more than 80 authors (Appendix A). After this, we look to a couple of the papers (outliers from the results) and highlight the common limitations and challenges associated with the inclusion of nanoparticles into different parts of the OSCs (Section 2.2.5).

The third part of this chapter looks at common modelling methods used within the literature, where we focus specifically on: The optical modelling of OSCs and multi-layered structures (Section 2.3.1); modelling of plasmonic nanoparticles (Section 2.3.2); then the modelling of nanoparticles in OSCs (Section 2.3.3). In this chapter we also give justification for why Matlab provides a good modelling environment, suited to these types of numerically intensive methods and the vectorised nature of the models (Section 2.3.4).

2.1. Organic Solar Cells

In OSCs, the morphology, energy levels, interface interactions, etc. all play important roles in the device performance [8]. In this section, we discuss the fundamentals of OSCs, commonly reported metrics and parameters, and different materials and device configurations that have been used.
2.1.1. Fundamentals of Organic Solar Cells

Organic Solar Cells (aka. Polymer Solar Cells, or Organic Photovoltaics), like dye-sensitised solar cells (DSSCs), are excitonic solar cells. Excitons can be thought of as tightly bound electron-hole pairs [14], and can be excited under the conditions that the incident energy \( E_i = \frac{hc}{\lambda} \), where \( h \) is Planck’s constant, \( c \) is the speed of light, and \( \lambda \) is the incident light’s wavelength) is greater than the band-gap energy \( E_g \) [36]. These excitons need to then be dissociated into quasi-free charges, transported, and finally extracted from the device.

Figure 2.1 demonstrates the processes that lead to the conversion of photons into separate charges, that lead to the production of electrical energy by the OSC. Excitons require a strong electric field to dissociate the electron-hole pair, hence a polymer blend, in a bulk heterojunction configuration is required (Section 1.2). The effective band-gap for a donor-acceptor polymer blend can be estimated by the difference between the HOMO level of the donor to the LUMO level of the acceptor. The following processes relate to the points within Figure 2.1 [14], [17]:

1. If the energy of the incident photon is greater than the band-gap of the material blend, then an electron-hole pair can be excited into an exciton. An exciton is a tightly bound electron-hole pair (Frenkel exciton [37]) with a binding energy \( E_b \approx \frac{e^2}{4\pi\varepsilon_0\varepsilon_\text{r}R} \), where \( \varepsilon_\text{r} \) is the relative permittivity of the media, \( e \) is the charge of an electron, and \( R \) is the equivalent radius of the molecule [38]). Typical values for the exciton binding energy for organic semiconductors are \( E_b \approx 0.3 \text{ eV} \) [39].

2. The created exciton will diffuse towards an interface between the donor-acceptor, where a strong electric field is present.

3. To overcome the exciton binding energy to dissociate the electron-hole pair, a strong electric field at the interface aids in the dissociation into charges; which are then transferred to their respective domains (electrons – acceptor, holes – donor).

4. The charges then need to be transported to their respective contacts, where charge collection and extraction can occur.
Recombination is the predominant efficiency limiter, as every step shown in Figure 2.1 can also lead to recombination [17], [40], [41], rather than charge separation:

1. If the photon energy is not greater than the band-gap, then the excited electron will relax back to the HOMO energy level.

2. Exciton lifetimes are very short in organics, leading to short diffusion lengths of typically (~12 nm in P3HT:PC\textsubscript{70}BM blend [42]). The diffusion length is governed by the exciton lifetime, which is in the order of 100 ps – 1 ns [43]. If the exciton diffuses from where in the blend it is generated, but never reaches an interface, or another area of high energy, the exciton will relax, resulting in recombination.

3. There is a probability that the exciton at the boundary will not dissociate into charges and hence recombine at the interface.

4. There is also a probability that the charges can recombine during transport, as the lifetimes of the charges are short (~\(\mu\)s) [44]. Furthermore, charges can also recombine at the contacts.

There are a multitude of factors that affect the performance of the devices. The morphology of the polymer blend, for example, is an important factor. The size of the domains needs to be such that they are small enough that the excitons can reach an interface, but also large enough to create paths to the contacts for the charges. This is a trade-off and has been a focal point of many studies. If the domains are too big, the probability that the excitons will reach and interface (for dissociation) will decrease, if the domains are too small, the charges cannot find...
their way to the contacts and will relax back to their ground state. Trap states such as defects (through intermediate energy levels, or pockets of densely packed charges) will lead to the increased recombination of the charges. The inclusion of nanoparticles can lead to increased trap states due to the net charge density at the surface, a higher dissociation probability, and changes in the morphology of the polymer blend – more information on this is provided in Section 2.2.4.

Metals are conductor materials, which have a work function and no split in the conduction and valence band (bandgap is 0). Polymers have a work function and bandgap (the exception is PEDOT:PSS, which is metal-like and hence has a bandgap of 0). The function of energy level matching in OSCs is two-fold: HTL and ETL materials are chosen to act as a buffer layer for specific charges between the active region and the contact. The materials are also chosen to block the opposing charges from reaching the contact. Hence, the choice of materials is an important factor, and care should be taken to ensure energy level matching for hole/electron blocking. If the energy levels do not match they will cause charge injection at the contacts, which will increase recombination. The effective band-gap affects the ability to generate excitons: when the band-gap is large, then a smaller proportion of the solar spectrum is absorbed; the optimal bandgap is around 1.1 eV [40]. The electronic properties of the materials need to be balanced; if there is a large discrepancy between the electron and hole transport properties of the materials, then the number of charges that will recombine before reaching a contact will increase.

The choice of materials is discussed in more depth in Section 2.1.3, where we look at the most commonly used materials and configurations thereof. Throughout this work we are mostly concerned with how we can maximise the number of excitons generated within the active layer (Figure 2.1). The transport layers are designed to absorb the least amount of the incident light, to maximise the amount of incident light absorbed, and hence excitons generated, within the active region.

2.1.2. Useful Parameters and Metrics

Throughout this work we refer to metrics taken from literature and experimental work, these include the open-circuit voltage ($V_{oc}$), short-circuit current density ($J_{sc}$), fill factor ($FF$), power conversion efficiency ($PCE$), external quantum efficiency (EQE), internal quantum efficiency (IQE), and exciton generation rate ($G_{opt}$). This section provides some background into where these metrics arise from, and/or how we can calculate them from experimental data.

$V_{oc}$ describes the apparent voltage of the device in an open circuit configuration, or when the device is in equilibrium and there is no apparent current ($V_{oc} = V(J = 0)$). This is one of many parameters that can be obtained from a current-voltage (J-V) characteristic, shown in Figure
2.3 (a). The current-voltage characteristics can be obtained using a solar simulator, which simulates solar irradiance. The bias voltage is changed in small steps and the current from the device is measured.

The open circuit voltage can also be estimated from the energy levels of the materials. Scharber et al. [45], for example, demonstrated that for fullerene-based OSCs (e.g. PC_{60}BM – Section 2.1.3), the $V_{OC}$ can be approximated by taking the difference between the HOMO level of the donor material and the LUMO of the acceptor (Eq. 2.1). The 0.3 eV value is added to correct for deviation between the theoretical minimum calculation and the measured open circuit voltage [45].

$$V_{OC} = V(I = 0) \approx \frac{1}{e} \left( |E_{HOMO}^{Donor}| - |E_{LUMO}^{Accepter}| \right) - 0.3$$  \hspace{1cm} 2.1

Likewise, the short circuit current ($J_{SC}$) can be drawn from the J-V characteristics, when the open circuit voltage matches the internal bias voltage of the device, or $J_{SC} = j(V = 0)$ [36]. This can also be seen in Figure 2.3 (a).

The example given in Figure 2.3 is taken from an experimental device with Glass / ITO (150 nm)/ PEDOT:PSS (40 nm)/ PCDTBT:PC_{70}BM (120 nm)/ TiO_{2} (10 nm)/ Aluminium (~100 nm). The materials, and associated performance, are described in more depth in Section 2.1.3, their optical properties are given in Appendix E.

![Figure 2.2 The basic equivalent circuit (non-capacitive) for a solar cell, $V_{oc}$ is the open circuit voltage, $J$ is the current density, $J_{dark}$ is the diode dark current density. $R_{sh}$ is the shunt (parallel) resistance, and $R_{s}$ is the series resistance.](image)

The current density and voltage, at the maximum power point ($J_{m}$, and $V_{m}$ respectively) are also useful metrics, and are used to calculate the fill factor ($FF$). The $FF$ describes the squareness of the J-V characteristics, and is affected by the parasitic resistances ($R_s$, and $R_{sh}$, demonstrated in Figure 2.2); the best performing devices will have the lowest series resistance, and the highest shunt resistance, as possible [36]. This can be seen in Figure 2.3 (a) as the greyed square, and the equation is given in Eq. 2.2. Notice that as $J_{m}$ and
Organic Solar Cells

$V_m$ approach $J_{SC}$ and $V_{OC}$, the $FF$ approaches 1, or 100%, which would represent an ideal device.

$$FF = \frac{J_mV_m}{J_{SC}V_{OC}} \quad 2.2$$

The power conversion efficiency (PCE, $\eta$) is a metric of performance for the device, the ratio of the power utilised by the device to the amount available. Eq. 2.3 demonstrates this, where $P_{tot}$ is the total incident irradiance (1000 W m$^{-2}$ for the AM1.5 solar spectrum). This can also be calculated from the external quantum efficiency (EQE), by integrating the product of the spectral irradiance and the EQE (Eq. 2.3).

$$\eta = \frac{J_{SC}V_{OC}FF}{P_{tot}} = \frac{1}{P_{tot}} \int_0^\infty P_{AM1.5}(\lambda) \cdot EQE(\lambda) d\lambda \quad 2.3$$

The EQE can be described as the ratio of the number of electrons out to the number of photons in [46], whereas the IQE can be described as the ratio of the number of electrons out to the number of absorbed photons [47]. Eq. 2.3 shows the relationship between the EQE, IQE, and the absorption of the device (ABS).

$$IQE = \frac{EQE \text{ (electrons extracted/s)}}{Absorption \text{ (photons absorbed/s)}} \quad 2.4$$

![Figure 2.3 Experimentally obtained (a) J-V light characteristics and (b) Absorption, IQE, and EQE for the device Glass/ITO/PEDOT:PSS/PCDTBT:PC$_{70}$BM/TiO$_2$/Aluminium.

The EQE can be found experimentally by illuminating a device with a monochromatic incident light source with a known energy, and measuring the current from the device. The absorption of a device can be found by measuring its reflection and transmission, using UV-VIS spectroscopy for example.
When reporting efficiency, it should be with respect to a standard illumination, usually under air-mass AM1.5 illumination for terrestrial applications, and AM0 for extra-terrestrial applications, such as satellites [48]. The standard takes into consideration the absorption from the earth’s atmosphere (AM1.5 would be the spectra after a path length at 48.2° through 1.5 atmospheres) [49]. Figure 2.4 demonstrates the difference between the standards, where the G stands for global. The total irradiance ($P_{tot}$) from the AM1.5 spectrum is 1000 W m$^{-2}$.

Due to the band-gap of the materials used for OSC applications, only a small portion of the total irradiance is utilised, where the cut-off wavelength of the absorption generally happens in the NIR region (~750 nm for a PTB7:PC70BM active layer [50]). However, this is material dependent and some materials are designed to absorb more of the red/NIR region.

As we intend to look at how to maximise the optical absorption of devices in this work, a useful parameter would be the exciton generation rate (Eq. 2.5) [14], which describes the number of excitons per volume per second generated within a device. This can be calculated from the energy dissipation within the device, which stems from the absorption profile (more information on this is provided in Chapter 3). This is normalised to the solar intensity (from the AM1.5 spectral irradiance shown in Figure 2.4) and the incident wavelength. Where, $\hbar$ is the reduced Plank’s constant; $\lambda$ is the incident wavelength; and $z$ is the position in nm through the device.

Figure 2.4 Air Mass standard spectral irradiance for AM0, AM1.5G (includes contributions from scattering and indirect illumination) and AM1.5 (based on direct illumination from the sun at a 37.5° [12]. The highlighted area (green) demonstrates the range of wavelengths commonly absorbed by organic donor-acceptor materials (see Appendix E for optical properties of materials).
Maximising the exciton generation rate is the basis of optical optimisation of solar cells for terrestrial applications. To realise high efficiency solar cells, electrical optimisation also needs to be conducted, focused on tackling the associated challenges described in Section 1.2. From the exciton generation rate (Eq. 2.5), the charge distributions, the drift and diffusion currents can be calculated, where the dissociation probability, transport properties, interfacial layers etc. all have an impact on the device performance. The exciton generation profile is usually considered the cross-over point between optical and electrical simulations [14], hence, electrical optimisation will be out of the scope of this work.

2.1.3. Materials and Device Configurations

In OSCs, a polymer blend of an electron donor material and an electron acceptor material (commonly a fullerene derivative) is used for the active layer [51]. This configuration is favoured due to the exciton diffusion length being small (~12 nm [42]), so having smaller domains will ensure the excitons can find an interface to dissociate (Section 2.1.1).

For the incident photons to be absorbed into the active layer, a transparent conductive electrode (TCE) is used. This is optically transparent, but also conductive, to extract the charges from the device. The most commonly used material for this is indium tin oxide (ITO), however, suitable alternatives are being researched, such as fluorine tin oxide (FTO) [52], [53], aluminium-doped zinc oxide (AZO) [53], and silver nanowires [54]. The requirement for this layer is to be as transparent as possible over the visible spectrum, typically >90% transmissivity, and be as conductive as possible (<100 Ω/□), with a suitable work function (close to the HOMO/LUMO levels of the active/transport materials).

Transport layers (hole transport layer – HTL, and electron transport layer – ETL), are used for energy level alignment, to avoid unnecessary losses due to miss-matching energy levels between the active layer and contacts (Section 2.1.1) [55], [56]. They also should be conductive, with suitable hole/electron mobilities, and generally optically transparent (no complex refractive index). The most commonly used HTL material in a standard configuration is PEDOT:PSS\(^1\) [56]. Other HTL materials include molybdenum trioxide (MoO\(_3\)) [57], and graphene oxide (GO) [56]. Common materials used for the ETL are and zinc oxide (ZnO) [14], and bathocuproine (BCP) [58]. Different materials work better with different material systems.

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\(^1\) PEDOT:PSS – Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)
A standard device structure (Figure 2.5 (a)) consists of a TCE on top of a glass substrate, a HTL separating the TCE from the active layer (BHJ). An ETL is used to separate the top contact (or back electrode, BE) from the active layer. In most applications, the BE also acts as a reflective contact (usually Ag or Al) to reflect the remaining light that is not absorbed back into the device. In other applications, such as semi-transparent cells, this is not the case (Section 4.3). In contrast, an inverted device structure (Figure 2.5 (b)) has the ETL and HTL switched; in this case, the charges within will be collected at the opposite contact to the standard configuration. There are reported cases of inverted devices being more efficient than their standard counterparts [59]. Inverted devices were developed to address stability issues with using PEDOT:PSS [60], [61], as PEDOT:PSS is acidic in nature and hence oxidises in-air over time [60].

The most commonly used electron acceptor material is the fullerene PC_{60}BM, although more recently IC_{60}BA has been shown to be a better alternative with some material configurations. HOMO/LUMO levels for these acceptor materials are given in Table 2.1.

Table 2.1 shows the most commonly used materials for OSCs, giving their type, bandgap, HOMO/LUMO levels and the references for each. P3HT has values within brackets due to the large range of values throughout the literature and should be taken as an approximate range.

<table>
<thead>
<tr>
<th>Material</th>
<th>Type</th>
<th>Bandgap (eV)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT</td>
<td>Donor</td>
<td>1.67 (2.02)</td>
<td>-5.20 (4.76)</td>
<td>-3.53 (2.74)</td>
<td>[62], [63]</td>
</tr>
<tr>
<td>PCDTBT</td>
<td>Donor</td>
<td>1.85</td>
<td>-5.45</td>
<td>-3.60</td>
<td>[64]</td>
</tr>
<tr>
<td>PTB7</td>
<td>Donor</td>
<td>1.84</td>
<td>-5.15</td>
<td>-3.31</td>
<td>[65]</td>
</tr>
<tr>
<td>PCDTT-C-T</td>
<td>Donor</td>
<td>1.86</td>
<td>-5.11</td>
<td>-3.25</td>
<td>[66]</td>
</tr>
<tr>
<td>PC_{60}BM</td>
<td>Acceptor</td>
<td>1.70</td>
<td>-6.00</td>
<td>-4.30</td>
<td>[45]</td>
</tr>
<tr>
<td>PC_{70}BM</td>
<td>Acceptor</td>
<td>1.80</td>
<td>-6.10</td>
<td>-4.30</td>
<td>[67]</td>
</tr>
<tr>
<td>IC_{70}BA</td>
<td>Acceptor</td>
<td>1.89</td>
<td>-5.61</td>
<td>-3.72</td>
<td>[63]</td>
</tr>
</tbody>
</table>

2 PC_{60}BM - [6,6]-Phenyl C(61/71) butyric acid methyl ester
3 IC_{60}BA – Indene C_{60/70} Bis Adduct
Some of the typical electron donors include: P3HT, PCDTBT, PTB7, and PBDTTT-C-T, their associated HOMO/LUMO levels are given in Table 2.1. P3HT:PC60BM being the most commonly used material system in literature due to it being the most understood and researched material system [68]. However, P3HT:PC60BM is also one of the poorer performing material systems, with efficiencies rarely breaking the 5% barrier [68]. Efficiencies of up-to 6.7% have been achieved from a P3HT:IC70BA material systems in larger area OSCs [58].

In contrast, PCDTBT, PTB7 and PBDTTT-C-T are all high performing materials, where efficiencies of above 7% have been consistently achieved [59], [69], [70]. He et al. [59] showed how using inverted structures (Figure 2.5 (b)) with a PFN8 ETL, PTB7:PC70BM active layer and MoO3 HTL, can lead to increase in device performance ($\eta = 9.22\%$). Wang et al. [71] developed a stamping technique for graphene oxide, which they combined to form the ETL in their device ($\eta = 7.5\%$).

**Figure 2.5** OSC device configurations demonstrating: (a) A standard configuration, where the hole transport layer (HTL) is on top of the transparent conducting electrode (TCE), and the electron transport layer (ETL) above the bulk-heterojunction (BHJ). (b) An inverted device structure showing the ETL on top of the TCE and the HTL after the BHJ.
2.1.4. Semi-transparent OSCs

In Section 2.1.3 we gave a brief overview of the most common materials used currently in OSCs and we also discussed the different, and parts of, configuration (standard vs inverted), which we will refer to throughout in this work. In this section, we show how OSCs have been applied to the alternative area of energy-harvesting from decorative windows.

The thin-film nature of OSCs means that they can be made to be flexible, lightweight and semi-transparent [72]. One alternative application for these attributes is in glass office buildings and greenhouses [5], which both have large areas of glass windows. The wide variety of different materials (Section 2.1.3) that can be used in OSCs provides a wealth of different combinations, all with their unique optical properties. Exploiting this enables us to control the colour of the devices, whilst still being able to maximise the efficiency (Chapter 5). We discuss research conducted in this area, focusing on techniques and material combinations used for semi-transparent OSCs.

There are a few tricks that can be used to reduce the reflectivity of the top contact, with one of these being the use of an index matching layer, such as Ag/ITO [1], Ag/LiF [6] and Ag/MoO3 [73]. Another method is to create a grid structure, making a proportion of the contact transparent, such as a Ag grid [72]. Others solutions include: ultra-thin metallic films [74], nanowire films [75], and other novel transparent conducting oxides [76] (i.e. not using standard transparent conducting oxides, such as ITO).

Chen, C. et al. [75] demonstrated that it is possible to create a visibly transparent OSC (average ~60%), whilst maintaining a 4% PCE, by using an infra-red absorbing material (PBDTT-DPP9) for the electron donor material. This, in conjunction with their Ag nanowire top contact, allowed them to provide a colourless device with high efficiency and transmissivity.

Betancur et al. [6] utilised a PTB7:PC70BM active layer in conjunction with a Ag/LiF contact. In their work, they also implemented a Bragg grating (LiF/MoO3) on the back contact to increase absorption in the red/NIR region, and could control the visible colour of the devices. Using this method, they achieved 30% transparent cells with a PCEs of 5.6%.

Chen, K. et al. [74] created their cells using a PBDTTT-C-T:PC70BM active layer, with an ultra-thin Ag top contact. They managed to achieve 4.25% efficient cells with an average of 50% transmission. In this case, it seems that the addition of an index matching material would have

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9 PBDTT-DPP - poly[2,6′-4,8-di(5-ethylhexylthienyl)benzo[1,2-b;3,4-b]dithiophene-alt-5-dibutyloctyl-3,6-bis(5-bromothiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4-dione
benefited their design, and increased the transmission and allowed for a slightly thicker contact, improving their results (Chapter 5).

There are many different approaches to developing semi-transparent OSCs, each of these methods have shown to work as intended, however, they lead to different device dynamics through the introduction of additional layers, novel materials, and nanostructures. This adds extra complexity when trying to pin-point which of the limitations and challenges (Section 1.2) it addresses, or augments. We discuss the limitations and challenges associated with creating semi-transparent devices further in our study in Chapter 5, using the model we have produced to enable the optimisation of such structures in Chapter 3.

2.2. Plasmonic Nanoparticles

The inclusion of plasmonic nanoparticles in OSCs is one method to tackle some of the associated challenges discussed in Section 1.2, such as exciton generation and dissociation, charge transport and collection, and recombination. However, the mechanisms involved are complex and the effect it has on the device performance is still not fully understood. In this section, we give a background on plasmonic modes and their use in OSCs (Section 2.2.1) and we provide some basic theory on the quasi-static approximation and the associated limitations in Section 2.2.2. We discuss briefly some of the most commonly used metrics for plasmonic phenomena in Section 2.2.3, leading on to a review of the field of plasmonics in OSCs and analysing the trends in performance increases (Section 2.2.4). We close this section by giving the reader an overview of the limitations and challenges involved in the inclusion of nanoparticles in OSCs, Section 2.2.5.

2.2.1. Plasmonic Modes

Figure 2.6 demonstrates the plasmonic modes that have been used for improving the efficiency of OSCs, Figure 2.6 (a) shows the effects of scattering from nanoparticles, Figure 2.6 (b) demonstrates the localised electric field created close to the nanoparticles and Figure 2.6 (c) shows a Surface Plasmon Polariton (SPP) mode where an evanescent wave (Figure 2.6 top-right) propagates across the surface creating a strong field. As the size of the nanoparticles increase (>50 nm for Ag) light scattering effects will start to dominate over absorption. For SPPs, the spacing between the particles plays the most important role, which determines the conditions for the plasmons.
Figure 2.6 Different nanoparticle in device configurations demonstrating (a) light trapping from wide angle scattering of the nanoparticles. (b) appearance of strong Electric field close to the nanoparticles aiding dissociation, and transport of charges at the interface of the HTL/Active layers, (top-centre) demonstrates how the localised electric field is formed in relation to the nanoparticle, and (c) Surface Plasmon Polariton effects across the surface of a periodic grating, which is implemented to aid the dissociation and extraction of charges, (top-right) demonstrates the evanescent wave created in the case of SPPs, where the direction of travel is also identified. Reprinted from Materials Today, 14 (4), Emmanuel Stratakis and Emmanuel Kymakis, Nanoparticle-based plasmonic organic photovoltaic devices, pp. 133 - 146, Copyright (2013), with permission from Elsevier [22].

SPPs occur when the incident wave-vector (or momentum of) phase-matches the boundary conditions at interface between two materials. SPPs are such that no propagating modes can exist under then condition $\omega_{SP} < \omega < \omega_p$, where $\omega_{SP} = \omega_p/\sqrt{2\varepsilon_d}$ is the surface plasmon frequency, $\omega_p$ is the plasmon frequency, and $\omega$ is the frequency of interest. Hence the conditions that $\text{Re}(\varepsilon_m < 0)$ and $\varepsilon_m < -\varepsilon_d$, should be satisfied for SPPs to exist, where $\varepsilon_m$ is the complex permittivity of the metal (nanoparticle) and $\varepsilon_d$ is the permittivity of the surrounding media (usually assumed to only have a real part [23]). When wavevector of the incident wave ($k_0$) matches the surface plasmon wavevector ($k_{SPP}$) at the interface of the metal dielectric, the wave couples in the direction of the interface creating an evanescent propagating wave [23].

Structures such as the Kretschmann configuration, or gratings can be used, where the conditions for SPP modes can be met for freely propagating waves. For example, using a grating, the periodicity plays an important part of phase matching the incident wave-vector (Eq. 2.6) [23], which would be visible in practice by a minima in the reflection from the device. The equation stems from the boundary condition for the coupling of the incident and SPP wave-vectors at the interface ($k_x = \beta_{spp} \pm vG$, where G is the wave-number of the grating).

$$\beta_{spp} = \sqrt{\varepsilon_d k_0 \sin(\theta_0)} \pm v\left(\frac{2\pi}{d}\right), \quad v = 1,2,3 \ldots N$$ 2.6
The SPP propagation constant ($\beta_{\text{spp}}$) is a function of the refractive index at the interface, the free space wave-vector ($k_0$), $\theta_0$ is the incident angle of the incident wave-vector ($k_\perp$), and the spacing of the grating ($d$). When the incident wave-vector ($k_\perp$) matches the SPP propagation constant, coupling occurs and a strong evanescent wave at the interface travelling in the direction of the grating will be apparent.

Experimentally, in OSCs these conditions can be achieved by patterning the contacts [77], or by creating a periodic pattern throughout the whole device [78]. Li et al. [77], for example, created a periodic grating structure from the top contact (Ag), and included nanoparticles in the HTL (TiO$_x$). They demonstrated improvements in the optical absorption within the visible region, increased fill factor, reduced series resistance and increased short circuit current. Jin et al. [78] demonstrated how a periodically corrugated substrate, and hence device, could lead to improved absorption in OSCs through localised field enhancements from SPPs, ultimately leading to an increase in the short circuit current of the devices. SPP effects can be invoked from periodically spaced nanoparticles, such as demonstrated in Figure 2.6 (c) [22].

When nanoparticles interact with light, two things happen: incident light is scattered by the particle to wider angles and some of the incident light is absorbed by the nanoparticle, causing a strong localised electric field to occur close to the surface [23]. In OSCs, these techniques are used to manipulate and trap incident light within the device: At wider angles, the light is scattered at different angles within the device, increasing the effective path length of the light. This would in turn increase the absorption of the OSC, and hence the device efficiency. Section 2.2.4 gives an overview of the field of plasmonics in OSCs, giving some examples of how this has been used to increase PCEs. Atwater et al. [21] give a review of the techniques used to improve the efficiency of solar cells through the inclusion of plasmonics. Stratakis et al. [22] provide a more focused review on the inclusion of nanoparticles in OSCs, where they also state that more work needs to be done to further the understanding of how the inclusion of nanoparticles (with different size, shape, distribution etc.) will affect the performance of OSCs. The effect on the performance of OSCs generally comes from improving on one, or more, of the associated challenges, whilst also introducing more complex effects, and even worsening of other associated challenges. Therefore, an approach that simulates the effects from the inclusion of nanoparticles included in OSCs should be developed, which can be used to improve understanding of the underlying effects.

When applied to excitonic solar cells, such as OSCs and DSSCs, nanoparticles with no functional coating act as trap centres for the exciton, causing increased recombination at the surface [25], [79]. A dielectric spacer (usually an insulating material, such as SiO$_2$ [80] or TiO$_2$ [81]), is used to reduce the surface recombination when including such nanoparticles into excitonic solar cells [21]. This has some additional effects on the plasmon response of the
particle, where the inclusion of a dielectric coating will cause the resonance peak to red-shift and the cross-sections to reduce, as the total size of the particle and the material properties are change. This does, however, add another layer of tuneability, where the ratio of the thickness of the dielectric layer to the core nanoparticle will have different effects on the resonance. We explore this further in Chapter 6, where we look at the effects on the plasmon resonance from single, multiple and graded coatings.

2.2.2. Nanoparticles and Localised Surface Plasmon Resonance

When the particles are much smaller than the wavelength of light \( (d \ll \lambda) \) LSPR effects appear as a dipole, which can be explained simply through the polarisation of the sphere. The widely accepted approximation [23], [82], [83] for this problem is the quasi-static approximation, which shows the dipolar resonance from a nanoparticle when it is much smaller than the wavelength. The polarizability of a mixture of materials can be found by using the Clausius-Mossoti relation [23]. The polarizability of a sphere (Eq. 2.7) has a cubic relationship with the radius of the particle (like the absorption cross-section \( C_{\text{ext}} \), shown in Eq. 2.9), which means that a sphere with a 10 nm radius would have a polarizability 8 times lower than that of a 20 nm sphere. The polarizability is also highly dependent on the Fröhlich condition \( (\varepsilon_m = -2\varepsilon_d) \), which would lead to the internal field exhibiting a resonance [84]. As the denominator (based on the Fröhlich condition) tends to zero the polarisation would tend to infinity giving the maximum radiative plasmon resonance effects. The permittivity of Drude metals \( (\varepsilon_m \text{ in Eq. 2.7}) \) relates the plasmon frequency \( (\omega_p) \) to the frequency of interest \( (\omega) \) and the damping factor \( (\gamma) \). Drude metals include materials such as Ag and Au. Under the condition that \( \omega \gg \gamma \), which would be the case for visible light and representative of the free-electron model, the damping term can be assumed to be negligible. The surface plasmon resonance frequency, where the polarizability is maximum, in this case can then be approximated as \( \omega_{SP} = \omega_p/\sqrt{1 + 2\varepsilon_d} \) [23].

\[
\alpha_p = 4\pi r^3 \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d}, \quad \varepsilon_m = 1 - \frac{\omega_p^2}{\omega^2 - i\gamma\omega} \approx 1 - \frac{\omega_p^2}{\omega^2} \quad 2.7
\]

The Poynting vector of the scattered electric \( (E_{\text{sca}}) \) and magnetic \( (H_{\text{sca}}) \) fields are taken with respect to the surface of the sphere \( (S = E \times H) \) [85]; this leads to the form of the scattering cross-section in Eq. 2.8. More information on how this is derived can be found in Nolte’s [85] work on Dipoles and Rayleigh Scattering. Relating the polarizability (Eq. 2.7) to the scattering and absorption of spheres, it is found that the absorption is still dependent on the \( r^3 \) relationship. However, the scattering follows a \( r^6 \) relationship (Eq. 2.8), which means that as the size of the particles increase, scattering will start to dominate at a specific radius (dependent on material properties and wave-vector). Depending on the position within an OSCs, scattering or absorption may be preferred (Section 2.2.5). The related absorption
cross-section can be found in Eq. 2.9, where the total extinction cross-section is \( C_{\text{ext}} = C_{\text{sca}} + C_{\text{abs}} \) [23].

\[
C_{\text{sca}} = \frac{k^4}{6\pi} |\alpha_p|^2 = \frac{8\pi}{3} k^4 r^6 \left| \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d} \right|^2
\]

\[
C_{\text{abs}} = k \text{Im}[\alpha_p] = 4\pi k r^3 \text{Im} \left[ \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d} \right]
\]

This approximation assumes that the scattering element is much smaller than the incident light’s wavelength. When the particle size increases, we cannot treat it only as a dipole (the first term of the Taylor’s expansion of the polarizability) and should include multipole terms. In practical terms, this shows as a red-shift, and a reduction in the amplitude, compared to the dipole approximation [86]. The effects from higher terms of the Taylor’s power series (multipolar effects – quadrupolar, octopolar etc.) can be seen in Figure 2.7 (b). Figure 2.7 (a) shows the extinction cross-section of a Ag nanoparticle with a radius of 10 nm, where both the methods (Mie Theory and the quasi-static approximation) agree with each other. However, as the particle size increases (radius > 25 nm for silver), higher order resonances occur. An example of this is in Figure 2.7 (b), where the extinction cross-section of a Ag nanoparticle with a radius of 50 nm is shown: The quasi-static approximation is no longer representative of the result obtained via Mie Theory and the dipolar resonance for the Mie result now lies at ~500 nm and the smaller peak seen at ~400 nm is the quadrupolar resonance [87].

![Figure 2.7 A comparison between the extinction coefficient from our Mie model (described in depth in Chapter 4) and the Quasi-Static approximation for a 0.4 volume fraction of Ag (complex refractive index from Rakić et al. [88], we also assume \( \mu_r = 1 \)) nanoparticles in water (n = 1.33) for particles with radii (a) 10 ± 1 nm and (b) 50 ± 1 nm. The cross-sectional value for the quasi-static approximation has been scaled by an arbitrary value to match the same scale as the Mie theory solution; as we are interested in the peak position rather than the cross-section value.](image)
The dipole approximation also does not hold true for when we have multi-layered coatings around the core particle, where we start to see competing effect (red and blue shift) on the plasmon resonance peak position, even when the particle size is very small compared to the wavelength. This is part of our investigation in Chapter 6, based on the recursive Mie model described in Chapter 4.

2.2.3. Useful metrics and parameters

As briefly demonstrated in Section 2.2.2, cross-sections can be an effective way to characterise the plasmon resonance from nanoparticles. The scattering cross-section is a geometric quantity given as an area (m²). A total cross-section will be the contribution from a collection of particles, as shown in Figure 2.7, which demonstrates the total extinction cross-section for \(1.3 \cdot 10^{23} \text{ (m}^{-3}\)) particles, based on a 0.4 volume fraction of Ag nanoparticles with a radius of 10 nm, in water. This is calculated by taking the sum of the cross-sections of each of the particles, and we cover this in more depth in Chapter 4.

Other ways of reporting plasmonic effects are energy rates and efficiencies (scattering, absorption and extinction), which are usually denoted as \(W_Z\), and \(Q_Z\), respectively, where the Z changes depending on whether it relates to either extinction, scattering or absorption [89]. The efficiencies can be found by normalising the cross-section by the size factor \(Q_{sca} = \left(\frac{2}{x^2}\right)C_{sca}\) of the particle, which is given by \(x = 2\pi r/\lambda\), where \(r\) is the radius of the particle. The energy rates \(W_Z\), which can be calculated directly from the Poynting vector, can also be found by normalising the efficiencies to the incident energy upon the surface of the sphere \(W_Z = I_0 \pi r^2 Q_Z\) [90]. The calculations for the cross-sections, efficiencies and energy rates need to be corrected, when considering an absorbing surrounding medium, due to the additional absorption of the incident light. We explain the origin of these in more depth in Section 5.2.1.

2.2.4. Nanoparticles in Organic Solar Cells

To get an overall picture of some of the research in the field of plasmonics in OSCs, and how the overall performance increase is reported. We have compiled a wide list of papers where the authors have reported enough information on both their control devices and plasmonic devices to draw a relationship. Our requirements for this were that the devices need to be identical in material configuration (the same order of materials between the control and plasmonic devices), report an average rather than a single device Power Conversion Efficiency (PCE) and give full transparency of the materials that they have used. We have compiled a list that can be found in Appendix A, which includes all the information that we have used within this section.
To be able to compare OSCs with a similar technology, a shorter list of authors that have included plasmonic structures in Dye-Sensitised Solar Cells (DSSCs) has also been included, sticking to the same requirements for selecting the data. DSSCs are another type of excitonic solar cell: although they use different materials, the main principles at the core of the working devices are the same, which is the reason for selecting this type of device. From the collected data, we hope to be able to extract trends in performance data for OSCs with nanoparticles included, compared to those without. The expected result is to see an overall increase in cell performance compared to the reference device (without nanoparticles) in all cases.

Figure 2.8 gives an overview of the results that we gathered from the authors’ research, which provided two interesting trends. The datasets used for each was 80 data points for OSCs and 20 data points for DSSCs: We expect the OSC data points to be more statistically significant than the data obtained for DSSC. The points in Figure 2.8 were fitted in Matlab using a linear fit tool: Eq. 2.10 and Eq. 2.11 are the equations for the linear fit. The $R^2$ values, 0.9796 and 0.9658 for the OSCs and DSSCs respectively, represent the square of the correlation coefficient (can be in the range 0 to 1, where 1 would be a perfect fit).

The equation for the fits follows the format $f(x) = \alpha x + \beta$. $\alpha > 1$ signifies that as the PCE of the control device increases, the PCE of plasmonic enabled equivalent devices would increase $\alpha$ times more. When we compare the linear fit for both OSCs (Eq. 2.10) and DSSCs (Eq. 2.11), we see that both values are very close to 1. This signifies that the improvement by the addition of nanostructures in these devices is not dependent upon the control device efficiency. The second term in the equation ($\beta$) signifies a fixed improvement amount (on average) on the device with the inclusion of nanostructures. What is significant about the results in Eq. 2.10 (OSCs) and Eq. 2.11 (DSSCs) is that there is a relatively large difference between the two (~0.84% PCE). This signifies that the inclusion of nanostructures in DSSCs would have a much bigger impact on the overall efficiency that it would for OSCs. However, there will always be exceptions to the rule, for example Sheehan et al. [91] report +2.71% on their control devices with the inclusion of core-shell-shell (Au@SiO$_2$@TiO$_2$) aggregates (core-shell and core-shell-shell structures are discussed in more depth in Section 6.1). For OSCs, Liu et al. [92] introduced core-shell-shell Nanocubes into the HTL of their control device, and achieved +1.76% PCE improvement. These are the most significant results in this area and, in both cases, contain a core-shell-shell configuration; In Chapter 6 we provide details of our study on core-shell-shell particles, and in Chapter 4 we provide our methods of being able to simulate such structures.
Figure 2.8 The data points in this figure were fit using a Linear fit ($\alpha x + \beta$) in the Curve Fitting tool in Matlab, using a 95% confidence interval. The plasmonic device PCEs against the control devices for (a) OSCs ($R^2 = 0.9796$) and (b) DSSCs ($R^2 = 0.9658$). A 1:1 reference (black-dashed) line, which represents no improvement, is also given in both graphs. A full list of efficiencies, including references are given in Appendix A.

Wu et al. [25] is the only point that we found throughout the literature that has reported a consistently lower result with the inclusion of Ag nanoparticles in the active layer (-0.1%). They report losses in the devices open circuit voltage, short circuit current, and the fill factor of the devices. The nanoparticles had a diameter of ~25 nm and no functional coating. The author reports that the losses are predominantly due to increased recombination affecting the exciton lifetimes (via exciton quenching [50], [79]). The functional coating of the nanoparticle is important, as it affects the charge transport dynamics, where Wu et al. [25] suggest that an insulating coating can be used to alleviate the problem of increased recombination, which agrees with our findings in Appendix A, which are displayed in Figure 2.8.

We have provided a side-by-side comparison in Figure 2.9 (a) and (b). The +% metric provides much more uniformity (determined by a low $R^2$ value of 0.1583) within the results, which means that a +1% PCE increase at 1% can now be comparable to a +1% PCE increase at 8%. When analysing the data points on a per year basis (Figure 2.9 (c)) we note that the average (red-lines) does not reveal a trend. The quartiles vary from year to year significantly, where the biggest inter-quartile range can be found in 2016 (also, showing a skewed distribution, where Q3 is further away from the mean than Q1. The only noticeable trend from this data is the maximum improvement (top of the range), on average, improves on a year to year basis.
Figure 2.9 The data points in this figure were fit using a Power fit ($a x^b + c$) using the curve fitting tool in Matlab, and was fit using a 95% confidence interval (bounds). (a) percentage increase between the control (reference) PCEs, calculated by (plasmonic/control) $\times 100$($\%$) ($R^2=0.7903$), (b) percentage increase, calculated by (plasmonic($\%$)-control($\%$)) expressed as $\pm$ PCE($\%$) ($R^2=0.1583$). (c) the red lines show the average percentage improvement from that year, which does not demonstrate a trend, the blue boxes are the quartiles (Q1, Q3), which demonstrate the statistical variability in the results increase over time, the dashed extensions show the range. (d) the position in the device that the authors have placed the nanoparticles does not seem to make a difference on average, shown by the overlapping colour dashed lines.

In Figure 2.9 (a) we display the percentage increase between the devices. The percentage increase is a very common method of presenting the improvement in the devices with the inclusion of particles; an example would be the review papers by Yang et al. [93] and Stratakis et al. [22]. As shown in Figure 2.9 (a), a trend appears when reporting the efficiency enhancement as a percentage – when the efficiency of the reference device (control) is low (< 3%), the reported percentage increases become inflated. A 200% increase on a reference device with 1% efficiency is not comparable to a 200% efficiency improvement of a cell of 8% efficiency. A better metric for reporting improvements in this case would be +/- PCE($\%$), shown in Figure 2.9 (b), where it shows a weak positive trend with increasing control PCE.
In summary, the results (Figure 2.9) have shown that on average, the inclusion of nanoparticles in OSCs could provide a +0.5% improvement upon the control device efficiency (+1.3% in DSSCs). Although, it is important to note also that this trend analysis (regression) from literature, which tends to focus on positive results. In the next section, we look at the limitations and challenges of including nanoparticles into OSCs.

### 2.2.5. Limitations and Challenges

The inclusion of nanoparticles in OSCs has been shown to improve the efficiency through improved optical absorption, increased short circuit currents from better charge dissociation, transport and extraction, and improved device lifetimes. However, to make full use of these effects certain challenges need to be overcome.

One of the challenges for increasing the optical absorption through the inclusion of nanoparticles into the interfacial layers (HTL and ETL, Section 2.1.3), is finding the correct size of the nanoparticles. As discussed in Section 2.1.3 typical layer thicknesses for interfacial layers are usually < 50 nm and scattering effects from nanoparticles are more dominant as the size of the particle increases. Therefore, to obtain the performance increase from light trapping, the thickness of the interfacial layer and the size of the particle need to be optimised for the material system [21]. The position of the nanoparticles in the device will also have different effects: placing them in the ETL of a standard device configuration (Section 2.1.3) should increase the reflection back into the active layer, hence increasing the absorption [94]. Whereas, including them into the HTL will scatter the light at wider angles increasing the mean path length of the light, and hence the absorption within the active layer [95]. The choice of functional coating also plays an important role, where un-optimised solutions will lead to increased recombination in the interfacial layers, before the charges are extracted.

The inclusion of nanoparticles in the active layer makes more use of the localised electric field effects enhancing the absorption, hence smaller nanoparticles are generally preferred to limit the scattering [22]. A limitation of this method is in the size range of the particles that can be used: As the particle size increases, changes in the morphology and an increase in trap states can be seen [79]; this is another reason why smaller nanoparticles are preferred. The nanoparticles also increase recombination of excitons [25], leading to reduced short circuit currents. The introduction of an insulating coating in a core-shell [21], [22], [25], or core-shell-shell [91] configuration has been shown to counteract the exciton quenching. However, this presents other, more complex, challenges in terms of optimisation of the plasmon resonance, including: particle size distributions, material configurations, layer thicknesses, and overall contribution to the performance.
One benefit of having a core-shell, or core-shell-shell, configuration, is the increase in the tuneability of the plasmon resonance. The addition of a coating around a metallic core has been shown to red-shift the plasmon peak proportionally to the thickness of the layer [86]. In a core-shell-shell configuration, competing effects start to appear (Chapter 6), leading to a resonance blue-shift with increasing size. A careful selection of materials and meticulous optimisation of a nanoparticle system can lead to substantial performance increases in OSCs. The biggest challenge is in understanding all the effects that arise from the inclusion of the nanoparticles into a OSC. This is the reason for developing an integrated model capable of simulating the optical response of a OSC containing nanoparticles (Section 7.2).

2.3. Modelling Methods

Optical modelling of multi-layered structures, plasmonic phenomena, and a mixture of the two, has proved to be a useful tool in understanding how the inclusion of plasmonic nanoparticles in OSCs can affect the optical response and the overall efficiency of the devices [21]. The inclusion of nanoparticles into OSCs is attempting to tackle some of the topical challenges seen to affect device performance, such as maximising the optical absorption, exciton dissociation, recombination, charge transport and extraction and the lifetime of the devices [95], [96]. The limitations and challenges have been discussed in Section 1.2 and reported impacts on device performance have been discussed in Section 2.2.4.

In this section, we look at some of the directions of research taken to model optical effects in multi-layered structures, such as OSCs (Section 2.3.1) and how the challenge of simulating plasmonic nanoparticles has been tackled (Section 2.3.2). Then we discuss briefly how nanoparticles are simulated in a multi-layered device (Section 2.3.3), focusing on the advantages and disadvantages of each method. Then we give a brief overview on using Matlab as a development environment for device modelling, showing how some of the in-built tools have been useful when developing a stable and robust algorithm.

2.3.1. Optical Modelling - Organic Solar Cells

Optical modelling is a powerful tool for looking at how light propagates through devices. In Organic Solar Cells, maximising the number of excitons generated in the active layer for a specific configuration is of maximum importance. OSCs that have not been optically optimised generally have much lower power conversion efficiencies (PCEs), as the two are proportional [36]. Therefore, in this section, we look at existing methods for modelling the optics within OSCs and how each method targets specific problems; these methods include: Finite-Difference Time-Domain (FDTD), Finite Element Modelling (FEM) and the Transfer Matrix Method (TMM).
Interference effects within the device are one of the biggest contributors to the absorption within an optical device. The interference effects depend on the phase and amplitude of more than one wave. With one source, multiple waves are produced by the multiple reflections from interfaces within a multi-layered structure. When dealing with layer thicknesses that are smaller than the wavelength, the phase becomes increasingly important, as even slight variations in the layer thicknesses can change the phase of the wave. Throughout this work, we will be using the terms ‘constructive’ and ‘destructive’ to describe the types of interference effects: ‘constructive’ would be when the waves are in-phase and hence the resulting amplitude at that point would be higher; and ‘destructive’, or when the waves are out-of-phase with each other and hence have a detrimental effect on the amplitude. Interference effects in OSCs, using the TMM, are explored in more depth in Section 3.4 and throughout Chapter 5.

All the methods that are used to simulate the optics of multi-layered structures, such as OSCs, take into consideration interference effects. Surface roughness will directly affect this, going from a completely coherent layer (flat-interfaces) to a more partially-coherent scenario [97]. Partially-coherent is used to describe the case when the interfaces are not flat, or have surface roughness – which causes specular reflections/transmissions. This can be simulated using FDTD and FEM methods, by changing the geometry at the interface to match the topography of a rough surface (or an approximation thereof). This comes with the disadvantage or requiring a finer mesh around this area and hence increased computational requirements. In contrast, there are two reported methods for accounting for these effects in the TMM: Random Phase method (Section 3.5.2) and an adaptation of the Fresnel reflection and transmission coefficients (Section 3.5.1), which have both been shown to be effective approximations of partially-coherent layers [97]–[99].

Numerical methods (e.g. FDTD and FEM) tend to make fewer assumptions and usually provide more accurate answers to complex problems – they are designed to be generic tools used for a multitude of different applications [100]–[102]. Analytical methods, such as the TMM, are usually more specific to the problem to be solved, and the assumptions made in the process should make physical sense. The major advantage of analytical methods, in general, over numerical, is the computational resource required: Numerical methods require orders of magnitude more computations than analytical methods – due to the number of iterations required to converge to an answer.

The advantages of using numerical approaches include: their accuracy is generally higher than that of analytical methods (due to the number of assumptions that are generally made); they can be used to simulate complex geometries effectively (a function of the fineness of the mesh, which determines the calculation points) and they can be used to look at transient behaviour. Disadvantages include having a computational domain does not work well for small
features in a large domain and it is resource-heavy, usually requiring a server or computer cluster to run efficiently [103]. In regards to OSC specific modelling, the difference in the size of the glass/PET substrate and the interfacial layers (~1 mm compared with ~10 nm) becomes very difficult to realise using these type of numerical methods and authors generally resort to not including this layer [104], [105] or changing the theoretical thickness to be of the same order (~100 nm).

In contrast, analytical methods (such as the TMM (Chapter 3)), are applied to more specific scenarios making some assumptions to simplify the calculations. One significant advantage of using methods, such as the TMM, is the required amount of computational resource is typically much lower than numerical methods, such that they can typically run on a standard desktop computer, or laptop. This allows for designing optimisation problems and studies that would require many different simulations (Chapter 5). Optimisation problems are much better suited to analytical methods than numerical ones predominantly because of the simulation time. Analytical methods have been used to verify results obtained by numerical methods [106], however, assumptions made in the process could have a negative impact on the accuracy of the model to the problem that is trying to be solved.

There are several readily available software packages for each of the methods that have been used to model OSCs; such as Lumerical (FDTD) [107], OPVDM (TMM/FDTD) [108], Setfos by Fluxim (TMM/FDTD) [109], and Comsol (FEM) [110].

**2.3.2. Modelling Plasmonic Nanoparticles**

Increasingly often, nanoparticles are being included into various layers of OSCs for different reasons. In practice, these nanoparticles are different size, shape, material within the same batch. They may even have functional coatings or similar, each with a statistical variation. We have shown in Section 2.2.4 reports of increases in efficiency through the inclusion of nanoparticles into the OSCs, with some research suggests that it is due to wide-angle light scattering that results in increased absorption [103], [111], [112], whilst others look at the strong localised near field created around the particles being responsible for increased exciton dissociation, charge transport and charge extraction [113], [114]. Some authors even report losses by the inclusion of nanoparticles [25], and NPs have also been shown to slow down the degradation process in some cases [26], [115].

One of the things to overcome with the inclusion of nanoparticles into OSCs is the increased exciton quenching, which has been observed by several authors [50], [79], [110], [116]. Recently, there have been increasingly more studies on the applications of oxide coatings (SiO₂, TiO₂, etc.) around the nanoparticles that serve to stop the exciton quenching (band energy trap states, where excitons can recombine) and also provide some plasmon resonance
tuning [50], [113], [117]. To further understand the changes in the optics when including plasmonic nanoparticles into OSCs, more in-depth modelling techniques for simulating many particles with different shapes, sizes, different coatings, and multiple coatings, and including realistic statistical distributions of each of these parameters should be developed (Chapter 4).

Some modelling techniques already exist that cover some of these: FDTD and FEM based simulations are capable of simulating different geometries, coatings and materials. However, a fundamental drawback of these methods is the defined nature of the geometries that does not allow for the simulation of a complete distribution of particles. Most FDTD or FEM based simulations tend to concentrate on one specific element, and no more than a few same-sized particles at the time [116], [118], [119].

Mie theory [120] has been extensively used to simulate the scattering properties of spherical objects under various conditions. This method has also been elaborated to include the ability to simulate single coatings [121], [122], absorbing surrounding media [123]–[125], particle size distributions [126], mixed media [126], among other scenarios. However, these have not been compiled into a single working theory, and the ability to create a recursive function for simulating N-number of coatings using Mie Theory has not been previously reported. We have tackled this in Chapter 4, where we describe our model before presenting an in-depth study using the model in Chapter 6.

2.3.3. Optical Modelling - Nanoparticles in OSCs

Optical modelling of nanoparticles in OSCs has been done before using FDTD and FEM based simulations. These simulations typically study single particle [103], [107], [127] or a small number of particles [116], [118], [128] in a single layer [107], [129] or a few-layered device [105], [128]. This is not representative of a complete system, which would generally have in the order of $10^{20} m^{-3}$ nanoparticles. Bastús et al. [130], [131] have shown that even rigorously controlled growth of nanoparticles results in a range of sizes that can be described through a probability distribution function. Hence, simulating OSCs with same-sized nanoparticles is a big assumption on its own, and a major drawback of using FDTD and FEM methods.

In this work, we show how we are working towards a complete device modelling scenario, where we can simulate many particles in a layer of a device. There will always be cases where this type of simulation is not suitable, such as for the study intra-dependent effects between the particles, or for the study of complex shapes etc. But, for generic modelling, and understanding of how the inclusion of nanoparticles will affect the device, this type of simulation is well suited.
2.3.4. MATLAB as a modelling environment

MATLAB is widely used within mathematical subjects as a platform for building proof of concept models, analysis of data etc. Matlab is efficiently built to work with vectors and matrices and this makes it ideal for running simulations with multiple input parameters and approaches such involving transfer matrices.

We have chosen to use MATLAB for some specific reasons:

- The time for development is short
- It is easy to use; with very good documentation and community
- Comes with libraries of in-built functions (besselj, for example)
- In-built plotting functions
- Object-orientated, allowing flexibility in programming
- Optimised for vectorisation

Disadvantages and reasons why ultimately moving to a different platform, such as Java/C++/Python would include:

- Only basic GUI framework available
- It can become resource heavy compared to other languages.

Time for development, during the proof of concept stage, is important for any project, and only those projects that rely on efficient calculations are generally built using more efficient languages (C++ etc.). In our case, the ideas behind the simulation are meant to be much more efficient than other techniques (e.g. FDTD, FEM, etc.) and making the program more efficient by porting it to another language is not going to be so beneficial for us.

Some important commands that we have used are included by default; for example, the example of the Bessel function of the first kind \( J_\nu(z) \) is the MATLAB representation (Eq. 2.12) [132], the second one is a textbook definition (Eq. 2.13) [82].

The time complexity of the calculation will still scale with both \( k \) and \( z \), such that in big-O notation this would be \( O(z \cdot N \cdot \log(N)) \), where the \( N \) originates from the summation to \( N \) terms. The \( \log(N) \) come from the factorial (\( k! \)), as it needs to be recalculated at every \( k \) term to \( N \) (starting with 1). However, the in-built function reduces the amount of computations done during the function (by using a scalar term outside of the summation (Eq. 2.13). In real terms, this means that the time taken to do \( m \) number of size parameters \( z \) scales linearly, and the real killer for performance would be the number of terms in the series that are required (\( N \log(N) \)). For nanoparticles and visible light, the size parameter is such that only a few terms
(\(N < 20\)) are required. This is another advantage of choosing the Mie Theory method for these specific applications (OSCs, biological, etc.).

\[
J_\nu(z) = (\frac{z}{2})^\nu \sum_{k=0}^{\infty} \frac{(-z^2)^k}{k! \Gamma(\nu + k + 1)}
\]

\[
J_\nu(z) = \sum_{k=0}^{\infty} \frac{(-1)^k}{k! \Gamma(k + \nu + 1)} \left(\frac{z^2}{2}\right)^{2k+\nu}
\]

One of the best things about this is that the algorithms used to calculate the Bessel functions are stable, and can include decimal values for \(\nu\), which when working with spherical Bessel function is extremely important; as spherical Bessel functions relate to Eq. 2.13 by a factor of \(\nu + 0.5\). \((z/2)^2\) is a scaler and hence it has been taken out of the summation.

To ensure efficiency, some of the calculation required need to be re-written using the terms available. An example of this is given in Appendix B, where we take the spherical Bessel functions and logarithmic derivative calculation and re-write them in terms of the Bessel functions of the first and second kind. Then we can calculate this once, and use the generated array for multiple calculations within the broader Mie calculations. This is just an example of how we have manipulated the mathematics to make it suitable for the type of computing we wish to do.

Overall, we believe that Matlab will be a good choice for a simulation environment allowing for the object orientated power of traditional programming languages, but also the added benefit of being able to explore the data, the useful documentation and in-built functions available etc.

In this chapter, we have reviewed the literature and provided some basic theory in preparation for the rest of this work. In Section 2.1, we discussed OSCs including basic operating principles. Then we elaborated on some of the useful parameters and metrics (Section 2.1.2), common material and device configurations (Section 2.1.3). Section 2.2 looks at plasmonic nanoparticles, where we discuss the different plasmonic modes concerned with OSCs (Section 2.2.1), description of localised surface plasmon resonance (Section 2.2.2), useful metrics and parameters (Section 2.2.3). Section 2.2.4 compiled data from more than 80 sources, which showed a fixed +0.4% improvement upon the reference device efficiency. Then in Section 2.2.5 we discuss the limiting factor associated with the inclusion of nanoparticles, aligning with some of the results shown in Section 2.2.4. We ended this chapter discussing different modelling methods for both OSCs (Section 2.3.1), plasmonic nanoparticles (Section 2.3.2), and plasmonics in OSCs (Section 2.3.3). The next chapter (Chapter 3) discusses the optical model that was built as a basis for the development of a simulation tool that can efficiently simulate nanoparticles in OSCs.
Chapter 3

3. Basic Optical Model

As described in Section 2.3, the modelling of Organic Solar Cells (OSCs) is an effective way to predict and optimise device performance. The most common approach for modelling the electrical characteristics of OSCs is the drift-diffusion model [14]. The drift diffusion model relies on knowing the exciton generation rate through the device (Section 2.1.2). To obtain this, an optical model is used to find the number of incident photons absorbed per second through the active layer.

As described in Section 2.3.1, modelling of thin-film devices can be conducted using methods such as the Finite-difference time-domain (FDTD) [133] method and Finite Element Modelling (FEM) [134]. However, these have a common disadvantage: The computational time needed to solve a simple structure can take anywhere from a few hours to a few days. This makes optical optimisation of simple problems extremely time consuming, because each iteration of the simulation, which requires a different geometry, needs to be re-meshed and then recalculated on an iterative basis.

Previous research has demonstrated [14], [19], [97], [99], [135]–[139] that the Transfer Matrix Method (TMM) - an analytical 1-D method - can be used to accurately model the transmission, absorption, and reflection of a multi-layered structure. The TMM calculates the propagation, and interference effects, of electromagnetic waves through a multi-layered system. The model that we have constructed is described within this chapter; where we highlight the assumptions and limitations of this method (Section 3.8). We also provide verification of the model, comparing the simulation results to experimental devices (Section 3.7). This section is important for understanding the principles, additions and alterations that have been made, which will provide a basis for proposed future work (Section 7.2): Integrating our plasmonic model (Chapter 5) with the TMM, to model the effects of nanoparticles in OSCs (including the increased surface roughness within the inclusion layer).

Due to the nature of the devices, where the thicknesses of the layers are usually smaller than the wavelength of light, the phase of the waves are especially important, leading to constructive (in-phase) and destructive (out-of-phase) interference effects. These effects occur in the form of Fabry-Pérot oscillations, due to interference between multiple reflections from the boundaries (interfaces), which only occur when the layer thickness is less than the wavelength of the incident wave. Therefore, the absorption in the active layer of the devices
is highly sensitive to the layer thickness and the complex material properties of all coherent layers.

In this chapter, we demonstrate a verified model that describes the propagation of a monochromatic electromagnetic wave. These can be separated out into their s- and p-polarisations. We also show how we can include the angular dependence, and extract useful information in regards to the device performance from an optical perspective. Then, we highlight two different methods for accounting for the scattering of light at the interfaces and surfaces (Section 3.5), showing the strength and weaknesses of both methods within this application.

3.1. Complex Fresnel Coefficients

To calculate the propagation through a multi-layered system, it is useful to firstly describe what happens at the interface between two materials, and secondly what happens within a layer of the multi-layered system. For the first part, we use Fresnel coefficients to describe the effects of transmission and reflection from a plane interface for both s-polarised and p-polarised waves. Layer $j$ is the layer of interest, and layer $k$ (or $j + 1$) is next layer in the system with respect to the incident wave. Throughout this work, we refer to the complex refractive indices of the materials as $\tilde{n} (n + ik)$, where a non-complex refractive index would be represented by the symbol $n$.

![Figure 3.1 The refraction and reflection from a wave at an incident angle ($\theta_i = \theta_r$) perpendicular to a plane interface between two materials with complex refractive indices $\tilde{n}_j$ and $\tilde{n}_k$. $\theta_i$ is the angle of refraction, $I_{j/k}$ shows the interface between layer $j$ and $k$, and the incident, reflected, and transmitted electric field vectors are $E_i$, $E_r$, and $E_t$, respectively.](image)
Two things happen at a plane interface: A proportion of light is refracted, and the rest is reflected (no absorption happens at the interface). The proportion, and angle of the refraction, are based on the ratio of the complex refractive indices of the materials either side of the interface, where \( \bar{n} = n + ik = \sqrt{\varepsilon \mu} \). Here, the assumption is that the materials used are isotropic and non-magnetic \((\mu = 1)\), and therefore \( \bar{n} = \sqrt{\varepsilon} \). Figure 3.1 shows visually what happens to electromagnetic waves at an interface, where \( \theta_i, \theta_t \) and \( \theta_r \) are the incident, refracted and reflected angles respectively, and \( \bar{n}_j \) describes the permittivity of the material in the \( j^{th} \) layer.

The Fresnel coefficients are based on Snell's law (Eq. 3.1), which describes the relationship between the angle of incidence and the angle of refraction with a change in refractive index, where \( \theta_i = \theta_r \) in Figure 3.1.

\[
n_0 \sin(\theta_0) = n_1 \sin(\theta_1) = n_j \sin(\theta_j) \quad \text{3.1}
\]

We can describe the transmitted and reflected amplitudes (Eq. 3.2 – Eq. 3.5), in terms of Fresnel coefficients. This enables us to keep the polarisations independent, and the phase information for both polarisations is therefore retained. Eq. 3.2 is the complex Fresnel coefficient for the transmission of s-polarised (TE) light, and Eq. 3.3 describes the complex reflection coefficient. Eq. 3.4 and Eq. 3.5 are for p-polarised (TM) Fresnel transmission, and reflection, coefficients respectfully. The derivation for these equations has been thoroughly documented by the text of Born and Wolf [83].

\[
t_{jk,\text{TE}} = \frac{2 \bar{n}_j \cos(\theta_j)}{\bar{n}_j \cos(\theta_j) + \bar{n}_k \cos(\theta_k)} \quad \text{3.2}
\]

\[
r_{jk,\text{TE}} = \frac{\bar{n}_j \cos(\theta_j) - \bar{n}_k \cos(\theta_k)}{\bar{n}_j \cos(\theta_j) + \bar{n}_k \cos(\theta_k)} \quad \text{3.3}
\]

\[
t_{jk,\text{TM}} = \frac{2 \bar{n}_j \cos(\theta_j)}{\bar{n}_k \cos(\theta_j) + \bar{n}_j \cos(\theta_k)} \quad \text{3.4}
\]

\[
r_{jk,\text{TM}} = \frac{\bar{n}_k \cos(\theta_j) - \bar{n}_j \cos(\theta_k)}{\bar{n}_k \cos(\theta_j) + \bar{n}_j \cos(\theta_k)} \quad \text{3.5}
\]

The total reflection is given by \( R = |r|^2 \), where \( r \) is given for both polarisations in Eq. 3.3 and Eq. 3.5. The differences between p-polarised and s-polarised reflection using complex Fresnel coefficients can be seen in Figure 3.2. Figure 3.2 (a) demonstrates the case when the refractive index of the second medium \((n_2)\) is higher than the first \((n_1)\), where anything with an incident angle higher than the critical angle is totally internally reflected. Figure 3.2 (b)
demonstrates the second case, where $n_1$ is higher than $n_2$: The light is never totally internally reflected. The critical angle can therefore be defined as $\theta_c = \sin^{-1}(n_2/n_1)$.

\[ \theta_c \]

**Figure 3.2** The reflection from an interface for s-polarised and p-polarised waves travelling from material $n_1$ to $n_2$, over a range of incident angles from $\theta_i = 0$ to $\theta_i = \pi/2$ rads. $\theta_c$ denotes the critical angle at which total internal reflection occurs. (a) $n_1 = 1.2$ and $n_2 = 1$, (b) $n_1 = 1$ and $n_2 = 1.5$.

It is now possible, using Snell's law (Eq. 3.1), to describe the angle of refraction as a function of the incident angle in ambient conditions (Eq. 3.6), more on how this was obtained is given in Appendix C.

\[ \tilde{n}_j \cos(\theta_j) = \sqrt{\tilde{n}_j^2 - \tilde{n}_0^2 \sin(\theta_0)} \quad 3.6 \]

### 3.2. Transfer Matrix Method

In the previous section, we showed how the complex refractive indices can be used to determine Fresnel's transmission and reflection coefficients for a given incident angle and polarisation. This allows us to integrate over the solar spectrum and see how the solar cell performs over a range of angles. In this section, we show how this can be formalised into a matrix describing the electric field propagation through a multi-layered system.

The transfer matrix should take the form given by Eq. 3.7, where $\mathbf{E}^{+\ast}_{OR}$ is the incident electric field propagating in the forward boundary, the $\kappa$ represents that it is positioned at the interface (or at the right of the layer, in a left-to-right configuration, demonstrated in Figure 3.3). $\mathbf{E}^{-\ast}_{OR}$ describes the backwards propagating electric field. When dealing with the TMM, the notation follows that of Jung et al. [136].

\[
\begin{bmatrix}
\mathbf{E}^{+\ast}_{OR} \\
\mathbf{E}^{-\ast}_{OR}
\end{bmatrix} = \mathcal{S} \cdot 
\begin{bmatrix}
\mathbf{E}^{+(m+1)\ast L}_{(m+1)\ast L} \\
\mathbf{E}^{-+(m+1)\ast L}_{(m+1)\ast L}
\end{bmatrix} \quad 3.7
\]
Figure 3.3 A schematic of a multi-layered stack, showing the electric field directions at each of the boundaries in the forward propagating direction (+) and backwards propagating direction (−). Also, \(d\) corresponds to the thickness of each layer, in the direction of propagation, where \(d_j\) would be the thickness of the \(j\)th layer.

In the TMM there are two type of matrices, the first is the interface matrix, which is described by \(I_{jk}\), and describes the electric fields at either side of the interface; as shown in Eq. 3.8. The second is a layer matrix, which describes the coherent propagation within a layer dependant on its optical path length. This also holds the phase information for calculating the interference effects, which is denoted as \(L_j\) and is shown in Eq. 3.9.

\[
\begin{bmatrix}
E_{jR}^+ \\
E_{jL}^+
\end{bmatrix}
= I_{jk} \cdot \begin{bmatrix}
E_{kL}^+ \\
E_{kL}^+
\end{bmatrix} = \frac{1}{t_{jk}} \cdot \begin{bmatrix} 1 & -r_{kj} \\
t_{jk} & t_{jk} - r_{kj}t_{kj}
\end{bmatrix} \cdot \begin{bmatrix}
E_{kL}^+ \\
E_{kL}^+
\end{bmatrix} \quad 3.8
\]

To calculate the wavelength-dependant phase length \((k \cdot r)\) of the propagation of light through a layer, we need the complex refractive index, and the layer thickness. Using trigonometric functions, we can find the optical path length of the incident wave, where \(|r| = d_j \cos(\theta_j)\), where \(\tilde{n}_j \cos(\theta_j)\) is given in Eq. 3.6. The phase length is then given by the wave vector \(k\), which in this case would be \(k \cdot r = \beta_i d_j = \frac{2\pi}{\lambda} \tilde{n}_j \cos(\theta_j) d_j\). This quantity describes the wavenumber of the directional wave within the layer, which will be less than 1 for thicknesses smaller than the wavelength. The propagation of a wave through the layer can be described as a linearly polarised wave \(e^{-i(k \cdot r)}\), which is what is used within the layer matrix (Eq. 3.9).

\[
\begin{bmatrix}
E_{jR}^+ \\
E_{jL}^+
\end{bmatrix}
= L_j \cdot \begin{bmatrix}
E_{jL}^+ \\
E_{jL}^+
\end{bmatrix} = \begin{bmatrix} e^{-i\beta d_j} & 0 \\
0 & e^{i\beta d_j}
\end{bmatrix} \cdot \begin{bmatrix}
E_{jL}^+ \\
E_{jL}^+
\end{bmatrix} \quad 3.9
\]

As can be seen from Eq. 3.8 and Eq. 3.9, the input to the next interface matrix is the output of the layer matrix in this form. It is now possible to describe light propagation through a coherent stack of thin-films, using the Layer and the Interface matrices. From this, it is possible obtain the transmission and reflection, and hence the absorption from the whole device.
Chapter 3 - Basic Optical Model

The method of calculating the interference within the layer assumes that the layers are coherent (constructive and destructive interference effects occur within the layers, determined by the phase, \( \beta_j \) in Eq. 3.9), and perfectly flat with a constant thickness. When fabricating films, they have a surface roughness value, which is proportional to the change in height from the measured thickness. Therefore, assuming the layers are perfectly planar is incorrect. We have presented methods to introduce partial coherence into the model, which are described in Section 3.5. It also assumes that all the materials are homogeneous and isotropic, and non-magnetic. Jungho et al. [140] came up with a method of including the permeability into the TMM, allowing the inclusion of magnetic materials, and meta-materials. They gave a rigorous method for modelling meta-material structures, which can be used as a tool to develop understanding of such structures. Although this is currently beyond the scope of this work, for application in OSCs, it would be a great addition to the tool; as discussed in the Future Work (Section 7.2).

![Figure 3.4](image)

**Figure 3.4 Optical path length through a layer in polar co-ordinates from layer thickness \( (d_j) \) and refraction angle \( (\theta_j) \), where the optical path length is a real distance denoted by \(|r|\).**

To calculate the transmission \((T)\) shown in Eq. 3.10), reflection \((R)\) shown in Eq. 3.11) and absorption \((A)\) from the TMM we can use the description of the electric field vectors, where \( A = 1 - R - T \).

\[
T = |t|^2 = \left| \frac{E_{(m+1)L}^+}{E_{OR}^+} \right|^2 \tag{3.10}
\]

\[
R = |r|^2 = \left| \frac{E_{OR}^-}{E_{OR}^+} \right|^2 \tag{3.11}
\]

This type of problem is particularly well suited to the MATLAB environment due to the already vectorised nature of the problem, as explained in Section 2.3.4. The efficiency of the calculation, and hence lower computational requirements, allows for solutions to optimisation
problems, making it ideal for rapid development and characterisation of devices with new materials.

As discussed in Section 2.1.2, we wish to obtain the exciton generation rate ($G_{\text{opt}}$). In this case the optical model needs to provide information such as the spatial distribution of the electric and magnetic fields, and the absorption profile within each individual layer. To achieve this, we need to describe the propagation of light within each layer, taking into consideration the layers on either side. The standard TMM only describes the input and output of a multi-layered structure, therefore, we describe the Partial TMM method and demonstrate how we can use this to obtain the information from within each of the layers.

### 3.3. Partial Transfer Matrix Method

The partial TMM is used to extract spatial information about the electric field within the individual layers. This information relies on the amount of reflection and transmission from the packets of layers either side. As described by Pettersson et al. [19] the system can be described by two sub-scattering matrices, which we will denote as $S_j'$: For the subsystem to the left of the layer of interest (layers $n_0 \rightarrow n_{j-1}$ in Figure 3.3), and $S_j''$ for the subsystem to the right (layers $n_k \rightarrow n_{m+1}$ in Figure 3.3). The interfaces between layers $n_{j-1}$ and $n_j$ ($I_{(j-1)j}$), and layers $n_j$ and $n_k$ ($I_{jk}$), are also taken into consideration. Eq. 3.12 shows the physical meaning of the subsystem parameters; this allows us to obtain the amount of incident energy that is reflected and transmitted through the layer.

$$S = \left( \prod_{v=1}^{j-1} I_{(v-1)v} L_v \right) I_{(j-1)j} \cdot L_j \cdot \left( \prod_{v=j+1}^{m} I_{(v-1)v} L_v \right) I_{m(m+1)} \tag{3.12}$$

The complex reflection and refraction values can now be defined for both parts of the system using Eq. 3.2 – Eq. 3.5 applied to the two subsystems, where $S_{j(11)}'$ denotes the first element of the first subsystem of the scattering matrix, and $S_{j(21)}''$ describes the first element on the second row of the scattering matrix of the second subsystem. These values can be used to find the spatially-resolved electric field vector (Eq. 3.13), given by [19].

$$E_j(z) = E_j^+(z) + E_j^-(z) = [t_j^+ e^{i\beta jz} - t_j^- e^{-i\beta jz}] E_0^+ \tag{3.13}$$

$$t_j^+ = \gamma \frac{t_j'}{1 - r_j' t_j'' e^{i2\beta j d_j}} \tag{3.14}$$
Where \( r_{j-}' = \frac{-S_{j(21)}'/S_{j(11)}'}{1 - r_{j-}' r_{j-}'' e^{i2\beta_j d_j}} \) is the backwards propagating reflection coefficient from the first subsystem, which describes the second order reflection back into the layer of interest. A note here, that the generalised quantities given by Jung et al. [136] for \( t_{j+}' \) and \( t_{j-}' \) are incorrect and do not yield the same answers that they gave in their results. Hence, we provide the corrected values, where \( \gamma \) is the correction factor for the glass, and represents the energy dissipation within this thick incoherent layer. More information on these corrections will be given in Appendix D.

\[
t_{j-} = \gamma \frac{t_{j+}' r_{j-}'' e^{i2\beta_j d_j}}{1 - r_{j-}' r_{j-}'' e^{i2\beta_j d_j}} \quad \text{(3.15)}
\]

Figure 3.5 shows the s-polarised electric field through the device as a function of distance from the glass. This is after treating the glass as incoherent, which will be discussed in Section 3.4. The sum of the complex forward and backwards propagating waves creates interference, both constructive and destructive; this is what causes peaks in the electric field through the device. Optically tuning this then becomes viable by changing the peripheral layer’s thickness. It is possible to centre the peak of the electric field within the active layer (Section 4.1); as the electric field is proportional to the power dissipation (Section 3.6). An optimised OSC would have a maximum peak in the power dissipation within the active layer.

Figure 3.5 The (s-polarised) electric field through a multi-layered stack, shown as a function of distance from the glass, the colours of the layers are representative of the same colours in the device structure image. The peak of the electric field is within the HTL (dark-pink layer), where an optimised device would usually have the peak occur within the active layer (light-pink layer). Therefore, this device could be optimised further, just by changing the layer thicknesses. The light is incident on the left hand side of the structure propagating from left to right.
3.4. Coherent and Incoherent Packets

One of the main problems with the TMM is the treatment of purely coherent layers (single phase leading to constructive or destructive interference effects), which is only accurate for layers that appear flat when compared to the wavelength of light. The substrate, when included, will have a variation of thickness larger than that the wavelength of light, and the Fabry-Pérot oscillations that you would normally see with coherent layers are not experimentally visible in the substrate. For this reason, we integrate over all phases to compensate for this, which leads to a more experimentally representative result.

The most common way of doing this is removing the phase (complex part) for the calculations of the incoherent layers by working with the general intensity matrix, instead of treatment using electric fields. This approach has been well documented [97], [99], [135], [136]. Jung et al [136] give a detailed description of the system, which describes the propagation through incoherent layers using the electric field intensities, which for the $j^{th}$ would be given as $U_{jR}$, and $U_{jR}^{-}$, respectively.

We can now express the transfer matrix in terms of intensities, as shown in Eq. 3.16, where $I_{1/(m+1)}$ is the modulus square of the coherent reflection and transmission coefficients, which are calculated using Eq. 3.18, converting the electric field amplitudes to intensities, where $U = |E|^2$.

$$\bar{s} = \bar{i}_{0/1} \bar{l}_{1}(m+1)$$  \hspace{1cm} 3.16

These matrices become real, and not complex, which removes the complex phase component and describes the intensity passing through the layer only.

The intensity matrix description at an interface is given in Eq. 3.17 and Eq. 3.18, which describe the transmitted and reflected intensities as a function of the modulus square of the Fresnel coefficients. This means that there will not be any change in the phase from the interface.

$$\begin{bmatrix} U_{jR}^+ \\ U_{jR}^- \end{bmatrix} = \bar{i}_{j/k} \begin{bmatrix} U_{kL}^+ \\ U_{kL}^- \end{bmatrix}$$  \hspace{1cm} 3.17

$$\bar{i}_{j/k} = \frac{1}{|t_{j/k}|^2} \begin{bmatrix} 1 & |r_{k/j}|^2 \\ -|r_{k/j}|^2 & |t_{j/k}t_{k/j}|^2 - |r_{j/k}|^2 \end{bmatrix}$$  \hspace{1cm} 3.18

Eq. 3.19 and Eq. 3.20 describe the transmission of intensity from one side of the layer to the other. This is done by taking the absolute value squared of the Layer matrix elements. This then makes the total reflection from the system $R = U_{0R}/U_{0R}^+$ and the transmission $T =$
$U_{(m+1)L}^+/U_{0R}^+$, which can be calculated easily from the generalised scattering matrix $\tilde{S}$, shown in Eq. 3.16.

$$\begin{bmatrix} U_{jL}^+ \\ U_{jL}^- \end{bmatrix} = \prod_j \begin{bmatrix} U_{jR}^+ \\ U_{jR}^- \end{bmatrix}$$ \hspace{1cm} (3.19)

$$\prod_j = \begin{bmatrix} |e^{i\beta j d_j}|^2 \\ 0 \\ 0 \\ |e^{-i\beta j d_j}|^2 \end{bmatrix}$$ \hspace{1cm} (3.20)

Figure 3.6 (a) Simulated device structure with layer thicknesses and (b) complex refractive index ($\tilde{n} = n + i k$), where $n$ (solid) is the real part and $k$ (dashed) is the imaginary part of the refractive index (Appendix E). (c) Standard TMM with the Glass substrate treated as coherent and (d) the substrate is treated as an incoherent layer. Oscillations, resulting from interference effects (c), are apparent when treating a thicker layer as coherent. These oscillations reduce significantly when the much thicker glass layer is treated as incoherent (d), which is what you would expect as the scattering from the internal interfaces increases.

Figure 3.6 gives an example of the simulation accounting for and not accounting for the incoherent glass substrate, where Figure 3.6 (a) gives the schematic of the simulated device structure including the names of the materials, and the thickness of each of the layers. The
refractive indices of the materials used are shown in Figure 3.6 (b), which gives both the real and complex parts ($n$ and $k$). Finally, Figure 3.6 (c) shows the result of the model given in Section 3.2, which shows the Fabry-Pérot oscillations from the glass substrate that are not apparent in experimental results because the thickness, and surface roughness is not perfectly flat. To account for this, we can make the substrate incoherent as part of the partial system shown in this section, Figure 3.6 (d) shows the transmission, reflection and absorption of the simulated device.

### 3.5. Partial Coherence (Surface Roughness)

When something is partially coherent, it is not completely coherent, or completely incoherent, it shares elements of both. Where previously we had to deal with the incoherent layers using the intensities, with partial coherence we can treat them using electric fields still. This is useful for keeping phase information. In thin-film device structures, experimental variation would appear due to contaminants, layer thickness variation, measurement errors, and surface roughness. We would like to account for some of these effects to make the simulation more realistic.

There are two well-known methods to account for surface roughness in the thin films, the first is by modified Fresnel coefficients using the Root Mean Squared (RMS) surface roughness value [97], which can be measured. The second is by a random phase method [139], which integrates over a random selection of phases within limits set to be proportional to the surface roughness. The second of these methods is applied in the layer matrix, and therefore does not require any modification of the Fresnel coefficients [139]. The modified Fresnel coefficients is the most understood and popular method used.

In this section, we give a brief description of how each of the methods work and give an example of the use of both methods before evaluating them for use within the final model.

#### 3.5.1. Surface Roughness – Fresnel

The modification of the Fresnel coefficients used in the interface matrix (Eq. 3.8) results in changes in the reflection and the transmission properties at an interface. This is done by introducing a Gaussian distribution describing the phase variation at the surface/interface; as a function of the change in height [97]. These are in the form of exponents, based on the RMS surface roughness ($\sigma_{RMS}$) between layers $j$ and $k$, and the wavenumber ($k_z = \frac{2\pi}{\lambda} n_j$). The changes in the transmission coefficient can be described by the correction factor given in Eq. 3.21 [97], where it would be the same for light propagating in either direction, whereas for the reflection coefficients it is different and needs a separate coefficient for forwards (Eq. 3.22) and backwards (Eq. 3.23) propagations. To experimentally obtain the surface roughness, we
can use Atomic Force Microscopy (AFM) on several areas of the device and obtain the RMS surface roughness value \[47\], which can then be used in the calculations.

\[
s_t = e^{-\frac{1}{2} \left( \frac{2\pi \sigma_{jk}(n_k-n_j)}{\lambda} \right)^2} \tag{3.21}
\]

\[
s_{r(jk)} = e^{-2 \left( \frac{2\pi \sigma_{RMSn_j}}{\lambda} \right)^2} \tag{3.22}
\]

\[
s_{r(kj)} = e^{-2 \left( \frac{2\pi \sigma_{RMSn_k}}{\lambda} \right)^2} \tag{3.23}
\]

The equations for adapting the Fresnel coefficients (Eq. 3.21 – Eq. 3.23) can be implemented into the interface matrix \( I_{j/k} \) as demonstrated in Eq. 3.24. This can be simplified dramatically in the case of a single incident linearly polarised wave (with forward directional propagation), which becomes Eq. 3.25 \[97\], \[138\], \[139\].

\[
I_{j/k} = \frac{1}{s_{t}t_{jk}} \cdot \begin{bmatrix}
1 & -s_{r(kj)^{T}k}
n_{(jk)}^{T}ky_k - s_{r(jk)^{T}k}s_{r(kj)^{T}k}
\end{bmatrix} \tag{3.24}
\]

\[
I_{j/k} = \frac{1}{s_{t}t_{jk}} \cdot \begin{bmatrix}
1 & s_{r(jk)^{T}j}
s_{r(jk)^{T}j}n_{(jk)}^{T}ky_k
\end{bmatrix} \tag{3.25}
\]

A major observation from the addition of partial coherence into the model, is the increase in the absorption with increased surface roughness. This is due to a decrease in the transmission with increasing surface/interface roughness. The light is scattered at an interface, which reduces the diffusive reflection/transmission, increases the optical path of the light within the layer and, hence increases the absorption. Overall, the transmission should not increase. A way to mimic the increase in the optical path length of the light through the layer can be achieved with a random phase method can be used. One of the advantages of using this method is that it directly relates to a measurable quantity (surface roughness), it is also analytical too, which fits in with the aims of the model (allowing for efficient and accurate simulations). In the next section, we look at a different method, which utilises a stochastic process to predict the effects from surface and interface roughness to produce partial coherence.
Partial Coherence (Surface Roughness)

Figure 3.7 (a) Simulated device structure with layer thicknesses; including ZnO, which is a commonly used Electron Transport material in OSCs. (b-d) Transmission, reflection and absorption from the devices including (c) and (d) partial coherence, and not including (b). (b) is completely coherent, no surface roughness, (c) ITO/ZnO interface with RMS 10nm, and ZnO/Air interface has 20nm. (d) ITO/ZnO interface with RMS 50nm, and ZnO/Air interface has 100nm. The additional surface roughness introduced in the calculations removes the coherent oscillations, seen in (c), resulting in a flatter Abs/Tra/Ref spectra (d), which is what you would expect as the scattering from the internal interfaces increases.

3.5.2. Surface Roughness – Random Phase Model

The layer matrix is built from taking the optical path length using different refraction angles (Eq. 3.6); if a surface roughness is introduced, the optical path through the layer will increase due to scattering of the light. This scattering of light can be described using the refraction angle, and is the basis of the Random Phase Method [99]. Also, as when transitioning between perfectly flat and rough surfaces, the Fabry-Pérot oscillations, which arise due to the reflections at the surface causing constructive/destructive interference effects, reduce significantly, up to a certain value of the roughness ($\sigma_{RMS}$) where they are no longer visible.
The random phase method adjusts the optical path length in the TMM calculations with an additional factor ($\phi_{\text{rand}}$). The random refraction factor is used to describe the changes in the transmission from both specular and diffusive refraction, however it does not take into consideration the reflection of the incident light on the surface of the device. In this case, the random refraction angle takes the form $\phi_{\text{rand}} = \beta_n \cdot \text{Rand}$, where $\beta_n$ is a number between 0 and $\pi$, which describes the severity of the surface roughness, and the random number (Rand) between -1 and 1. To obtain realistic results with this method, it should be repeated multiple times, with the average of all the iterations being the final output [139]. This has the disadvantage of computational time increase in comparison to Section 3.5.1, where it only needs to be calculated once. The other disadvantage with this method is the relation of the refraction angles to the RMS surface roughness parameter. For this method to work effectively, a weighted value attached to the random process should be modelled, which would relate the amount of ‘randomness’ (phase fluctuation) to the surface roughness. This is something that needs to be investigated further (Section 7.4).

Figure 3.8 shows the results from the random phase method, where the device structure used is given in Figure 3.7 (a). As can be seen, the average value of all the metrics does not change; as the random phase increases, the Fabry-Pérot oscillations are still supressed (compared with the original, Figure 3.7 (b)), which is what is expected in an experimental system.

\[
\frac{2\pi}{\lambda} \tilde{n}_j \cos(\theta_j) d_j \rightarrow \frac{2\pi}{\lambda} \tilde{n}_j \cos(\theta_j) d_j + \phi_{\text{rand}}
\]

Figure 3.8 Transmission, reflection and absorption from the devices including partial coherence from the random phase approach using (a) $\beta_n = \pi/4$ and (b) $\beta_n = \pi$. There is minimal difference between (a) and (b) due to the mean of the random value being the same.
3.6. Outputs from the Model

In the previous sections of this chapter, we discussed how the model was realised with emphasis on the methods used and the concepts behind them. In this section, we explore the outputs of the model and how they can be used to study the optics of thin-film devices. These outputs have been generated by using the layer thicknesses, surface roughness parameters and wavelength dependant optical properties for each of the layers (Appendix E).

In Section 3.2 we introduced the method used to calculate the Transmission (Tra), Reflection (Ref) and Absorption (Abs) of devices using the TMM. Now we look at how we can draw relationships between inputs and outputs. Figure 3.9 (a) demonstrated the Abs, Tra and Ref of a device over a range of wavelengths. This metric can be directly compared to UV-Vis spectroscopic results taken from experimental devices, as we demonstrate further in Section 3.7.3. Figure 3.9 (b) looks at a different angle, where we change the angle of incidence and look at the reflected and transmitted results from the devices. These modelling results could be obtained experimentally by using a solar simulator and measuring the change in performance with change in incident angle (from $0^\circ$ to $90^\circ$ [141]. Although, the most common method for investigating the angular dependence is through the use of the TMM [141], [142]. The outputs can show the different results for different polarisations (TE or TM, Figure 3.10) or the output assuming a plane wave (Figure 3.9). At an angle of incidence of 0, the results for TE and TM are the same and only one is given.

![Graphs](image.png)

*Figure 3.9 The Absorption, Transmission and Reflection for a device consisting of Glass (700 μm) and ITO (150 nm), which typically would have between 80 and 90% transmissivity over the visible spectra. (a) shows the wavelength dependent results, and (b) shows the angular dependence at a wavelength of 420 nm, which demonstrates how the absorption and transmission fall-off as the incident angle increases.*
The Transmission, Reflection and Absorption of a device under different polarisations, (a) s-polarised, and (b) p-polarised, with an incident angle $\theta_i = 60^\circ$. The p-polarised spectra is, on-average, higher than that of the s-polarised, with the exception of the peak at 430 nm, where the absorption in the s-polarised case reached 100%.

As discussed in Section 2.1.2, the exciton generation rate needs to be calculated before the electrical characteristics can be computed, as it is one of the required parameters. In this case, we need a way of describing the exciton generation profile through the active layer, which is spatially dependent due to interference effects within the layer. To achieve this, we first need to calculate the electric and magnetic field strengths throughout the device, following the notation of Pettersson et al. [19] and Jung et al. [35] (Appendix D).

\[
E_{jTE}(z) = E_{jTE}^+ (z) + E_{jTE}^- (z) = [t_{jTE}^+ e^{i\beta j z} + t_{jTE}^- e^{-i\beta j z}] E_0^+ \tag{3.27}
\]

\[
E_{jTM}(z) = E_{jTM}^+ (z) + E_{jTM}^- (z) = \tilde{n}_j [t_{jTM}^+ e^{i\beta j z} + t_{jTM}^- e^{-i\beta j z}] E_0^+ \tag{3.28}
\]

The description of the magnetic field (Eq. 3.30 and Eq. 3.29) has been found by taking the spatial derivative of the electric field (Eq. 3.26 and Eq. 3.27), according to Maxwell.

\[
H_{jTE}(z) = H_{jTE}^+ (z) + H_{jTE}^- (z) = c\varepsilon_0 \tilde{n}_j [t_{jTE}^+ e^{i\beta j z} + t_{jTE}^- e^{-i\beta j z}] E_0^+ \tag{3.29}
\]

\[
H_{jTM}(z) = H_{jTM}^+ (z) + H_{jTM}^- (z) = c\varepsilon_0 [t_{jTM}^+ e^{i\beta j z} + t_{jTM}^- e^{-i\beta j z}] E_0^+ \tag{3.30}
\]

Figure 3.11 shows the optical intensities for the electric ($|E|^2$) and magnetic fields ($|H|^2$). When designing photovoltaic cells, we want to optimise the optical intensity within the active region (Section 4.1); as this is directly proportional to the exciton generation rate.
Figure 3.11 (a) Electric field optical intensity through the device as a function of the distance from the glass. (b) Magnetic field optical intensity, and (c) is the time-averaged Poynting vector, normalised to the incident energy, these were taken at a specific wavelength ($\lambda = 550 \, \text{nm}$). This demonstrates that the peak in the E-field distribution (a), and the minima in H-field (b), relates to the biggest drop in the power dissipation (c), which is characteristic of an optimised cell.

The time averaged power dissipation, given by Eq. 3.30, is the Poynting vector of the Electric and Magnetic fields in both polarisations. This directly relates to the spatial absorption, where the relationship is shown in Eq. 3.31. This provides us with useful information, the difference in the time-averaged power dissipation between two points provides us with the integral of the power dissipation. The power dissipation ($Q$) can give us a spatial representation of the generated excitons as a function of wavelength.

This also allows us to run the simulation to obtain the maximum number of excitons generated in the active layer, which is the basis of the optical optimisation routine adopted in this work (Chapter 4). Further to this, we can then do this as a function of wavelength and angle, to find the optimum for angular operation and specific wavelength.

In both Pettersson’s [19] and Jung’s [136] papers, they only assume and treat (a) normal incidence, and (b) one single polarisation. This is because, due to the symmetry when the incident angle is normal to the surface, the TE and TM modes will yield identical results. In
Chapter 3 - Basic Optical Model

In this study, we do not make these assumptions, as this neglects essential information about the response of the devices over multiple angles. It also allows us to incorporate physical processes that only occur in one of the two polarisations, mainly Plasmonics, which has been shown to only appear in TM polarisations [23], [143]. For this reason, it is of great benefit to adapt the equations given to allow for this in preparation for adding gratings, nanoparticles and other plasmonic enabled materials (Section 7.2). Therefore, it is essential that we correctly treat the calculation of the power-dissipation accounting for the difference in polarisations. Hence, we re-write the Poynting vector assuming asymmetry between the polarisations (Eq. 3.30), this affects the calculations for the optical-dissipation (Eq. 3.31).

\[ \mathbf{P}(z) = \mathbf{E}(z) \times \mathbf{H}(z) = 0.5[\mathbf{E}_{TE}(z) \cdot \mathbf{H}_{TM}^*(z) + \mathbf{E}_{TM}(z) \cdot \mathbf{H}_{TE}^*(z)] \]  \hspace{1cm} 3.31

\[ Q(z) = - \frac{\partial \mathbf{P}(z)}{\partial z} \]  \hspace{1cm} 3.32

The exciton generation profile (Eq. 3.33) [14] can be obtained from the time averaged energy dissipation \( Q(z) \), Eq. 3.32) by normalising to the incident energy, which for solar cells in general would be the AM1.5G spectra (Section 2.1.2). This method assumes the best-case scenario, that the quantum efficiency is 1. The exciton generation profile can be seen in Figure 3.12 (a), with the distance from the PEDOT:PSS, hole transport layer, to the ZnO, electron transport layer, over a range of wavelengths (Units: \( \times 10^{28} m^{-3} \)).

\[ G_{opt}(z, \lambda) = \frac{\lambda}{2\pi \hbar} I_{AM1.5}^{\lambda}(\lambda) Q(z, \lambda) \]  \hspace{1cm} 3.33

We can take this further and look at how we can optimise the devices, over a wavelength range, or over an angular range. Figure 3.13 (a) demonstrates a 3-D plot of layer thickness dependence on the absorption over wavelength, this could also be done as an average over a set of wavelengths and shown spatially through the device. Figure 3.13 (b) shows the same result, but with varying the angle of incidence, showing how the cell absorption changes with increasing angle.

Now we have demonstrated some of the outputs that we can obtain from the optical model, we now demonstrate the accuracy of the model compared with experimental results. We can verify that elements of the model are working by obtaining experimental measurements for the layer thicknesses, and measuring the absorption and reflection of the devices giving us some direct comparisons.
Outputs from the Model

Figure 3.12 (a) The simulated device structure, where the optical properties of the materials can be found in Appendix E. (b) The spatially resolved exciton generation rate, and (c) layer absorption following the same colours presented in (a) with the addition of red – reflectance of device. (b) demonstrates that most of the excitons will be generated closest to the glass (within the first 50 nm, within the wavelength range 450 nm and 650 nm). A second hot-spot further into the active-layer shows a peak of the exciton generation at ~600 nm. (c) shows the residual incident energy, and where in the device it has been absorbed. The colour scheme used in (c) is the same colours used in the schematic (a), where the red area in (c) is the additional reflection.
3.7. Verification of the Model

To test that the optical model agrees with experimental results we performed extensive characterisation on a set of devices, including: AFM, Ultra-Violet Visible Spectroscopy (UV-Vis), External Quantum Efficiency (EQE) and Current-Voltage (J-V) characteristics. A commonly used [69] active layer material (PCDTBT:PC71BM [144]) was used, with interfacial layers (PEDOT:PSS [145] and PFN [59]; the complex optical properties can be found in Appendix E). These layers were deposited using the spin coating method enabling consistent layer thicknesses and uniformity. All the complex refractive indices for the materials used are given in Appendix E.

As the model takes into consideration the layer thicknesses and surface roughness parameters (Section 3.5), we perform AFM characterisation as realistic inputs to the model, allowing for statistical variation. We ran the model in two different modes: The first was the direct method, where we use the mean values from the AFM characterisation; for the second method, we loaded the experimental optical data, provided by UV-Vis characterisation, and ran an optimisation routine with the limits including the variation of the thicknesses and surface roughness, which gave the best fit. We show that, in both cases, the model produced comparable results to the experiments. The following section demonstrates the characterisation of the devices followed by a direct comparison between the model and the experimental results.
3.7.1. Fabrication and Performance of Devices

We use pre-fabricated ITO (Lumitech, 130±5 nm) on glass substrates (1.2 mm thickness, 1 cm² total area, 0.633 cm² active device area), which go through a multistage cleaning process, finishing with plasma ashing to lower the work function of the ITO. The subsequent layers, except for the aluminium contact, were deposited using the spin coating technique. The PEDOT:PSS was spun at 4000 RPM for 60s followed by annealing for 30 mins at 150°C. PCDTBT:PCBM, which was mixed with a 1:4 ratio was spun at 5000 RPM for 30s followed by 10 mins annealing at 80°C and finally PFN (0.25 mg/ml in Methanol) was spun at 2000 RPM for 45s and was solvent annealed in the glove box for 10 mins. The aluminium was then evaporated to achieve a layer thickness greater than 60 nm.

The devices were then characterised using a solar simulator to measure the light and dark currents. This was done under AM 1.5G (1000 $W/m^2$) conditions and the results from this can be seen in Figure 3.14. EQE was obtained using a monochromatic quantum efficiency measurement system. We will use the data collected here to calculate the resulting IQE using the absorption from the devices in Section 3.7.3. The 6 fabricated devices demonstrated consistent characteristics with $V_{oc} = 0.86 \pm 0.01 \, V$, $J_{sc} = 11.09 \pm 0.03 \, mA/cm^2$, $FF = 61.45 \pm 1.02 \%$, and $R_s = 13.15 \pm 0.92 \, \Omega$. These characteristics resulted in an averaged PCE of 5.88 ± 0.18%, giving a consistent set of devices to compare with the modelling results.

![Figure 3.14 (a) J-V of a single device, showing the light and dark current density, where $V_{oc} = V(I = 0)$ and $J_{sc} = J(V = 0)$ in the light current density graph ($\eta_{eff} = 5.88 \pm 0.18\%$). (b) The EQE spectra taken for the same device, showing a characteristic peak at around 400 nm as is the case with other devices using a PCDTBT based active material [69]. The active device area in this case is 0.633 cm².](image)

Verhage of the Model
3.7.2. AFM and UV-Vis Characterisation

Figure 3.15 AFM height profiles of (a) Glass/ITO/PEDOT:PSS, (b) Glass/ITO/PEDOT:PSS/PCDTBT:PC_{71}BM, and (c) Glass/ITO/PEDOT:PSS/PCDTBT:PC_{71}BM/PFN, showing where the corresponding line profiles (b), (d) and (f) have been taken. The line height profile (dotted) also shows where the height profile averages have been taken from. It is also clear from figure (d) that we can identify the PEDOT:PSS layer thickness from the profiles. The artefacts on the images (c) and (e) have resulted from scoring the sample.
The model requires the layer thicknesses and optical properties of the materials used within the device to accurately represent the results. In this case, to obtain the layer thicknesses, we used the AFM to measure step sizes at multiple points, on multiple devices and took the arithmetic average of the results, which we have used within the model. The AFM height profile was analysed in the Gwyddion software package to extract line profiles and measure the step size; the height profiles of the PEDOT:PSS, PCDTBT:PCBM and PFN layers are shown in Figure 3.15 (a), Figure 3.15 (c) and Figure 3.15 (e) respectively. The corresponding line profiles, which show the step heights are given in Figure 3.15 (b), (d) and (e). The resulting values are given in Table 3.1, where the value of the ITO thickness has been taken from the datasheet of the glass/ITO substrates that we used within the experiment.

Table 3.1. Averaged AFM results from 20 line profiles taken from 5 different sections on the device. These have been arithmetically averaged and the standard deviation has been found by taking the variance in the results.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Mean Thickness ($\mu [nm]$)</th>
<th>Std. Deviation ($\sigma [nm]$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO</td>
<td>130</td>
<td>± 5</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>23</td>
<td>± 3</td>
</tr>
<tr>
<td>PCDTBT:PC71BM</td>
<td>40</td>
<td>± 5</td>
</tr>
<tr>
<td>PFN</td>
<td>10</td>
<td>± 2</td>
</tr>
</tbody>
</table>

Figure 3.15 (d) shows an independent step for two different materials, where the step closest to the substrate can be associated with PEDOT:PSS since it falls within the same range measured on other devices. The PFN layer does not do the same, which makes it more difficult to estimate accurately, in this case, we subtracted the height of the PCDTBT layer, where the PEDOT:PSS is still visible in the step profile (Figure 3.15 (f)).

The absorbance spectra (Figure 3.16 (a)) was obtained by taking the transmission and reflection spectra of the devices using a UV-Vis spectrometer (Varian Cary 5000), where Absorption = 1-Transmission-Reflection. The IQE (Figure 3.16 (b)) was obtained by using the absorbance spectra (Figure 3.16 (a)) and the EQE spectra previously obtained (Figure 3.14 (b)). The data in Figure 3.16 shows the mean and the standard deviation over the 6 devices. This data will be used in Section 3.7.3 for comparing the modelling results to the experimentally obtained results.
3.7.3. Comparison between Model and Experiment

The simulation required knowing the layer thicknesses, which we obtained using AFM (Section 3.7.2) and the optical properties of the materials (Appendix E). We specified the optical properties in the model and applied limits to the layer thicknesses (based on the range of values obtained from the AFM analysis), then we ran an optimisation routine, which uses the absorption spectra as an input. The model iterates through changing each of the layer thicknesses and the result (Figure 3.17 (a)), where the simulation was closest to the experimental then provides the layer thicknesses used in that case.

This method demonstrates good experimental agreement (Figure 3.17 (a)) for the absorption spectra and layer thicknesses that the optimisation routine found, we can now assert that the model is working correctly. In Chapter 4, we look at how we can apply the model to semi-transparent devices and how we can optimise organic solar cells applied to the windows of buildings.

Figure 3.16 (a) The Average absorption over 6 devices for the experimental device described in this section. (b) The IQE spectra taken for the same device. The average IQE value over the visible region is ~70%.

Figure 3.17 (a) Experimental averaged range of absorption for the set of devices described in Section 3.7.1, (b) the simulated structure including the layer thicknesses.
3.8. Limitations and Assumptions

The model relies on a set of limitations and approximations to provide efficient and accurate modelling of organic solar cells. To start, the model assumes that all the materials used are isotropic and non-magnetic. Further extensions to the model, such as that given by Kim et al. [140], can be applied, which can take into consideration the permeability, as-well as the permittivity of the materials (Section 7.4). The biggest limitation with this form of simulation is the 1-D nature of the problem: We have explored statistical and stochastic methods to include 2-D – 3-D elements such as surface roughness, however variations in the layer thicknesses, defects and other such elements are not taken into consideration.

Differences between our model and experimental results (demonstrated in Figure 3.17) can be put down to differences in the optical properties: We decided to use values that can be found within the literature to make the model accessible to the scientific community. This assumes that the mixtures, materials, concentrations, packing, and ratios are identical, which they are not. For this reason, there will be discrepancies within the results between the simulation and experimental results, however we have proven that even by taking this approach, we can still provide good experimental agreement and useful data that can be used for developmental and optimisation purposes.

Finally, when calculating the Exciton generation profile for the devices, we assume there to be 100% quantum efficiency (Figure 3.12 (b)). This would, however, not be the case in realistic devices: We showed that our experimental devices provided on average 70% IQE throughout the visible region (400 nm - 800 nm, Figure 3.16 (b)). This assumption was originally made by Tress [14], where he stated that over the visible spectra, the quantum efficiency in organic materials would be close to 100%. However, in reality recombination rates within organics is generally very high, hence the IQE is usually much lower.

3.9. Summary

In this chapter, we discussed how we can model the propagation of light through a multi-layered device. Where we have provided the principles, corrections and integrations taken throughout. Additionally, the effect of incorporating the surface roughness into the devices in two different ways was demonstrated. The commonly used Fresnel coefficient approach (Section 3.5.1) alters the interface properties, which results in a decrease in the transmission, and an increase in the absorption in the devices. The random phase method takes a different approach and changes the refraction angle by a random factor and changes the optical path length of the light through the layer. This method did not increase, or decrease any of the
characteristics, rather it reduced the Fabry-Pérot oscillations as the random factor was increased.

In Section 3.7 we compared the model against experimental results, giving a breakdown of the methods used in fabricating the devices and the characterisation steps taken to obtain the layer thicknesses. The comparison between simulation and experimental devices proved to be in good agreement. However, it did highlight the advantages with experimentally obtaining the complex refractive indices for the materials that you are using, instead of taking them from the literature. This asserts that the model is calculating things correctly and can be used as a good estimation and optimisation tool for OSCs.

In Chapter 4, we utilise the model for the optimisation of colour specific decorative windows, and show how it can be used in the case of semi-transparent devices, with further verification and comparisons to literature results (modelling and experimental).

The model has been described in depth to provide a solid foundation for the implementation of plasmonic nanoparticles into the TMM. In the Chapter 5, we look at a breakdown nanoparticle model that we have developed and the verification steps that we took. In the next chapter (Chapter 4) we apply the model developed within this chapter to optimisation of OSCs and the development of semi-transparent OSCs.
Chapter 4


In Chapter 3 an optical model, based on the Transfer Matrix Method (TMM), which is capable of simulating multi-layered structures has been demonstrated. This model took into consideration: complex-dielectric material systems and incoherent, coherent and partially coherent layers – in the form of surface roughness. It also gave us a set of useful outputs, such as the transmission, reflection and absorption spectra and a breakdown of the absorption, and hence power dissipation, within each of the layers. Also, we could change input parameters, such as the incident angle, solar spectra (for exciton generation profiles) and different material properties/configurations. The nature of this type of simulation provides a useful tool for the design and optimisation of Organic Solar Cells (OSCs). The algorithms designed allow for low simulation times (orders of seconds), in contrast to other methods such as Finite-Difference Time-Domain (FDTD), Ray Tracing and Finite Element (FEM) modelling, that are generally a lot more resource intensive and can take up to orders of magnitude longer to achieve the same results.

In this Chapter, we take the simulation tool that we have designed and apply it to investigate the optimisation of OSCs, optical spacing effects and design of semi-transparent OCSs, such as windows with specific colours. These can be used for specific architectural and design purposes, such as greenhouses [5], whilst generating electricity at the same time. The investigations require many independent simulations, working with a range of layer thicknesses and/or angles. We show how we can utilise the simulation to optimise material configurations in the case of an P3HT:IC_{60}BA active layer [58], where parts of the device already have fixed material properties and thickness values (Section 4.1). Section 4.2 is an in-depth investigation into optical spacing effects of the electron transport layer (ETL) thickness, where we draw a relationship between the power dissipation within the active layer, and hence the exciton generation rates, and the spacing between the beginning of the active layer and the back contact. Limitations and an explanation of why optical spacing effects would not be taken full effect of within standard OSC applications is explored. Section 4.3 explores the use of the model for application in colour specific semi-transparent OSCs, showing how we can extract the approximate colour from reflectance and transmission spectra (Section 4.3.1), how we can optimise the cells to specific parameters, and the angular dependence of
semi-transparent OSCs. We also demonstrate a material shadowing effect that became apparent during the modelling of semi-transparent solar cells (Section 4.3.2). This shadowing effect could block parts of the incident light from even making it to the active layer to be converted into excitons, and then free charges – affecting device performance.

After modelling colour-specific semi-transparent effects, we looked at how we can realise this through experimental work, demonstrating a single working device with ~17% transparency over the visible spectra and 4.45% Power Conversion Efficiency (PCE), and demonstrate some of challenges involved in realising high-performance semi-transparent OSCs (Section 4.3.7).

### 4.1. Optical Optimisation of OSCs

When designing OSCs for high performance, especially with novel material systems, one of the things to look at optimising is the layer thicknesses with respect to the maximum exciton generation rate. Although the exciton dissociation, charge-transport, charge collection, and recombination all influence the performance, the first step in optimising cells is obtaining the maximum generation rate possible (Section 2.1.1). When dealing with a known material configuration, the thicknesses of the interfacial layers and contacts is usually known before. This makes the optimisation of the active layer a less computationally heavy task, being able to sweep over many different thicknesses to find the optimal peak.

In this section we look at how the model can be used to find the optimal range of active layer thicknesses for a given material configuration, utilising P3HT:ICBA (Idene-C60 Bisadduct) as an active material blend. There are certain constraints to consider when designing a structure such as this, for example: the performance will start to degrade if the active layer is too thick, or too thin, for different reasons. Firstly, when the active layer is too thin, the light reflected from the back contact isn’t absorbed on a second pass through the active layer, and hence the device is not optically optimised. Secondaly, when the active layer is too thick, not all the charges can reach the contacts to be extracted and therefore recombine.

The results from the simulation, where we optimise a P3HT:ICBA-based device using material properties that can be found in Appendix E, are given in Figure 4.1. The device structure (shown in Figure 4.1 (d)) consists of: ITO [146]; PEDOT:PSS [147]; P3HT:ICBA [148]; BCP [149]; and Aluminium [88]. Figure 4.1 (a) shows the total power dissipation within the active layer with increasing thickness. There is an initial peak in exciton generation at ~ 90 nm active layer thickness, where the light is constructively interfering within the active layer. The second peak at 220 nm – 230 nm is where the thickness of the layer is optimal [58], where the active layer is thick enough to generate the maximum number of excitons before being too thick to be able to extract them efficiently. The formation of the blend also plays an important role in
the charge dynamics: as the layer thickness increases, so does the size of the domains within the polymer blend [148].

![Optimal Thickness](image)

Figure 4.1 (a) Simulated total power dissipation within the active layer, (b) Reflectance, transmission and absorption spectra for the device shown in (d), the fall-off in the absorption is due to the band-gap energy of the polymer blend (P3HT:IC_{60}BM). (c) The power dissipation through the active layer over a wavelength range. The optimal thickness; as verified experimentally is shown in (a) at ~225 nm. Most of the excitons are, in this case, generated within the first 80 nm of the active layer (c), within the wavelength range 400 nm - 650 nm.

When the active layer thickness exceeds 250 nm, the performance of the device starts to degrade. This is because the P3HT:IC_{60}BA blend does not produce completely interpenetrating domains, which increases the overall recombination within the device; due to the cell’s inability to transport and extract the charges from the device (See Section 2.1.1 for more details). This has been verified experimentally by Kutsarov et al. [58] This is relevant to the simulations; as it provides a maximum thickness value (and hence a range) to search through for the maximum peak value, as shown in Figure 4.1 (a), where we show the total power dissipation as a function of the active layer thickness.
4.2. Optical Spacing Effects in OSCs

Bragg gratings and mirrors work through coherence effects, both constructive and destructive. In these systems, you would generally have multiple layers alternating between the same selection of materials, hence creating a filtering effect. In OSCs we have several layers, of different materials and thicknesses, which makes this story a bit more complicated. By changing one of the layer thicknesses, you can change the whole optical response of the device. An area of interest [35], [150]–[152] in the field of OSCs is optical spacing effects. Particularly from changing the thickness of the electron transport layer (ETL), where the use of the interface materials serve the purpose of creating an optical spacer, and to provide hole/electron-blocking layers. Here we use the model, described in Chapter 3, and investigate the extent of the optical spacing effect in OSCs.

In this investigation, we have opted for a TiO$_2$-based ETL, within a pre-defined device configuration (shown in Figure 4.2 (a)): Simulated device structure, with refractive indices: ITO [146], PEDOT:PSS [147]/PTB7:PC$_{70}$BM [5] /TiO2 [153]/Ag [88]. The same investigation was repeated for a different material system - utilising ZnO as the ETL material, where we found very similar results, in terms of optical spacing effects. These additional results can be found in Appendix H. The range of ETL thicknesses was repeated for different active layer thicknesses, which demonstrates the conditions when the optical spacing effects have the most pronounced effect on the device performance. Each simulation (per active layer thickness) has 120 data points, over a range of 10 nm to 300 nm for the ETL thickness.

Figure 4.2 (b) shows the total power dissipation within the active layer against the ETL thickness, the coloured crosses on the graph represent the data points shown in Figure 4.2 (c) – (e). The reflection (Figure 4.2 (c)), absorption (Figure 4.2 (d)) and transmission spectra (Figure 4.2 (e)), for each of the crosses in Figure 4.2 (b), are given for the same device structure shown in Figure 4.2 (a). Figure 4.2 (d) shows the total power dissipation spectra over wavelength. Firstly, we investigate what happens at the minima and maxima of the power dissipation (Figure 4.2 (b)) within the active layer, when increasing the ETL thickness.

What is most interesting about this is the region between 500 nm and 700 nm, where this seems to be where most of the differences in the total power dissipation originate from. The peaks (blue and yellow crosses) in Figure 4.2 (b) correlate to a period of low reflection from the device within this range (Figure 4.2 (c)), and hence higher absorption (Figure 4.2 (d)) and power dissipation (Figure 4.2 (f)), whereas the local minima (orange and purple crosses) in Figure 4.2 (b) relate to much higher reflectance values within this range. The spectra beyond 700 nm remains consistent in all cases, with very little difference between them. Also, the transmission spectra show negligible differences between the different layer thicknesses.
Figure 4.2 (a) Simulated device structure showing the material configurations. (b) Power Dissipation ($Q$ [W/m$^3$]) integrated over wavelength. The coloured crosses (all are done using a 100 nm active layer thickness) in (b) represent points where each of the coloured lines in (c)-(f) are taken from, the exact thicknesses for the TiO$_2$ layer are given in the legends. (c) reflectance spectra, (d) absorption spectra, (e) transmission spectra and (f) Active layer (PTB7:PC$_{70}$BM) Power Dissipation integrated over the thickness of the layer ($Q$ [W/m$^3$]).
Changes in the optical spectra directly relate to changes in the layer thicknesses (predominantly the active and interfacial layers) and optical properties, where the constructive and destructive interference, play the biggest role. When the layers are thick enough (e.g. more than 150 nm) that most of the light is absorbed on the first pass, these effects play less of a role, and hence the effects seen in Figure 4.2 would be less significant.

Figure 4.3 (a)-(d) Power Dissipation (colour scale) over wavelength and through the device (Q [W/m²]). The red boxed area is the PTB7:PC70BM layer, the green boxed area is the TiO₂ layer, shown in Figure 4.2. Glass is not included; as it is much larger than the other layers and is also incoherent. Each of these graphs represents a point (cross) on Figure 4.2 (b): Blue – (a); Orange – (b); Yellow – (c); and Purple – (d).

Figure 4.3 (a) – (d) show the power dissipation as light propagates through the device and as a function of the wavelength, one for each of the crosses in Figure 4.2 (b). What has become apparent from these graphs, is the pattern formed within the active layer by the distinct maxima and minima in Figure 4.2 (b) - (d). In the case of the minima, or lower total power dissipation, these are the large blue streaks across the visible wavelengths. They show that the device is not optically optimised and deconstructive interference effects are dominant. In the case of the maxima (Figure 4.2 (a)), the device is optimised for that specific active layer thickness, where constructive interference effects are dominant. The light blue streaks seen in Figure 4.3 (b) – (d) appear because of destructive interferences; caused by phase differences between the internal transmissions and reflections within the device. For example, the device with 150 nm ETL thickness (Figure 4.3 (c)), which is a local maximum in the total power dissipation.
Optical Spacing Effects in OSCs

(Figure 4.2 (a)), has a lower total power dissipation than the case of a 10 nm ETL thickness (Figure 4.3 (a)). Therefore, as the ETL layer thickness increases, the local maxima of the total power dissipation will continue to decrease. In the other cases (local minima, Figure 4.3 (b) and (d)), there is more destructive interference over the region of interest (400 nm – 650 nm – where the active layer has the highest absorption).

To see how the transmission, reflection, and absorption spectra change, and effects on the total power dissipation change, we look at the middle peak for each case of active layer thickness – demonstrated by the crosses shown in Figure 4.4 (b), for the same device structure shown in Figure 4.4 (a). Figure 4.4 (b) shows that when the active layer thickness increases, the spacing effects of the layers thereafter get smaller; as we go further than this to 200 nm, we see that the curve flattens off as there is less light to interact with the ETL and back contact.

Before (Figure 4.2 (c) – (f)) we noted that, with different TiO₂ layer thicknesses, the most affected part of the optical spectra was between 500 nm – 700 nm. In this example (Figure 4.4), when we consider the maximum point of the power dissipation for each active layer thickness, we see that the biggest changes in the transmission and reflectance spectra are now between 400 nm and 550 nm, and there is very little change after this point. In each case, there is a specific reflectance peak (absorption dip) between 450 nm and 500 nm, where the amplitude of the reflected peak becomes greater the smaller the active layer thickness is. The overall line-shape between each of the spectra in Figure 4.4 (c) – (d) does not change significantly, as the predominant peaks do not shift significantly in wavelength.

When we use ZnO as the ETL and PCDTBT:PC₇₀BM as the active layer (Appendix H), we see the same resulting pattern, with the exception of the 120 nm active layer thickness case. Because PCDTBT:PC₇₀BM has a higher extinction coefficient than PTB7, we see that the flattening of the total power dissipation in the active layer is more pronounced (for an active layer thickness of 120 nm) and the peak at 150 nm ETL thickness is no longer identifiable. Hence, the limitation, where the light is nearly completely absorbed on a first-pass through the active layer, which supresses optical spacing effects, has been found in this material system (ZnO, Appendix H) when the active layer exceeds a thickness of 150 nm.
Figure 4.4 (a) Simulated device structure showing the material configurations. (b) Power Dissipation (Q [W/m²]) integrated over wavelength. The coloured crosses (Blue – 180 nm; Orange – 170 nm; Yellow – 150 nm; Purple – 130 nm) in (b) represent points where each of the coloured lines in (c)-(f) are taken from, the exact thicknesses for the PTB7:PC_{70}BM layer are given in the legends. (c) reflectance spectra, (d) absorption spectra, (e) transmission spectra and (f) Active layer (PTB7:PC_{70}BM) Power Dissipation integrated over the thickness of the layer (Q [W/m²]).
Figure 4.5 (a)-(d) Power Dissipation (colour scale) over wavelength and through the device ($Q$ [W/m²]). The red boxed area is the PTB7:PC$_{70}$BM layer, the green boxed area is the TiO$_2$ layer, shown in Figure 4.4. Glass is not included; as it is much larger than the other layers and is also incoherent. Each of these graphs represents a point (cross) on Figure 4.4 (b): Blue – (a); Orange – (b); Yellow – (c); and Purple – (d).

Figure 4.5 shows the power dissipation through the device, calculated at the maximum efficiency conditions depicted by the crosses in Figure 4.4 (b), as a function of the distance from the glass substrate and wavelength. What is particularly interesting in this optimised case, compared with the study shown in Figure 4.3, is that the pattern between devices seems to be the same between all optimised active layer thicknesses. It appears that the pattern is invariant and more, or less, of it is revealed as we increase, or decrease, the thickness of the active layer. Moreover, the total thickness (active layer thickness + ETL thickness) is the same (245 ± 5 nm). Looking back at Section 4.1, we note that even in the case of a P3HT:IC$_{60}$BA material system, the total thicknesses of the ETL (BCP) and active layer fall within the same range. This signifies that what gives us the best control over the efficient conversion of light in the active layer is the distance between the start of the active layer and the start of the back contact (Aluminium in both cases). If the spacer material – separating the active layer and the contact – does not have a high extinction coefficient, then it will demonstrate some optical spacing effects.

In standard OSC applications, the use for optical spacing beyond device optimisation (predominantly the active layer thickness), is unrealistic. The thicknesses of the ETL that the
effects appear to be most beneficial at ~150 nm, which is an order of magnitude thicker than what would typically be used (5 - 30 nm) – due to the electrical properties, namely the transport properties and energy level alignment with the other materials being a limiting factor.

However, in semi-transparent applications, when the active layer thickness is typically much thinner, these effects play an important role. In some cases, this difference between a 10 nm layer and 100 nm layer could lead to a halving of the device performance \( (3.6 \times 10^8 \text{ W/m}^2 \text{ at } 10 \text{ nm vs. } 1.8 \times 10^8 \text{ W/m}^2 \text{ at } 100\text{nm}) \). Optimisation of the layers for the highest power dissipation in the active layer, and hence the exciton generation rates, will lead to better device performance overall. The charge transport properties (mobility, energy levels etc.) must also be taken into consideration, as these also impose other restrictions on the layer thicknesses.

### 4.3. Semi-transparent OSCs

A growing area is the use of thin-film technology in applications such as windows [2], [74], where the devices can both harvest energy and be semi-transparent. One of the selling points for organics is that they are both thin-film, and hence low cost, but also can be made to be semi-transparent [2], [5], [72], [76]. Chapter 3 gave a full description of the optical model that has been created; in this section, we use the model for optimising colour specific semi-transparent OSCs. As demonstrated in Section 4.1, by using a set of pre-defined parameters, such as minimum and maximum layer thicknesses, wavelength range and material configuration, we can optimise for the highest achievable Power Conversion Efficiency (PCE).

In this section, we take this one step further and now add parameters for the required transparency and colour preferences. The model will then change each of the layer thicknesses within the defined parameters to match the colour preferences; as close to as it can get within the bounds.

To be able to optimise a colour preference, we first need to define a method to enable the extraction of colour from transmission and reflection spectra (Section 4.3.1).

#### 4.3.1. CIE and RGB Colour Spaces and Optical Spectra

A method for converting optical spectra (e.g. transmission or reflection) to an approximate colour is to use a convolution method with a set of three predefined curves (Figure 4.6). Each of these curves relate to a coordinate in the CIE 1931 colour standard; the coordinates are denoted as X, Y and Z [154]. The transformation is based on a standard-observer and takes into consideration the perception of colour by humans.
The curves, denoted in Figure 4.6, are written as wavelength dependent parameters $\bar{x}(\lambda)$ (red), $\bar{y}(\lambda)$ (green) and $\bar{z}(\lambda)$ (blue). The convolution can be re-written in terms of integral functions (shown in Eq. 4.1), with a normalising factor ($\bar{N}$), shown in Eq. 4.2, which normalises the X, Y and Z values to a range between 0 and 1. The integral is done over the entire visible spectra, which in this case is between 350 nm and 750 nm; the convolution is 0 beyond these limits. In Eq. 4.1, $E_s(\lambda)$ represents the wavelength solar energy spectrum and $T(\lambda)$ is the wavelength dependent transparency. The transparency calculations were done using the model described in depth in Chapter 3, where an incident plane wave is assumed. The transparency can be replaced with the reflection ($R(\lambda)$) to approximate the reflected colour, where both $T(\lambda)$ and $R(\lambda)$ have been previously defined in Section 4.2.

$$\begin{bmatrix} \bar{X} \\ \bar{Y} \\ \bar{Z} \end{bmatrix} = \frac{1}{\bar{N}} \int_{\lambda_{350 \text{ nm}}}^{\lambda_{750 \text{ nm}}} \left[ E_s(\lambda)T(\lambda) \right] \cdot \begin{bmatrix} \bar{x}(\lambda) \\ \bar{y}(\lambda) \\ \bar{z}(\lambda) \end{bmatrix}$$  \hspace{1cm} 4.1

$$\bar{N} = \int_{\lambda_{350 \text{ nm}}}^{\lambda_{750 \text{ nm}}} \bar{y}(\lambda)E_s(\lambda)$$  \hspace{1cm} 4.2

A transformation, using a transformation matrix ($M^{-1}$) can be used to obtain RGB values from the XYZ coordinate (shown in Eq. 4.3). The transformation matrix is defined as a set of real positive numbers that map the colour XYZ (CIE 1931) coordinates to RGB values for different applications, the values within the matrix also depend on the type of incident light (White Point – The equivalent energy from a defined source). We chose to use the International Colour Consortium (ICC) standard (D65 White Point) with a sRGB (a standard RGB colour space...
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output values, which are used for monitors and printers) \[155\]. Eq. 4.3 shows the values used for the transformation from XYZ coordinates to RGB values.

\[
\begin{bmatrix}
R \\
G \\
B
\end{bmatrix} =
\begin{bmatrix}
m_{11} & m_{12} & m_{13} \\
m_{21} & m_{22} & m_{23} \\
m_{31} & m_{32} & m_{33}
\end{bmatrix}
\begin{bmatrix}
X \\
Y \\
Z
\end{bmatrix}
\]

\[4.3\]

To test the transform from optical spectra (transmission \(-T(\lambda)\)), a device was fabricated with the structure shown in Figure 4.7 (c). A comparison between the experimentally obtained and simulated results are shown in Figure 4.7 (d), showing a peak at \(~450\) nm and then again at \(~750\) nm; using the colour space transform, we obtain the colour in Figure 4.7 (b), where a photo of the experimental cell is shown in Figure 4.7 (a). The cell in Figure 4.7 (a) was illuminated from behind with a white light and taken using the camera on a Sony Xperia Z3 phone (un-edited).

\[\text{Figure 4.7 (a)} \quad \text{A photograph from a transmission perspective, with a white light behind the device and a diffuser. (b) shows the predicted colour for devices with the same layer thicknesses. The colour that spans the predicted colour will be represented of the active region of the device; which is the centre part of the device shown in (a). (c) The device structure created both experimentally and used for modelling purposes; the device is composed of BK7 Glass (700µm - Incoherent) /ITO (150 nm) /PEDOT:PSS (40 nm)/PCDTBT:PC70BM (80 nm)/ZnO (10 nm)/Ag (10 nm), (d) the results transmission spectra from the simulation and experimental device.}\]
As demonstrated in Figure 4.7 (d), using the model described in Chapter 3, it is possible to accurately determine the transmission, and hence obtain a good approximation for the predicted colour of the device. Further investigation into experimentally achieving working semi-transparent cells is shown in Section 4.3.7, where we obtained a single working device with a 20 nm back silver contact, instead of the 10 nm shown in Figure 4.7.

### 4.3.2. Material Shadowing Effects

Whilst investigating semi-transparent material configurations and the effects of changing each of the layer thicknesses (Section 4.3.3), it was observed that using some material configurations would cause parts of the spectrum to be blocked before reaching the active region. In this section, we explore the conditions under which this can occur and the resulting changes to the device performance.

Active materials, such as PTB7:PC$_{70}$BM, have a peak absorption range within the visible spectra (~450 nm – 680 nm, [5]). Within this range, to reach optimal performance, the more incident light that is provided to the active region of the device, the higher the number of excitons that are generated and hence, the higher the efficiency. In some cases, using specific transport layer materials, such as ZnO or MoO$_3$ can lead to parts of the visible spectra being absorbed before reaching the active region. Hence, in these cases, we would expect to see lower device performance due to a non-optimised device structure.

Figure 4.8 (a) shows an inverted device structure using PTB7:PC$_{70}$BM blend for the active material, to ensure that the device is semi-transparent, we simulated the back contact to be a thin layer of PFN (HTL) and ITO. Three different ETL materials have been used in this simulation, TiO$_2$ (Figure 4.8 (b)), ZnO (Figure 4.8 (c)), and MoO$_3$ (Figure 4.8 (d)), in each of these cases, the thickness of the ETL has been kept constant at 20 nm. Figure 4.8 (b)-(d) demonstrates the Power Dissipation ($Q$) over wavelength and distance through the device, which is proportional to the exciton generation profile.

Shadowing effects are visible in this data representation, seen as darker parts in the active region (e.g. Figure 4.8 (c)). The difference between TiO$_2$ as a ETL, and ZnO or MoO$_3$, is that between 350-400 nm the power dissipation within the active layer goes from \( \sim 5-6 \times 10^7 \text{ W/m}^3 \) to \(< 3 \times 10^7 \text{ W/m}^3 \). This is clearest in Figure 4.8 (c) as a dark blue streak. This is due to the absorption properties of ETL materials (shown below), where both ZnO and MoO$_3$ have larger absorption coefficients than TiO$_2$ over these wavelengths. This will in-turn reduce the total exciton generation rates (proportional to the power dissipation) within the active layer, and hence reduce the power conversion efficiency, disregarding transport effects and energy level alignment (injection/blocking).
Figure 4.8 (a) Simulated inverted device structure, where the ETL layer material is (b) TiO2, (c) ZnO and (d) MoO3. The red box highlights the area of interest, where the material shadowing effects take place for each of the materials. A dark blue streak demonstrates this effect for specific wavelengths, most pronounced. (b), (c) and (d) are Power Dissipation ($Q \text{ [W/m}^3\text{]}$) plots over distance from glass and wavelength (the area of interest has been focused and enlarged in the red box).

These effects are visible when running a simulation of a device, which can only be fully diagnosed and avoided with optical modelling methods, such as what is presented in Chapter 3. This will not be apparent in spectroscopic methods, and prior knowledge of the optical properties of the materials and a deep understanding of how the layers interact with each other would be needed to identify these things experimentally.

Material shadowing effects could impact heavily on the device performance, depending on the material structure. If there is a transport layer, between the incident light and active layer that is highly absorbing then, depending on the thickness, this will reduce the amount of available light to be absorbed within the active layer, and hence the device performance. Section 4.3.3 details how we can use the model defined in Chapter 3, to optimise material configurations for colour specific, and semi-transparent, applications.
4.3.3. Colour Specific Optimisation

In Section 4.1, optical optimisation of standard and inverted device structures was demonstrated. In these cases, we optimised specific material configurations to find the best set of layer thicknesses to achieve the maximum power dissipation within the active layer. In this section, the focus moves towards semi-transparent devices, where we now have a transparency value – before the back contact would have been thick enough (> 100 nm) to fully reflect the remaining light back into the device.

In applications, such as energy harvesting from decorative windows (Appendix G – NANOTECH Presentation 2016), the importance shifts from achieving maximum efficiency to being able to select specific transparencies and/or colours. By specifying a set of constraints for the simulation, we can run a simulation with a set of target parameters. These parameters are the transparency (minimum and maximum), layer thicknesses (minimum and maximum), RGB values (target values) and material configuration (no. of layers, material properties etc.).

Before demonstrating some results from using the algorithm, we first consider how variations in the layer thicknesses change the transparency and colour, which has not previously been demonstrated. The material configuration that has been chosen for this investigation is BK7 Glass (700 μm) /ITO [146] (50 nm) /PEDOT:PSS [147] (80 nm) /PCDTBT:PC\textsubscript{70}BM [156] (70 nm) /MoO\textsubscript{3} [157] (10 nm)/ Silver [88] (10 nm)/ ITO [146] (Back, 80 nm). The refractive indices for each of the materials have been obtained from the literature, which are presented in Appendix E.

The effects of altering the active layer thickness, whilst maintaining the layer thicknesses for all other layers, are shown in Figure 4.9. Over the range of active layer thicknesses (10 nm – 110 nm), the average reflection (Figure 4.9 (a)) does not exceed the 10-20% range, however, the approximate colour from the reflection of the device does change significantly, from a pale green (10 nm) to blue (50 – 70 nm) and back to a green (110 nm). This primarily comes back to Fabry–Pérot oscillations that have been previously discussed in Chapter 3, which are more pronounced in semi-transparent solar cells.

The effects on the transparency are shown in Figure 4.9 (b), where there is a significant increase in the average transparency when reducing the active layer thickness, from ~30% (110 nm) to ~50% (10 nm). The biggest increase happens at 430 nm, going from ~20% transmission to 60%. The transmitted colour in this case goes from a light-purple (10 nm) to a pastel orange (50 nm) to a dark-pink colour (110 nm). This is predominantly because of the absorption coefficient (complex part of the refractive index responsible for the absorption within the layer) of the active layer (PCDTBT:PC\textsubscript{70}BM), which can be seen clearer in Figure 4.9 (d) – the power dissipation within the active layer. At very thin layer thicknesses (10 nm -
30 nm) the absorption, transmission and reflection spectra change significantly (peak positions and intensities). Then at larger thicknesses (> 100 nm) there are smaller changes in the peak positions and intensities within the spectra, mainly due to the amount of the incident light that is primarily absorbed by the active layer, and hence not reflected/transmitted from the back contact. The changes in the absorption of the whole device can also be seen in Figure 4.9 (c), where Figure 4.9 (d) just shows the power dissipation within the active layer as the thickness increases. They both follow the same increase pattern, meaning that changing this layers’ thickness does not directly affect (increase/decrease) the power dissipation within the other layers.

\[ \text{Figure 4.9 Simulated reflection (a) and Transmission (b) spectra for changing the PCDTBT:PCBM layer thickness, where the line colour represents the approximate colour calculated using the method shown in Section 4.3.1. (c) shows the absorption spectra of the simulated device for the same active layer thicknesses and (d) demonstrates the power dissipation within the active layer.} \]

(a) the colour changes from an olive colour, to a deep blue, back to a mint-green colour, and in (b) it goes from a pale pink to a darker red-pink colour.
Figure 4.10 Simulated Reflection (a, c and e) and Transmission (b, d and f) of the device (Glass /ITO /PEDOT:PSS /PCDTBT:PC\textsubscript{70}BM /MoO\textsubscript{3} /Ag, showing how the spectra varies when different layer thicknesses are changes; Back Contact - Ag (a and b), ETL – MoO\textsubscript{3} (c and d) and HTL – PEDOT:PSS (e and f). The line colours represent approximate colour based on the methods described in Section 4.3.1. The transmissivity of the devices averages between 30% and 50% in (a) – (f), which is found by taking the average over the visible region. The reflectance colours change between a purple, to a deep-blue, and green depending on the layer thickness that was changed. The transmission remains in the pink/red regions throughout.
Figure 4.10 shows the changes in the reflection and transmission spectra when changing the thickness of different parts of the device, where all the layers take on their default values as previously shown and only the layer of interest is changed for a layer thickness range of 10 nm – 110 nm. In all cases, the colour of the reflected light changes the most significantly within this material configuration, and is the most pronounced when changing the back contact (Silver), which changes from blue (10 nm) to green (50 nm – 70 nm) and then to purple (110 nm), as shown in Figure 4.10 (a). The average reflectance does not change significantly with the change in the contact layer thickness, remaining at ~15%. The average transmission, however, changes a lot more, going from ~25% (110 nm) to ~50% (10 nm), shown in Figure 4.10 (b). The change in the thickness does not lead to a change colour as dramatically for the transmission – pink (10 nm) to pastel-brown (110 nm).

Changes in the thickness of the transport layers (ETL (MoO₃), Figure 4.10 (d), and HTL (PEDOT:PSS), Figure 4.10 (f)) do not have a major impact on the colour in this case; they all appear to be shades of orange-pink. Changing any of the layers seems to have some degree of optical spacing effect (see Section 4.2 for more details), changing both the reflectance and transmission spectra, and hence the absorption within the active layer.

### 4.3.4. Case Study: PBDTTT-C-T:PC₇₀BM

Unlike the most common, high efficiency, electron donor materials such as PCDTBT, PTB7, and PBDTTT-C-T have different optical properties. More specifically, it has an absorption peak in the red and near infra-red regions (> 600 nm, Figure 4.11) making it an idea candidate for colour specific semi-transparent applications – particularly for blue and green colours.

![Figure 4.11 Refractive Index (a) and Extinction Coefficient (k) for a selection of active layer materials (PBDTTT-C-T:PC₇₀BM [158], PCDTBT:PC₇₀BM [5], and PTB7:PC₇₀BM [5]). Showing characteristic peak absorption within the materials (b).](image-url)
The material configuration used within this simulation has been loosely based on a device described by Sun et al. [2], where they describe the use of PBDTT-T-C-T as the material that can be semi-transparent and also high efficiency (~5% PCE with 40% Transparency). This is because other materials, such as PCDTBT:PC$_{70}$BM and PTB7:PC$_{70}$BM have peak absorption within the visible range and PBDTT-T-C-T:PC$_{70}$BM blend has it in the red and NIR regions (Figure 4.11 (a)). ITO on top of the Ag contact has been chosen for index matching reasons [1], avoiding too much unnecessary reflection from the contact.

Figure 4.12 Example optimised simulated device utilising a PBDTT-T-C-T:PC$_{70}$BM active layer, the inverted device structure is shown in (d). The associated Reflection, Transmission and Absorption are given in (a where the line colours for the Transmission and Reflection are approximated using the method demonstrated in Section 4.3.1, the Absorption is shown by a black line). The Power Dissipation in each of the layers is shown in (b) and a 3-D representation of this is provided in (c) over the distance from the glass substrate and the wavelength.

The parameters for the simulation were to keep the transparency within the range of 30% - 40%, make the device as green (in transmission) as possible, whilst optimising the power dissipation within the active layer and keeping the specified material configuration. We also defined the steps for the layer thicknesses to be 5 nm and set minimum and maximum values for the layer thicknesses. The resulting device structure following the optimisation routine is shown in Figure 4.12 (d).
The resulting device was a pastel-green in colour (RGB (154, 173, 165)) with a 33.5% transmissivity (Figure 4.12 (a)). The device was also optimised to give the highest power dissipation within the active regions (Figure 4.12 (b)), where Figure 4.12 (c) demonstrates that most of the generated excitons will be towards ITO/ZnO end of the device, with a peak absorption at 700 nm. The reflection is kept to a minimum (~20%) and is blue in colour (RGB (109, 105, 163)). The power dissipation within the silver contact is kept to a minimum due to the refractive index matching role that the thin film of ITO plays.

**4.3.5. Case Study: PCDTBT:PC<sub>70</sub>BM-based**

Using a similar method as shown in Section 4.3.4, instead of the active material blend being PBDTTT-C-T based, a PCDTBT:PC<sub>70</sub>BM active layer was chosen in a standard configuration. This has a higher extinction coefficient within the blue-green region of the visible spectra (Figure 4.11) and the extinction coefficient also falls-off to zero after 550 nm, making is a candidate for making a red coloured cell.

![Figure 4.13 Example optimised simulated device utilising a PCDTBT:PC<sub>70</sub>BM active layer, the device structure is shown in (d). The associated Reflection, Transmission and Absorption is given in (a), the Power Dissipation in each of the layers (b) and 3-D demonstration of the this (c). The line colours for the Transmission and Reflection are approximated using the method demonstrated in Section 4.3.1, the Absorption is shown by a black line.](image-url)
The simulation parameters used were 40% - 50% transmissivity, red in colour, and the material configuration shown in Figure 4.13 (d), where we had a layer thickness step of 10 nm. The materials used, and the reference for their associated optical properties, are ITO [146], PEDOT:PSS [147], PCDTBT:PCBM [5], MoO3[157], and Ag [88].

The optimised layer thicknesses for the parameters are shown in Figure 4.13 (d), and the transmission, reflection (with their approximate colours), and absorption are shown in Figure 4.13 (a). With 48% transmissivity, the resulting colour is red (RGB (182, 127, 133)), with the reflected colour being blue (RGB (103, 115, 150)). The device was also optimised for maximum power dissipation within the parameters. Figure 4.13 (b) shows the power dissipation within the active layer compared with the other layers, and Figure 4.13 (c) demonstrates that the exciton generation rates would be maximum in the middle of the device for most of the visible spectra.

Hence, we have shown how we can control the transparency and colour of semi-transparent device using different material system and layer thicknesses (Section 4.3.4 and Section 4.3.5). We also have shown how we can optimise device performance based on specific transparencies and preferred colour (Section 4.3.3). Now we look to how the incident angle of light affects the performance, colour, and transmissivity of the devices.

4.3.6. Angular Dependence in Semi-transparent cells

Up until now, we have based the colour dependence and transmissivity on the incident light being normal to the surface of the device. In this section, we look at how this changes as the angle of incidence changes. In Chapter 3, we have a full description of the model that has been used, including how we take into consideration the incident angle. Here we take the same material configuration and layer thicknesses that we obtained during the optimisation in Section 4.3.5, where we have demonstrated a red coloured cell with 48% transmissivity when the angle of incidence is 90 degrees (normal to the surface of the device).

We simulated the device shown in Figure 4.13 (d) for a range of angles between 0 and 180 degrees, not inclusive of 0 and 180 degrees, as they are completely parallel to the surface and hence no direct interactions would occur. We are looking at plane-wave interactions (\((s\text{-polarised} + p\text{-polarised})/2\)), the Brewster angle for the p-polarised case would appear at ~60 degrees for the air/glass interface. At 90 degrees, we obtain identical results as shown in Figure 4.13, where we have 48% transmission, and a red colour (Figure 4.14 (a)). As the angle approaches 0 or 180 degrees, the amount of transmission falls off to become negligible. However, at 30 degrees (150 degrees) we still achieve 25% transmission, with a slight darkening of the red-colour due to the increased reflection from the device.
The most affected parameter here is the reflection (Figure 4.14 (b)); as the incident angle approaches 0 or 180 degrees, the reflection from the device approaches 100%. The colour also changes with the angle, going from blue (90 degrees) to a purple colour at 30 degrees (150 degrees) and then approaches a white colour as would be expected as it approaches 100% reflection.

(a)

Figure 4.14 Angular dependence on the Transmission (a), Reflection (b) and Absorption (c), the arrows point to the incident angle of the light, the length of the arrows represents the Transmission, Reflection and Absorption respectively (a.u.) and approximate colours have been given for the Transmission and Reflection (a and b respectively). At 0° and 180° the incident light does not interact with the surface of the device and therefore no results can be obtained.
The least affected mode is the absorption, which begins at around 40% and at 30 degrees (150 degrees) is still > 30%. Falling off as the incident angle approaches 180 degrees (0 degrees). This gives the device a wide operating range in terms of incident angles and ideal for applications in windows, where the incident angle throughout the day will also change. This allows us to design a semi-transparent OSC, which can maintain 30% - 40% absorption from the incident energy throughout most of the day.

### 4.3.7. Experimental Results

In the previous sections in this chapter we have shown how we can use the simulation, described in Chapter 3, as a tool for designing colour specific semi-transparent OSCs. In this section, we show how we can start to realise this through experimental results. In Section 4.3.1, we briefly demonstrated how we can extract an approximate colour from optical spectra, where we have shown a side-by-side comparison between an experimental device and an output from the model – also how the spectra for that device matches in transmission mode. Here we take the same material configuration to obtain a working device.

The material configuration, shown in Figure 4.15, is based on a similar case to the case study on PCDTBT:PC_{70}BM (Section 4.3.5), with the exception of an additional layer of ITO on-top of the Ag contact for refractive index matching purposes. In this case, the goal was to be able to design and create a working cell with a uniform thin-film of Ag (< 20 nm). It was found that the silver did not form a uniform layer, and hence charges from the device could not be extracted at all. Figure 4.15 shows a comparison of the transmission between three identically constructed devices (mean ± standard deviation – black dashed lines in Figure 4.15 (a)), and simulated results that fit between the two experimental lines (simulated device structure is shown in Figure 4.15 (b)).

The device shown in Figure 4.15 (b) did not work in any of the three cases, due to the contact not being uniform enough. The decision was made to increase the thickness of the contact until we had a working device. Without changing any of the other layers, the thickness of the Ag contact was extended to 23 nm and the results for this are shown in Figure 4.16.
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**Figure 4.15** (a) The experimentally obtained results range for the transmission over three devices – the black dashed lines represent the mean ± the standard deviation across all devices. The blue line represents the simulated results for the device structure, shown in (b).

Figure 4.16 (a) shows a direct comparison between the transmission spectra of the simulated device structure and the experimental device with the thicker contact. The same simulated transmission result is shown in Figure 4.16 (b) alongside the corresponding reflection and transmission, showing a large proportion of the red and NIR light is being reflected from the device. However, in the blue and green regions, the device is absorbing up-to 80% of the incident light, Figure 4.16 (c) shows how this absorption is accounted for in each of the layers, demonstrating that most of this is absorbed within the active layer. The second highest proportion of the incident light is absorbed in the Ag contact, which is due to there not being an index matching material (such as ITO), which would make the Ag seem visibly transparent.

Figure 4.16 (d) shows the J-V characteristics for the device, noting that the fill-factor (FF = 60.6%) is lower than what we would usually expect for devices made using this material configuration (we would expect a Fill Factor between 65% and 70% [69]). This is most likely due to having a perfectly uniform layer. However, the goal is to tune to specific colours and transmissivities, and the efficiency comes second to this.

The hardest challenge to overcome is the introduction of a second transparent contact; in this case, obtaining a layer of Ag thin enough to work as intended and be transparent proved to be very difficult. There has been a lot of work done in this area – looking at areas such as Aluminium-doped Zinc Oxide (AZO), Silver Nanowires (Ag-NWs) and other methods people have chosen to use [53], [159], [160].

However, achieving 4.46% PCE for a semi-transparent device with a single thin-film of Ag that was still ~20% transmissivity is a huge step forward in the right direction for this work. Considering that, with back contact Ag layer with a thickness of ~20 nm, we managed to achieve a 60% FF, which is 5% lower than the average literature values for standard devices.
Semi-transparent OSCs [69]; this shows that it is possible to maintain efficiency whilst reducing the thickness of the back-contact. Although, further investigative work needs to be done surrounding the fabrication of thinner, more uniform, Ag layers before the realisation of the semi-transparent devices, such as the simulated device shown in Section 4.3.5, can be efficiently made by thermal evaporation; increasing the wettability of the surface using a wetting layer such as PEI [161] could aid in achieving more uniform, and semi-transparent, ultra-thin films (Section 7.4).

Figure 4.16 (a) A comparison between experimental and simulated transmission spectra between 380 nm and 750 nm, for the device shown in Figure 4.15 (b) with a thicker Ag contact (23 nm). (b) The corresponding simulated reflection, transmission (with approximate colour) and absorption for the device, (c) The breakdown of the power dissipation for each layer within the device, and (d) J-V characteristics of working device, displaying also the open circuit voltage (Voc), the short circuit current density (Jsc), the fill factor (FF) and the power conversion efficiency (PCE, $\eta_{eff} = 4.46\%$).
4.4. Summary

In this Chapter, we apply the model described in Chapter 3 for optimisation of OSCs, specifically semi-transparent colour-specific OSCs, where optical spacing effects, layer thicknesses, material properties and other factors have an impact on the device performance. We demonstrated that we can use the model for optimising a standard device configuration (P3HT:IC_{60}BA active material) to find the optimal layer thickness. This was done by capturing the total power dissipation from each simulation with different active layer thicknesses. We found that the optimal thickness was between 220 nm and 230 nm with the specified material configuration, which had been confirmed experimentally by Kutsarov et al. [58].

We investigated in detail optical spacing effects (Section 4.2) in a standard OSC configuration, where we show visually how the thickness of the ETL can impact the device performance, where we found that you can have up to double the power dissipation in the active layer between having a 100 nm and a 150 nm ETL. Then we showed that at the peak (~150 nm ETL thickness) the total power dissipation within the active layer did not change much as different active layer thicknesses are simulated. This is because the distance between the start of the active layer thicknesses and the back contact (Aluminium) was the same distance in each of the optimised cases. This was also seen when we used a different ETL material (ZnO instead of TiO₂, results in Appendix H), however the active layer material used in that case has a higher extinction coefficient and above 120 nm active layer thickness, the clear optical spacing effects seen previously were no longer visible. Our conclusion here is that optical spacing effects play an important role in OSCs, however, the effects are mostly visible when the active layer is semi-transparent to the back contact (i.e. not absorbed on a first-pass through the active layer) and light can be reflected all the way back through the device. In ordinary applications, this generally would not be the case, as the active layer thickness would be thick enough to completely absorb the reflected light from the back contact – part of the optical optimisation of the OSCs.

During our study of colour-specific semi-transparent OSCs (Section 4.3) we gave our methods for obtaining an approximate colour from the transmission and reflectance spectra, we also found that some materials (those with an extinction coefficient) blocked portions of the incident visible spectra from reaching the active layer (Section 4.3.2). This part of the spectra is generally where the polymer blends, such as PTB7:PC_{70}BM and PCDTBT:PC_{70}BM have the highest extinction coefficient. We then took this into consideration during our study on optimising for specific colours with different material systems.

We demonstrated how we can use the model, and predicted colours, to design colour specific windows, setting parameters such as the layer thickness range, the material configuration etc.
(Section 4.3.4 and Section 4.3.5). Then we show how we can tune colours by demonstrating some early results for semi-transparent devices, where we discussed the challenges and limitations. The biggest challenge to overcome, before completely realising the gap between modelling and experimental devices, is the ability to create uniform thin-films (~10 nm) of silver. However, with ~20 nm of silver we could show a working device with 4.45% PCE and ~17% transmission, which agreed with our modelling results for the same configuration, which is a significant step in the right direction towards the realisation of optimised, colour specific, semi-transparent organic solar cells.
Chapter 5

5. Plasmonic Nanoparticles with Graded or Multiple Coatings

In Section 2.3.2, we discussed different ways that can be used to simulate plasmonic nanoparticles, including by using Finite Element Modelling (FEM) and Finite-Difference Time-Domain (FDTD) methods; we found these to be computationally heavy and limiting, as only a few nanoparticles can be simulated at one time. Nanoparticles have size distributions that cause significant changes in the plasmonic response of the particles, which we will demonstrate in Section 5.2.2. These changes cannot be simulated practically using FDTD or FEM methods easily due to computational time and complexity, hence we chose to work with the Mie method and adapt the theory to account for the absorbing surrounding media, particle size distributions and single, multiple and graded coatings around the nanoparticles. This is in preparation for Chapter 6, where we demonstrate how plasmonic nanoparticles can be included into the Transfer Matrix Method (TMM) to simulate layers containing multiple scatterers.

In this chapter, we give an introduction into Mie theory (Section 5.1), discussing its limitation and the assumptions made in the original theory. We then start to integrate all of the different effects, such as: the absorbing surrounding media, graded and multiple coatings and particle size distributions, to create a realistic model (Section 5.2), before verifying that the model gives good experimental agreement with data from the literature (Section 5.3). We demonstrate how, by using multiple coatings and effective medium approximations, we can simulate faceted particles, before further examining the implications of graded media and how the treatment of the nanoparticle coatings significantly affects the plasmon response (Section 5.4).
Gustav Mie [120] published his theory on the optics of colloidal metals in 1908, which described the extinction of a solution containing small concentrations of nanoparticles, with particular emphasis on Gold (Au). He attributed the colour change from the size of the particles to optical resonances, explaining the inaccuracies of Maxwell Garnett [162], [163] effective media theory. Mie theory is built around Maxwell’s theories described in spherical co-ordinates \((r, \theta, \phi)\), shown in Figure 5.1 from \((x, y, z)\) co-ordinates, using boundary conditions at the surface of a sphere.

Mie also referred to the work of Lord Rayleigh [164], who described the scattering and absorption of perfectly conductive spherical particles, only considering first order effects (dipolar). This is true for Au particles with a size <100 nm, after which they start to show resonances due to higher order effects (quadrupolar, octapolar, etc.). These effects can be accounted for through an expansion of the spherical harmonic terms that represent the electronic and magnetic vibrations of the particles; in this case, only a finite number of terms needs to be considered to obtain an small error from the exact solution [120], which will be explored further in Section 5.2.3.
The extinction rate \( (W_{\text{ext}}) \) describes the amount of incident energy that the nanoparticle scatters and absorbs per unit area, where \( W_{\text{ext}} = W_{\text{abs}} + W_{\text{sca}} \) [123], [124], [165]. By using Maxwell’s theory in spherical coordinates, we can describe the extinction rate of the particle by taking an integral of the Poynting vector \( (S = 0.5 \cdot \text{Re}(\mathbf{E} \times \mathbf{H}^*) \) at the surface of the sphere [123], [124]. This should incorporate both the incident \( (\mathbf{E}_i, \mathbf{H}_i) \) and the scattered fields \( (\mathbf{E}_s, \mathbf{H}_s) \). The relationship between the scattering and extinction rates to the electromagnetic fields is given in Eq. 5.1 and Eq. 5.2, respectively.

\[
W_{\text{sca}} = \frac{1}{2} \text{Re} \left[ \int_\Omega ((\mathbf{E}_s \times \mathbf{H}_i^*) \cdot \hat{r}) \, d\phi d\theta \right] \tag{5.1}
\]

\[
W_{\text{ext}} = \frac{1}{2} \text{Re} \left[ \int_\Omega ((\mathbf{E}_s \times \mathbf{H}_i^*) + (\mathbf{E}_s \times \mathbf{H}_i^*) + (\mathbf{E}_s \times \mathbf{H}_i^*)) \cdot \hat{r}) \, d\phi d\theta \right] \tag{5.2}
\]

Some useful outputs from Mie’s theory are the absorption cross-section \( (C_{\text{abs}}) \) and the loss-through-radiation (better known as the scattering cross-section \( (C_{\text{sca}}) \)), which are described in Eq. 5.4 and Eq. 5.3 respectively. These can also be related back to the scattering and extinction rates by normalising to the incident flux \( (C_{\text{ext}} = W_{\text{ext}}/I_0) \). The cross-section describes the coefficient of absorption or scattering per unit volume of solution, whereas the total extinction relates to the sum of both the integrated absorption and scattering cross-sections. The total cross-section of a concentration of particles can be found by multiplying the cross-section by the total number of particles per unit area \( (N) \), which assumes that all the particles are identically sized [120]. In Eq. 5.3 and Eq. 5.4, \( \lambda \) is the wavelength, \( n \) is the refractive index of the surrounding medium (non-absorbing, i.e. no extinction coefficient \( (k) \)), and \( a_n \) and \( b_n \) are Mie coefficients describing the amplitude of the spherical vector harmonics, and will be described in more detail in Section 5.2.3. Although written in terms of the Mie coefficients, the product of the cross-section with the incident energy will yield the same result as the corresponding energy rate (Eq. 5.1 and Eq. 5.2.), where \( C_{\text{ext}} = C_{\text{sca}} + C_{\text{abs}} \).

\[
C_{\text{sca}} = N \frac{\lambda^2}{2\pi n^2} \sum_{n=1}^{\infty} (2n + 1)(|a_n|^2 + |b_n|^2) \tag{5.3}
\]

\[
C_{\text{abs}} = N \frac{\lambda^2}{2\pi n^2} \text{Im} \sum_{n=1}^{\infty} (2n + 1)(-1)^n (a_n - b_n) \tag{5.4}
\]

As shown by Mie, the total extinction of the incident beam via scattering and absorption is the sum over the total inclusive effects of the number of particles per unit volume; this is if the particles are dilute enough so that inter-particle effects do not need to be accounted for (i.e. very small concentrations). Using this theory, we develop a method for accounting for particle
distributions, using distribution functions such as the log normal distribution, which will be explained further in Section 5.2.2.

Mie theory has its limitations caused by assumptions and simplifications in the original theory; these assumptions are: the particles are very dilute, spherical and have identical sizes. It also assumes isotropic, non-absorbing surrounding media, and a single core material for the sphere. Nanoparticles are faceted, they naturally form a size distribution, and usually require a functionalised surface for maintaining suspension in aqueous solutions. More specifically, the use of nanoparticles in solar cell application requires us to deal with absorbing surrounding media and, as explained in Chapter 2, the use of capping oxide layers and multi-layered structures in order to reduce exciton quenching and to tune the plasmon resonance, respectively [79]. Therefore, we present an adapted Mie theory that includes these effects; although some of these effects have been addressed throughout the literature, these effects have not been incorporated together before. Moreover, we look at the implications of accounting for multiple and graded coatings in more depth as this has also currently not been addressed in the literature, to date. We also show how we can simulate for N number of particles of different sizes using statistical methods, which is difficult to achieve using FDTD and FEM methods (Section 2.3).

5.2. Modified Mie Theory

In this section, we will be looking at the modifications we have applied to Mie Theory to be able to simulate nanoparticles in a more realistic scenario, which includes accounting for the absorbing surrounding media, particle size distributions and particles with a single coating. Then we developed a model for multiple and graded coatings, incorporating all the other effects in one inclusive simulation.

5.2.1. Absorbing Surrounding Media

For a non-absorbing medium, the incident energy at the surface of the sphere is required, and is accounted for using the incident energy rate, through the Poynting theorem [166] expressed in spherical co-ordinates, as shown in Eq. 5.5, where \( r^2 \sin(\theta) \) is the surface element at a radius \( r \).

\[
W_0 = -\frac{1}{2} \text{Re} \left[ \iint_s \left( \mathbf{E}_s \times \mathbf{H}_s^* \right) \cdot \mathbf{r} \cdot r^2 \sin(\theta) \, d\phi d\theta \right]
\]  

5.5

When the surrounding media is absorbing, it has a complex imaginary refractive index (\( \tilde{n} = n + ik \)). In this case, we need to correct the incident energy rate on the surface of the sphere. Methods of achieving this have been described in the literature [165]. However, there has
been some disagreement within the literature on this treatment [90], [123], [125], [126], [165]– [168]; we will briefly explore this argument here.

The most widely accepted treatment between authors is that of Chýlek [165] (Eq. 5.6), who demonstrated a solution very similar to that of Mundy et al. [90], with the exception of the description of the extinction rate ($W_{\text{ext}}$). Chýlek provided a correction factor ($\gamma$), which considers the total absorption of the surrounding medium (instead of assuming non-absorbing media) containing a plasmonic sphere inside [165]. Mundy et al. [90] described $W_{\text{ext}}$ as the change in extinction between an absorbing medium and non-absorbing medium ($\Delta W_{\text{ext}} = W_{\text{ext}}(r) - W_{\text{ext}}^0(0)$) [165], [169], which is considered to be incorrect, as one could obtain conditions where the extinction goes negative.

$$C_{\text{sca}} = \frac{2\pi e^{-\alpha r}}{\gamma k^2} \sum_{n=1}^{\infty} (2n + 1)(|a_n|^2 + |b_n|^2)$$  \hspace{1cm} \text{Eq. 5.6}

Quinten and Rostalski [166] added an exponential term to the solution of Chýlek that describes the extinction within the surrounding media as a function of the distance from the particle surface ($e^{-2\alpha(R-r)}$), where $R$ is the position in the surrounding medium, as function of the distance from the centre of the sphere. This is a useful parameter when we look at incorporating the plasmonic nanoparticles into the TMM described in Chapter 3 (Section 7.2).

However, to obtain the absorption and scattering rates of the particle (not including the additional absorption from the surrounding medium), the Poynting vector should be calculated at the particle surface ($r$ is particle radius in the case of Eq. 5.6). This is due to the boundary conditions of the Mie solution, where the surface of the sphere represents the point where the equations for the internal (absorption) and external (scattering) fields split. Hence, Quinten and Rostalski’s [166] treatment of the outer sphere absorbing medium is incorrect, as demonstrated by Lebedev et al. [168].

The corrected version of the scattering cross-section is shown in Eq. 5.6, where $a_n$ and $b_n$ are the Mie coefficients, which will be explored in more depth in Section 5.2.3. $k$ is the wavenumber in the surrounding media and $\gamma$ is the geometric correction factor for the absorbing media (Eq. 5.7) as originally defined by Mundy et al. [90], where $\alpha = 4\pi\text{Im}[\bar{n}]/\lambda$, is the absorption coefficient. As the imaginary part of the refractive index approaches 0, the correction factor approaches 1, which turns the equation back to the original form as shown in Eq. 5.3.

$$\gamma = \frac{2(1 + (\alpha - 1)e^{\alpha})}{\alpha^2}$$  \hspace{1cm} \text{Eq. 5.7}
The correction presented by Chýlek, is the most commonly used within the literature [90], [123], [124], [126] and is the method that we have chosen to adopt.

5.2.2. Particle Size Distributions

In Section 5.2.1 we showed how we can adapt the original Mie theory to include absorbing surrounding media. Now we will show how we can incorporate particle size distributions into the model, where any distribution function can be used. In Section 5.1, we showed that the total extinction cross-section can be described for a number (\( N \)) of identically sized nanoparticles per unit volume (Eq’s. 5.3 and 5.4).

We will use the scattering cross section as an example: from Eq. 5.3, we can express this as a summation of the particle cross-sections (Eq. 5.8), where \( N \) is the total number of particles per unit volume and \( n \) is the \( n^{th} \) particle. In this case, we can now define the scattering cross-sections for different sized particles. This form of equation also allows us to incorporate more than one type of material, as is the case with mixed Au and Ag nanoparticles.

\[
C_{sca,\,tot} = \sum_{n=1}^{N} C_{sca(n)}
\]  

5.8

We will use a log-normal distribution as an example before showing how any other distribution could be incorporated. This method has been demonstrated to work for larger particles by Frisvad et al. [126]. The log normal distribution for the number density of nanoparticles (\( N_d(r) \)) can be expressed as shown in Eq. 5.9. The \( \alpha \) and \( \beta \) coefficients are given in Eq. 5.10, where \( \mu \) is the mean particle radius and \( \sigma \) is the standard deviation of the particle sizes, which can be experimentally obtained using dynamic light scattering or electron microscopy techniques.

\[
N_d(r) = \frac{r^2}{\beta\sqrt{2\pi}} e^{-\frac{1}{2} \left( \frac{\ln(r) - \alpha}{\beta} \right)^2}
\]  

5.9

\[
\alpha = \ln(\mu) - \frac{1}{2} \ln \left( \frac{\sigma^2}{\mu^2} + 1 \right), \quad \beta = \sqrt{\ln \left( \frac{\sigma^2}{\mu^2} + 1 \right)}
\]  

5.10

Then we can apply this to Eq. 5.8 to obtain the scattering cross section for the particle distribution, shown in Eq. 5.11. The change in \( r \) (\( r \) is discretised) should be very small (~2 nm) to obtain accurate peak positions and extinctions in the absorption and scattering cross-sections. This is because the resonance peaks in the extinction spectra will shift based on the radius. \( r_{min} \) and \( r_{max} \) represent the range of nanoparticle sizes (minimum and maximum radii respectively). This has a significant effect on the cross sections, which we will demonstrate in Section 5.3; where we will verify the results by comparison to the literature.
By using Chýlek’s method to calculate the scattering cross-section in an absorbing surrounding medium (Section 5.2.1), we can calculate the total cross-section for a distribution of particles under the same conditions. We can adapt Eq. 5.9 to incorporate any other distribution function, normalised such that the integral of the number density over the radii should equal the total number of particles per unit volume.

For two or more materials, we can use the same principles and obtain the scattering cross-section, as shown for Au and Ag in Eq. 5.12. However, this does have a limitation that requires knowledge of the number densities of the separate particle sizes for accurate results. It also assumes that the concentrations will be sparse enough that the average particle spacing is greater than 3 – 5 nm and therefore co-operative effects will not be apparent.

\[
C_{\text{sca, tot}} = \lim_{\delta r \to 0} \sum_{r_{\text{min}}}^{r_{\text{max}}} N_d(r) C_{\text{sca}}(r) = \int_{r_{\text{min}}}^{r_{\text{max}}} N_d(r) C_{\text{sca}}(r) \, dr
\]

5.11

\[
C_{\text{sca, tot}} = \int_{r_{\text{min}}}^{r_{\text{max}}} N_{d, \text{Au}}(r) C_{\text{sca, Au}}(r) \, dr + \int_{r_{\text{min}}}^{r_{\text{max}}} N_{d, \text{Ag}}(r) C_{\text{sca, Ag}}(r) \, dr
\]

5.12

5.2.3. Single Particle Coating

In the Section 5.2.2, we showed how we can incorporate size distributions into Mie theory to obtain more realistic results from our model. To keep the nanoparticles suspended and avoid aggregation, a functional capping layer is introduced, usually a few nanometres thick. A functional coating is also used in applications such as solar cells, where pure nanoparticles can act as trap centres for excitons and free charges, increasing the recombination and affecting the device performance. As we are interested in using the model for simulating solar cell performance, it is therefore important that we account for an additional layer to simulate capping or coated layers.

In order to do this, we first need to define the Mie coefficients \(a_n\) and \(b_n\) for a single sphere, where \(\psi_n\) and \(\zeta_n\) are the Ricatti-Bessel functions, which require the recurrence relations shown in Appendix B. \(x\) and \(y\) are the size parameters of the sphere given in Eq. 5.15, which can be used for estimating how many terms need to be calculated in order to obtain accurate peak positions and intensities. \(\bar{n}_1\) is the complex refractive index of the sphere, \(\bar{n}_2\) is the complex refractive index of the surrounding medium (real for non-absorbing media), and \(X_n\) and \(Y_n\) are
the logarithmic derivatives of the Ricatti-Bessel functions shown in Eq. 5.16, where the apostrophe denotes the first derivative.

\[ a_n = \frac{\psi_n(y)}{\zeta_n(y)} \left[ \frac{\bar{n}_2 X_n(x) - \bar{n}_1 X_n(y)}{\bar{n}_2 X_n(x) - \bar{n}_1 Y_n(y)} \right] \quad 5.13 \]

\[ b_n = \frac{\psi_n(y)}{\zeta_n(y)} \left[ \frac{\bar{n}_1 X_n(x) - \bar{n}_2 X_n(y)}{\bar{n}_1 X_n(x) - \bar{n}_2 Y_n(y)} \right] \quad 5.14 \]

\[ x = \frac{2\pi}{\lambda} r_1, \quad y = \frac{2\pi}{\lambda} r_2 \quad 5.15 \]

\[ X_n(z) = \frac{\psi_n'(z)}{\psi_n(z)}, \quad Y_n(z) = \frac{\zeta_n'(z)}{\zeta_n(z)} \quad 5.16 \]

A detailed description of these coefficients has been given by Fu and Sun [123], and Stratton [82]. In order to describe the Mie coefficients for an additional sphere (coating) we need to redefine the size parameters \( x \) and \( y \) into two sub-systems \((x_1, y_1) \) and \((x_2, y_2)\): the first set is identical to Eq. 5.15, the second is shown in Eq. 2.12, where \( r_2 \) is size of the outer-sphere (coating). \( \bar{n}_1 \) is unchanged, \( \bar{n}_2 \) is now the complex refractive index of the coating and \( \bar{n}_3 \) is the complex refractive index of the surrounding medium.

\[ x_2 = \frac{2\pi}{\lambda} r_2 \bar{n}_2, \quad y_2 = \frac{2\pi}{\lambda} r_2 \bar{n}_3 \quad 5.17 \]

To calculate the Mie coefficients for the coated sphere, we use Eq. 5.16 and Eq. 5.17; extending the boundary conditions to the surface of the outer-sphere. Using the Mie coefficients for the original sphere (Eq. 5.13 and Eq. 5.14), we can now define them for the outer-sphere (Eq. 5.18). We use the form of Kaiser and Schweiger [170], who describe the Mie coefficients of a coated sphere. The vector spherical harmonics expansion for a coated sphere has been described in detail by Aden and Kerker [121], where they give a further breakdown of the other terms, also briefly discussed in Appendix G.

\[ a_n = \frac{\psi_n(y_2)}{\zeta_n(y_2)} \left[ \frac{\bar{n}_3 [\psi_n'(x_2) - a_n \zeta_n'(x_2)] - \bar{n}_2 X_n(y_2) [\psi_n(x_2) - a_n \zeta_n(x_2)]}{\bar{n}_3 [\psi_n'(x_2) - a_n \zeta_n'(x_2)] - \bar{n}_2 Y_n(y_2) [\psi_n(x_2) - a_n \zeta_n(x_2)]} \right] \quad 5.18 \]

\[ b_n = \frac{\psi_n(y_2)}{\zeta_n(y_2)} \left[ \frac{\bar{n}_2 [\psi_n'(x_2) - b_n \zeta_n'(x_2)] - \bar{n}_3 X_n(y_2) [\psi_n(x_2) - b_n \zeta_n(x_2)]}{\bar{n}_2 [\psi_n'(x_2) - b_n \zeta_n'(x_2)] - \bar{n}_3 Y_n(y_2) [\psi_n(x_2) - b_n \zeta_n(x_2)]} \right] \quad 5.19 \]

Eq. 5.18 and Eq. 5.19 work together with the absorbing media (Eq. 5.6) and particle size distributions (Eq. 5.11), where the new Mie coefficients \( a_n \) and \( b_n \) can be used in the scattering cross-section (Eq. 5.6) and absorption cross-section (Eq. 5.4), whilst the sum of the two yields the total extinction. Using the same methodology, we can move the boundary conditions to
include another coating. This is the basis we have used for developing a recursive method for \( N \)-layered systems (Section 5.2.4).

Only a finite number of iterations need to be done for the results to converge. Dave [89] showed that the number of iterations required to achieve good experimental agreement could be based on the size parameter \( (x) \), where he defined the number of iterations as \( N = 1.1(n^2 + k^2)x + 1 \). Later, the work of Wiscombe [171] also demonstrated the relationship between the size parameter and the required number of iteration in more depth, where he presented different formulae dependant on the size parameter (Eq. 5.20). In the case of coatings and multiple coatings, the outer-most sphere will always have the highest size parameter and therefore should be the one used in the formula.

\[
N = \begin{cases} 
\frac{1}{x + 4x^3 + 1}, & 0.02 < x < 8 \\
\frac{1}{x + 4.05x^3 + 2}, & 8 < x < 4200 \\
\frac{1}{x + 4x^3 + 2}, & 4200 < x < 20,000 
\end{cases} \tag{5.20}
\]

### 5.2.4. Multiple Coatings around Nanoparticles

Now that we have shown how we can incorporate a single coating with an absorbing surrounding medium and account for a specified particle size distribution, we look at how we can develop on this to account for \( N \) coatings. After understanding how the boundary conditions are expanded to account for one additional layer, as shown in Section 5.2.3, we can look at how we can further expand this for \( N \) coatings.

We need to re-define the size parameters for the \( m^{th} \) layer (Eq. 5.21), where the radius is measured with respect to the centre of the core particle \((r_{m+1} > r_m > r_{m-1})\).

\[
x_m = \frac{2\pi}{\lambda} r_m \tilde{n}_m, \quad y_m = \frac{2\pi}{\lambda} r_m \tilde{n}_{m+1} \tag{5.21}
\]

*Figure 5.2 Schematic view of how the layers are treated with respect to the centre sphere, showing the complex refractive index \( (\tilde{n}_m) \) and radii \( (r_m) \) of the layers.*
Then we re-define the Mie coefficients \((a_n^m \text{ and } b_n^m \text{ in Eq. 5.22 and Eq. 5.23 respectively})\) for the \(m^{th}\) layer using the size parameters before, noting that for the case where \(m = 1\) (center sphere), Eq. 5.13 and Eq. 5.14 should be used.

\[
a_n = \frac{\psi_n(y_m) \cdot \bar{n}_{m+1}'(x_m) - a_n^{m-1}\zeta_n(x_m)}{\zeta_n(y_m)} - \ldots
\]

\[
b_n = \frac{\psi_n(y_m) \cdot \bar{n}_{m+1}'(x_m) - b_n^{m-1}\zeta_n(x_m)}{\zeta_n(y_m)} - \ldots
\]

5.22

5.23

5.2.5. Graded Particle Coatings

Now we have implemented an algorithm capable of accounting for N coatings around the nanoparticle, we can then use it to analyse graded coatings, as would be the case for hybrid material systems, such as TiO\(_2\) : SiO\(_2\). We can describe the change in the refractive index over increasing radius by using Eq. 5.24 and 5.25 for linear and exponentially graded media. This requires the refractive index at the start (\(\bar{n}_{\text{start}}\)) and end (\(\bar{n}_{\text{end}}\)) of the section of interest. In this chapter, we will be mostly concerned with linear and exponential gradients, although other gradients may be included using a similar description, and we will also compare the results with typical arithmetically averaged and double layered approaches.

When the media is linearly graded, the rate of change in the refractive index will be constant throughout the layer. This can be described by using Eq. 5.24, where \(\bar{n}(x)\) is the refractive index as a function of distance from the centre sphere (core).

\[
\bar{n}(x, \lambda) = \bar{n}_{\text{start}}(\lambda) + \frac{(x - r_1)(\bar{n}_{\text{end}}(\lambda) - \bar{n}_{\text{start}}(\lambda))}{r_m - r_1}
\]

5.24

In the exponential case (Eq. 5.25) an error (\(\rho_{\text{err}}\)) is introduced for correction, the error describes how close to the asymptomatic value the function gets, where the smaller the number the more accurate it is, providing it remains positive and non-zero. In the case the introduced value for \(\rho_{\text{err}}\) is zero, the equation does not compute as the natural logarithm of 0 is undefined.

\[
\bar{n}(x, \lambda) = \left(\bar{n}_{\text{end}}(\lambda) - \bar{n}_{\text{start}}(\lambda)\right) \cdot e^{-\frac{x-r_1}{r_m-r_1}\ln\left(\frac{\rho_{\text{err}}}{|\bar{n}_{\text{start}}(\lambda)-\bar{n}_{\text{end}}(\lambda)|}\right)} + \bar{n}_{\text{end}} - \rho_{\text{err}}
\]

5.25
Figure 5.3 demonstrates how the refractive index changes through the coating, the linearly graded uses Eq. 5.24, and the exponentially graded example uses 5.25. We explore a specific case using TiO₂ and SiO₂ as a capping layer in each of these configurations in Section 6.4. Now we have defined how we vary the refractive index through a layer, we now look to some of the outputs that we can obtain from the model.

### 5.3. Model Outputs

In Section 5.2.5 we built the plasmonic model for a distribution of particles with multiple and graded coatings in an absorbing medium; in this section, we look at the useful outputs that we can use to quantify the plasmon resonance, such as: efficiencies, rates, intensities etc. from the model in Section 5.2.

#### 5.3.1. The Poynting vector and Energy Rates

Energy rates (described in Section 5.1) are commonly used to describe the plasmon resonance. In this case, we need to calculate the Electric and Magnetic fields incident on the surface of the sphere (\(E_i, H_i\)) and we also need the scattered fields (\(E_s, H_s\)) at the surface. The Poynting vector (\(S = 0.5 \Re (E \times H^*)\)) is used to calculate the scattering and extinction energy rates (Eq. 5.1 and Eq. 5.2, given in Section 5.1). A vector spherical harmonic expansion of these terms is described in detail by Fu et al. [123], which we have based this work on.

The solutions to the Poynting vectors at the surface of the sphere using Mie coefficients are given in Eq. 5.26 and Eq. 5.27. \(a_n\) and \(b_n\) are the Mie coefficients calculated in the last section (Eq. 5.22 and Eq. 5.23). The absorption energy rate is given by the difference between the scattering and extinction rates (\(W_{abs} = W_{ext} - W_{sca}\)) [123], [124], [165].
A useful quantity is the cross-section normalised to the geometric cross section (or the efficiency), or the ratio between the effective cross-section and the radius of the particle. The efficiency gives an indication to how well the particle can scatter ($Q_{\text{sc}}$) and absorb ($Q_{\text{abs}}$) the incident light.

Generally, in the literature, the results are presented as either a cross-section or efficiency normalised to the flux incident on the surface. When directly comparing results to the literature, you may be required to change the format of the results (efficiencies, cross-sections, arbitrary values); as this changes depending on the authors from efficiencies [172] to cross-sections [173], to normalised arbitrary values [168]. In terms of the extinction, the efficiency ($Q_{\text{ext}}$) is normalised to the cross-sectional area and the incident intensity, such that $Q_{\text{ext}} = W_{\text{ext}}/I_0\pi r^2$. While the extinction cross-section is just normalised by the incident energy, such that $c_{\text{ext}} = W_{\text{ext}}/I_0 = \pi r^2Q_{\text{ext}}$.

### 5.3.2. Scattering Matrix, Phase and Intensity Patterns

In solar cell applications, the amount of light that is reflected, absorbed and transmitted from a system of scattering elements is important. For this reason, we need to express the angular dependant scattering parameters, intensities, and the phase function. This will then be used in Chapter 6 for putting the nanoparticles into the Transfer Matrix Method, which was described in Chapter 3. In this section, for completeness, we show how the scattering matrix is formed from the Mie coefficients, then demonstrate how we can obtain the angular dependant scattering, phase and asymmetry of the nanoparticle distribution.

The TMM (Chapter 3) described the behaviour of linearly polarised light through a multi-layered structure, this means that we need to describe the scattering from a bulk of scattering elements in terms of polarisation. Eq.’s 5.28 and 5.29 are the angular scattering parameters based on the Mie coefficients described in Section 5.2, where $\pi_n$ and $\tau_n$ (shown in Eq. 5.30) are the angular functions based on the Legendre polynomial ($P_n^m(\theta)$) of the first degree (more information on this and how they are calculated are given in Appendix G), where $S_1$ (Eq. 5.28) relates directly to $p$-polarised and $S_2$ (Eq. 5.29) to $s$-polarised.
The scattering functions (Eq. 5.28 and Eq. 5.29) relate directly to the extinction cross section by the relationship
\[ C_{\text{ext}} = 4\pi \text{Re}[S(0)/k^2], \]
where \( S(0) = S_1(0) = S_2(0) \), and \( k \) is the wave number \( (k = 2\pi n_m/\lambda) \). Another relationship that can be drawn from this is the amount of incident energy that has been back-scattered (reflected), where \( S(\pi) = S_1(\pi) = -S_2(\pi) \), which can be used to determine the amount of the scattered light that would be reflected (scattered) back out of a device, such as a solar cell.

\[ S_1(\theta) = \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} \left\{ a_n \pi_n(\cos(\theta)) + b_n \tau_n(\cos(\theta)) \right\} \]
\[ S_2(\theta) = \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} \left\{ b_n \pi_n(\cos(\theta)) + a_n \tau_n(\cos(\theta)) \right\} \]

The intensities are taken from the scattering parameters, where \( i_1(\theta) = |S_1(\theta)|^2 \) and \( i_2(\theta) = |S_2(\theta)|^2 \) are the angular intensity of an \( s \)- and \( p \)-polarised plane wave, respectively, which is given by Eq. 5.31 [143]. The total intensity, given in Eq. 5.31, can be found from the angular intensities for both \( s \)- and \( p \)-polarisations \( (i_1 \text{ and } i_2, \text{ respectively}) \), where a normalising factor of \( 1/k^2r^2 \) is introduced.

\[ I(\theta) = \frac{1}{2} \left( \frac{i_1(\theta) + i_2(\theta)}{k^2r^2} \right) I_0 \]

In the TMM (Chapter 3), the intensities at either side of the layer are calculated for partially or completely incoherent layers. We can use the same principles from this, by changing the observation point of the intensity to the boundary conditions of the layer depending on where in the layer the particles are positioned. This is the basis of Chapter 6 and will be discussed further there. Now that we have shown how the outputs of the model are computed, we look at some of the outputs with comparison to the literature.

5.4. Verification of the Model

In Section 5.2 we built an integrated model capable of calculating the Mie coefficients of a nanoparticle distribution with multiple and graded coatings, in an absorbing media. We now demonstrate the outputs of our model with comparison to experimental and other theoretical results from the literature. This will cover many different areas, from biological applications (Contrasting agents, Cancer treatments etc.) to growth and plasmon resonance control, and to solar cell applications.
The model requires the complex refractive indices of the materials used in the examples and these are not always available within the papers. In the case that this information is not available, it has been taken from other literature sources. A full list of refractive indices and references used within the thesis are given in Appendix B.

5.4.1. Gold and Silver nanoparticle growth control

Table 5.1 Parameters used in the model for Ag NP distributions capped with 4.3 nm of PEG, taken from Bastús et al. [174]

<table>
<thead>
<tr>
<th>Diameter</th>
<th>Radius</th>
<th>SD (%)</th>
<th>SD (nm)</th>
</tr>
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<tbody>
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<td>5.0</td>
<td>9.7</td>
<td>0.5</td>
</tr>
<tr>
<td>12</td>
<td>6.0</td>
<td>10.0</td>
<td>0.6</td>
</tr>
<tr>
<td>13</td>
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<td>8.4</td>
<td>0.5</td>
</tr>
<tr>
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<td>7.5</td>
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<td>0.7</td>
</tr>
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<td>18</td>
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<td>9.5</td>
<td>1.0</td>
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<tr>
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<td>12.0</td>
<td>12.5</td>
<td>1.5</td>
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<td>1.2</td>
</tr>
<tr>
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<td>15.0</td>
<td>8.0</td>
<td>1.2</td>
</tr>
<tr>
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<td>16.0</td>
<td>8.8</td>
<td>1.4</td>
</tr>
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<td>1.3</td>
</tr>
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<td>7.0</td>
<td>1.5</td>
</tr>
<tr>
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<td>24.0</td>
<td>7.7</td>
<td>1.8</td>
</tr>
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<td>6.2</td>
<td>1.6</td>
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<td>2.1</td>
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<td>5.7</td>
<td>1.9</td>
</tr>
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<td>218</td>
<td>109.0</td>
<td>8.9</td>
<td>9.7</td>
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</table>
Due to the increased need to tune the plasmon resonance of nanoparticles in applications such as biosensors, OLEDs, and solar cells, there is a need for methods to accurately control the size, shape and coatings of metallic nanoparticles. Bastús et al [174] studied the effects of size, composition and surface coating on the plasmon resonance by controlling the growth conditions of Au and Ag nanoparticles. They controlled the growth by using different ratios of the reducing agents (sodium citrate and tannic acid), a method that they presented in earlier papers: [131] and [130] for Au and Ag respectively. They provided details of particle size distributions (TEM image analysis) for each different growth, giving the mean diameter and the standard deviation. We have already demonstrated the ability to include particle size distributions within the Mie model, which is given in Section 5.2.2. They also provide details as to the capping layers that they used: poly (ethylene glycol) with molecular weights ($M_W = 1000$ and $3500 \text{ g/mol}$) to stabilise the solutions, which yields thicknesses of $\sim4.3 \text{ nm}$ and $\sim7.9 \text{ nm}$ respectively. We can also add this information to the model by using the single coating solution presented in Section 5.2.3.

Table 5.2 shows the parameters that we used within the simulation taken from Bastús et al. [174]. While the refractive indices of Ag [88] and PEG are given in Appendix B. To demonstrate our model against their theoretical and experimental results we provide a side by side comparison.

**Table 5.2 Parameters used in the model for Au NP distributions capped with Sodium Citrate ~2nm, taken from Bastús et al. [130]**

<table>
<thead>
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<th>Diameter</th>
<th>Radius</th>
<th>SD (%)</th>
<th>SD (nm)</th>
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</tr>
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Figure 5.4 Silver nanoparticle size distributions from Table 5.1 for (top) Ag nanoparticles with a capping layer of PEG for experimentally obtained and calculated results. Reprinted with permission from Bastús et al.\cite{174}. Copyright 2015 American Chemical Society. (bottom) Au nanoparticles using same growth process (parameters given in Table 5.2). Reprinted with permission from Bastűs et al. \cite{130}. Copyright 2011 American Chemical Society.
Using our model we have been able to reproduce the results from Bastús et al. [130], [174], original results shown in Figure 5.4 and results from our simulation shown in Figure 5.5. There are no discrepancies between our model and the results that Bastús et al. [130], [174] obtained from their modelling. In this case, however, our model incorporates effects from the particle size distribution, absorbing surrounding media and multiple functional coatings. Although in this case there is no absorbing surrounding media, or multiple functional coatings, it has not affected the computed result, which verifies that for basic particle modelling our model remains accurate. The extinction efficiencies used are taken directly from the model and have not been normalised in any form.

5.4.2. Cancer Drug Delivery with multi-layered Au nanoparticles

In many cases [27], [175]–[177] Au nanoparticles have been used for targeted drug delivery systems, due to their biocompatibility, surface properties (drug carrying capabilities), and size (skin permeability) [27][178][179]. Labala et al. [176] provide optical spectra for their multi-layered nanoparticles that they used for Imatinib Mesylate (IM) for cancer drug deliver through the skin. They provided the nanoparticle size and distribution information from dynamic light scattering at each stage of their process, as well as the complementary optical spectra. We used the information given by Labala et al. [176] and simulated the multi-layered structure at each stage using the multi-layered method outlined in Section 5.2.4. We accurately (±1 nm) reproduced their peak positions from the optical spectra, utilising the particle size provided within the paper (see Figure 5.6).

Labala et al. [176] used Au nanoparticles that have a distribution (mean and standard deviation) of 26.6±2.6 nm. They introduced a layer of polyethylene imine (PEI) making the
distribution $34.5 \pm 0.9$ nm, then a layer of polystyrene sulfonate (PSS) resulting in particle size of $61.2 \pm 1.2$ nm. This was followed by an additional layer of PEI, resulting in a final particle size of $98.5 \pm 4.3$ nm. We apply the distribution to the core particle size and obtained refractive indices for PEI ($n = 1.44$) and PSS ($n = 1.37$) from Sigma Aldrich; the particles were monodispersed in water ($n = 1.33$) [176].

![Schematic view of multi-layered nanoparticle](image)

**Figure 5.6** (a) A schematic view of the multi-layered nanoparticle with Au core of $26.6 \pm 2.6$ nm. (b) The results from simulation for each step of the process outlined by Labala et al. [176], where the peak positions are $\text{Au@PEI} = 518$ nm, $\text{Au@PEI@PSS} = 525$ nm and $\text{Au@PEI@PSS@PEI} = 530$ nm, which match the peak positions from the paper.

We showed that we can reproduce the plasmon response of a multi-layered structure by comparing our model to the experimental work of Labala et al. [176], we obtained identical peak positions ($\text{Au@PEI} = 518$ nm, $\text{Au@PEI@PSS} = 525$ nm, and $\text{Au@PEI@PSS@PEI} = 530$ nm, shown in Figure 5.6), where the maximum extinction efficiency peak has been normalised to 1.

### 5.4.3. Polarisation and Phase

In order to show that the angular dependence of the calculation, demonstrated by polar plots (Figure 5.7) is correct, we gave a comparison to the work of Setién et al. [87]. They showed how the TE and TM modes differ with different materials and peak wavelengths, showing forward scattering patterns. Here we demonstrate the accuracy of our polar plots, where the radial axis is the angle, and the linear axis is intensity. We do this with and without a Silica shell, to demonstrate the effect on the model with an additional coating. Setién et al. [87] show the polar plot for both parallel (TE) and perpendicular (TM) modes, for a Silver nanoparticle of 25 nm radius and 50 nm radius. Their results are shown in Figure 5.7 (a) and (b).
Figure 5.7 Polar plots of intensity in both (a) TM mode and (b) TE, showing a strong forward scattering element for the 50 nm particle at 0° and in (b) at the same angle. The smaller particle just shows dipole behaviour and therefore does not demonstrate forward scattering. Re-print from Setién et al. [87], no permission required. (c) The simulation result for a 25 nm radius particle and (d) for a 50 nm radius. For both the 25 nm plots, the peak was taken to be at 430 nm and for the 50 nm plot it was at 400 nm.

In our model, we set the core particle size to have radii of 25 nm, and 50 nm, respectively. Then we calculate the intensities, using Eq. 5.31, for angles 0 to 2π radians. Setién et al. [87] specify that the nanoparticles are in water, therefore we will use the optical properties of Silver from Rakić et al. [88] (Appendix E) and a value for the refractive index of water at n = 1.33. We have also assumed that in this case that water is non-absorbing (k = 0). The results from this simulation are shown in Figure 5.7, where it demonstrates comparable results to that of Setién et al. [87] (Figure 5.7).
Differences in the polar plot can arise from the differences in the refractive indices of either the core or external materials. The peak value at which it was calculated will also have an important effect, where the polar intensities should be taken at the plasmon resonance wavelength. An important point to make here is that as the particle size increases, and quadrupole and other higher order effects start to play a role, forward scattering effects start to show more, as seen in Figure 5.7 (d). When you only have dipole interaction, there will not be any forward scattering, as is the case in the 25 nm radius particle. In OSCs we wish to maximise the forward light scattering effects, and hence larger particles would provide a better plasmon response, however, larger particles contribute to other losses (recombination), and realistically a trade-off needs to be found (Section 2.2.4). At 0 phase (0° or 180°) both modes equal each other, hence only one is needed to be calculated; when considering the dipolar interactions, they start to alter the phase angle, then you start to get differences in the spectra.

The phase polar plots for the Ag nanoparticles of 25 nm and 50 nm are shown in Figure 5.7, which agrees with the work done by Setién. We can be sure that the amendments that we have made to the model to take into consideration the distribution of particle sizes, and multiple coatings, does not affect the results for trivial configurations such as single particles with no coating.

### 5.5. Summary

In this chapter, we have given an overview of the methods incorporated together to form the basis of our plasmonic model. This includes particle size distributions (Section 5.2.2), single, multiple and graded coatings as well as mixed media (Section 5.2.4). We have also verified these results against the literature showing the accuracy of our integrated model to realistic, experimentally obtained, results (Section 5.4). We also have shown how the model extends further than the intended discipline, where we show how it can also be utilised in biological applications (Section 5.4.2). In the biological example, the model reproduced the correct peak positions with an accuracy of ±1 nm. This was the result from the simulation, taking into consideration multiple coatings around a core nanoparticle, where we have verified that the recursive Mie method (Section 5.2.4) functions correctly.

In Chapter 6 we develop on these theories and show the effects and implications of having graded media, and how we can obtain a blue-shift in the plasmon resonance with multiple coatings in larger particles than previously shown. This could have many useful applications in controlling the plasmon resonance just by changing the ratio of coating to core particle size.
Chapter 6

6. Plasmonic Blue Shift and Multiple and Graded Coatings

In Chapter 4 we discussed how we built an all-inclusive plasmonic nanoparticle model that takes into consideration: the distribution of the particle size; absorbing surrounding media; mixed media; and multiple and graded coatings. We also demonstrated the outputs that we can achieve from the model, such as the Extinction, Scattering and Absorption cross-sections ($C_{ext}$, $C_{sca}$ and $C_{abs}$ respectively) and energy rates ($W_{ext}$, $W_{sca}$ and $W_{abs}$), phase ($\phi$), and intensities ($I(\theta)$, where $\theta$ is the scattering angle). This allows us to explore various scenarios, such as hybrid material systems, oxidisation, and refractive index changes, that have not been previously possible with other modelling methods, such as FDTD and FEM.

In comparison to Finite-Difference Time-Domain (FDTD) and Finite Element Modelling methods, the model (described in Chapter 4) has been found to be orders of magnitude quicker. It can simulate a particle size distribution with multiple coatings (~200, discussed further in Section 6.2) in less than a minute on average, on a standard personal computer or laptop. This is especially important when looking at tuning the plasmon resonance, by running the simulation over several variables.

In this chapter, we explore multiple and graded coatings in more depth, with a focus on hybrid and mixed materials. We show that a hybrid TiO$_2$ Anatase and SiO$_2$ mixed coating, depending on the formation, could lead to a strong blue-shift in the plasmon resonance with increased particle size. This effect has been previously seen by Peng et al. [31] experimentally for small (~3-5 nm) coatings. With the structure that we are investigating, we are seeing blue-shifts occurring in much larger particles (~20 - 30 nm). This could lead to increased control over the plasmon resonance, increasing the tunability for optical applications.

This chapter also serves as a demonstration of the limitations and assumptions made and how this affects the modelling and results. We find that, after a certain number of sub-layers (~200) between the core and surrounding media, the change in the peak position becomes negligible, and hence the results are convergent. We start by discussing the modelling parameters and set up for the simulation (Section 6.1). A detailed explanation of the convergent behaviour, in regards to the number of sub-layers, to the accuracy of the answer is given in Section 6.2.
We show, using Scanning Transmission Electron Microscopy (STEM) Z-contrast analysis, that a log-normal distribution for the size parameters of the nanoparticles is a good assumption (Section 6.3). The outputs from the modelled system, describing where the differences are and their likely causes, are given in Section 6.4. Furthermore, we demonstrate how 3-D peak mapping is possible using the model (Chapter 4) and how this can be used for optimisation of a material system and/or plasmon resonance tuning (Section 6.5).

6.1. Nanoparticle Structures

In recent years, the development of novel nanoparticle systems with unique characteristics using a multi-layered approach has become increasingly common [30], [91], [180]–[184]. By considering the selection of materials (material configuration) and layer thicknesses, one can tune the plasmon resonance of a structure. Methods such as these provide more flexibility for plasmonic tunability.

![Illustrative examples](image)

Figure 6.1 Illustrative examples of (a) hybrid material configuration, where the orange circle represents a core nanoparticle, and the blue-green outer shell represents a mixture of two materials, and (b) which shows the core nanoparticle, with multiple coatings (other coloured coatings).

Multi-layered and hybrid material nanostructures have a promising future in a wide range of applications; from bio-sensing and bio-diagnostic applications [185], [186], to medical and cancer therapies [175], [176], [187], Magnetic Resonance Imaging (MRI) contrasting agents [179], [188] to photovoltaic technology [81], [91].

In medical and therapeutic applications, gold is preferred as a core material due to its inert, biocompatible and non-toxic properties [27], [187]. Both Ag and Au are used in photovoltaic applications [116], [189], [190], because their plasmon resonances fall within the visible region (~ 400 nm for Ag, and ~ 560 nm for Au). The plasmon resonance of metallic nanoparticles red-shifts as the particle size increase and this has been seen both theoretically and
When a capping layer is introduced, in order to keep NPs from aggregating for example, this effect holds \cite{174}, and as you increase the capping layer thickness, the plasmon resonance also red-shifts \cite{81}. For plasmon resonance tuning applications, the lower wavelength in the visible spectrum that the plasmon resonance is at for a specific material system, then the more flexibility you have for tuning; for this reason Ag (plasmon resonance of core silver nanoparticles is \(\sim 380 \text{ nm}\)) is commonly used as a core material.

A typical configuration would be the core-shell structure, usually with either a Ag or Au core surrounded by a functional capping layer that prevents aggregation, for example; further examples include Ag with a SiO\(_2\) capping layer (Ag@SiO\(_2\)) \cite{174}, or Au with a TiO\(_2\) layer (Au@TiO\(_2\)) \cite{191}, but the layers can also be reversed, with the metal as a coating \cite{192}, \cite{193}. Further to this, there has been an increase in the amount of fabricated structures that follow the core-shell-shell structure \cite{91}, \cite{181}, \cite{183}, or even core-shell-shell-shell (Au@PEI@PSS@PEI, as shown in Section 4.4.2) \cite{176}: An example of this is Au@SiO\(_2@TiO2\) (Figure 6.2 (a) and (b)) \cite{91}. Other configurations are hybrid coatings, still presented as a core-shell structure, but this time with two different materials mixed with a specific wt.% to give the optimum optical response, such as the Au@(SiO\(_2\), TiO\(_2\)), shown in Figure 6.2 (c) \cite{30}.

In Organic Solar Cells (OSCs), nanoparticles are commonly used to increase the optical absorption, exciton generation and dissociation, and charge transport and extraction \cite{79}, \cite{116}, \cite{194}. Non-capped nanoparticles have been shown to act as trap centres, increasing the recombination of excitons (exciton quenching), and therefore decreasing the performance of the OSCs \cite{25}, \cite{50}. A capping layer is introduced to get the benefits of the plasmonic enhancement, without the drawback of the increased recombination \cite{94}. Commonly, the capping layer is either TiO\(_2\) or SiO\(_2\) \cite{110}, \cite{113}, which will be explored within this chapter.

An example of such a system would be the use of TiO\(_2\) and SiO\(_2\) coated Au nanoparticles: Figure 6.2 (a) \cite{91} demonstrates a double layered approach, where the SiO\(_2\) is layered onto the Au nanoparticle core, and a further layer of TiO\(_2\) is coated around this. Figure 6.2 (b) \cite{91} demonstrates the formation of these particles using STEM – Energy-Dispersive X-Ray Spectroscopy (STEM-EDX) to show concentrations of TiO\(_2\) towards the surface and SiO\(_2\) between the core and shell. A second use of this material system utilises the mixed media approach, where a hybrid layer of both SiO\(_2\) and TiO\(_2\) are coated around a Au core (Figure 6.2 (c) \cite{30}). Lekeufack et al. \cite{7} demonstrated, using High Resolution Transmission Electron Microscopy (HR-TEM), that with 50 wt% of both TiO\(_2\) and SiO\(_2\), they achieved an even spread of both materials across the coating, which would affect the overall optical properties of the coating. It can also be possible that a densely-concentrated area towards the centre or surface
of the coating could cause more of an exponential-type gradient in material percentage, leading to a similar behaviour in the optical refractive index; this could be the case with oxidation/reduction mechanisms affecting the coating gradually, from the surface to the core of the particle. Another option could be to have a linear concentration and optical properties gradient, with material systems such as shown in Figure 6.2 (c), where one material slowly blends to another.

Figure 6.2 (a) and (b) [91] show a double coated (Core-Shell-Shell) approach using Au (Core), SiO2 (Inner Shell) and TiO2 (Outer Shell). (a) shows HR-TEM image analysis of a single nanoparticle showing where the SiO2 and TiO2 are situated in the structure. (b) STEM-EDX, which confirms the position of the SiO2 between the Au core and TiO2 outer-shell. (c) [30] HR-TEM image of mixed-media (hybrid) coated Au NP showing how the SiO2 and TiO2 have been mixed around the Au NP. (a) and (b) Reprinted with permission from S. W. Sheehan et al. [91] Copyright 2013 American Chemical Society. (c) Reproduced from D. D. Lekeufack et al. [30] with permission from the Royal Society of Chemistry.

To further explore the effects of these different material configurations, we look at four different structures using the same materials. Figure 6.3 shows the four structures that we will investigate within this chapter, they will be named as follows: (a) Exponentially Graded, (b) Linearly Graded, (c) Averaged Coating, (d) Double Coating. We will briefly discuss each of these configurations in this section.

For this reason, we investigate the use of the recursive Mie Method presented in Chapter 5 and apply it to a similar system to the hybrid material system shown in Figure 6.2; we present four different ways of modelling this material system (These are approximations, but can be used to model more complex gradients etc.).

Now, synthesis of such material structures has been achieved [30] and more realistic modelling of the effects associated with the material structures becomes important, not only from a peak tuning perspective, but also from the associated characterisation of such systems. In practice, 3-D elemental mapping can be used to identify the structure and how the materials form around the nanoparticle.

Figure 6.3 (a) demonstrates the concept of an Exponentially Graded coating, which describes the situation where the first material very quickly grades into the second material. This is especially important for looking at effects from oxide coatings close to the surface, where the
complex refractive index changes rapidly over the first few nanometres from the surface. In this case, and throughout this chapter, we are interested in discerning the differences in the Plasmon resonances between each of the material configurations (Figure 6.3). The functional dependence for the Exponential Gradient has been given in Section 5.2.5, which demonstrates how we can obtain the $n$ and $k$ values over space for the two materials. The steepness of the exponential is determined by the area of interest; if it were confined to a few nanometres, then studies on oxide coatings would be possible.

Following on from the Exponentially-Graded coating, Figure 6.3 (b) shows a Linearly-Graded coating. In this case, there would be an even amount of material defined within a space that linearly changes from the optical properties of one material to the other. An interpolation algorithm has been implemented to calculate the refractive indices at each position. This is given in Section 4.3.3 and describes the relationship between the two materials’ optical properties as a function of distance from the core nanoparticle. Figure 6.3 (c) shows an arithmetically-averaged coating composed of a mix of two materials, using $(n_1 + n_2)/2$. As we will show in this chapter, treating special cases using the averaged configuration (Section 6.4) can lead to incorrect approximations. Lastly, in Figure 6.3 (d), we demonstrate a Double Coating, were two separate layers are used for each of the materials, with a sharp, defined interface between the two layers. In all cases, the same volume ratio of the materials used (i.e. 50:50) has been used for each of the examples.

### 6.2. Recursion and convergence of number of layers

In the previous section, we introduced the material configurations, common applications and materials used and a description of the configurations. In this section, we look at how the model developed in Chapter 4 calculates the optical properties for the multiple layers and the significance that the number of sub-layers has on the results. One reason for choosing to
demonstrate the material configurations using SiO\textsubscript{2} and TiO\textsubscript{2} Anatase is that they are commonly used in photovoltaic applications \cite{80, 193}, and their optical properties are substantially different. At 350 nm for example, the real part refractive index ($n$) for TiO\textsubscript{2} is 3.25 and for SiO\textsubscript{2} is 1.5. Figure 6.4 (a) shows the different configurations and how the refractive index should grade throughout the shell of the core-shell structure. This assumes that the number of sub-layers used to model the grading would be approaching infinity, as we are working in a discrete environment (as first mentioned in Section 5.2.4). Figure 6.4 (b) shows what the real part of the refractive index does throughout the shell layer; as the number of sub-layers increases, the change in the refractive index between each iteration decreases and smooths the gradient (no big changes in optical properties, causing unrealistic reflections at the boundaries of each sub-layer). Each of the functions for the lines shown in Figure 6.4 (a) have been described mathematically in Section 5.2.4.

![Figure 6.4](image)

**Figure 6.4** (a) TiO\textsubscript{2} Anatase:SiO\textsubscript{2} mixed layer using the different methods specified in Section 6.1: Exponential; Linear; Double and Averaged, this just demonstrates the real part refractive index, ranging from 3.25 for TiO\textsubscript{2} at 350 nm and goes to ~1.5 for SiO\textsubscript{2} for the same wavelength. The distance from centre defines the distance from the centre of the sphere, the first number here defines the size of the centre sphere and the difference between the last and first numbers shows the thickness of the coating. (b) demonstrates the effect of increasing the number of sub-layers. The higher the number (N), the closer to the function shown in (a).

To further demonstrate the impact of the number of sub-layers has on the answer, we demonstrate in Figure 6.5 (inset) how the spectra changes, and (main) the quantification of peak position and extinction efficiencies. These were obtained by fitting the spectra shown in the (inset) plot. What this demonstrates is a very quick convergence of both the extinction efficiency and peak position as the number of layers increases up until ~200 layers, where afterwards the values do not change significantly (much less than experimental precision using spectroscopic methods). Therefore, in all further simulations, we calculate using 200 sub-layers.
Figure 6.5 The absorption peak position (black) and the corresponding extinction efficiency (blue) show convergence once the number of sub-layers increases above 200, for an exponentially decreasing refractive index (Figure 6.4). The inset shows the amplitude and peak positions reduce and blue shift with an increased number of steps.

When you have an interface between two materials (different optical properties), reflection and refraction happen and the amount that is reflected, per the Fresnel equations (Section 3.1), is proportional to the difference between the refractive indices. We believe this to be the predominant reason we see the effect shown in Figure 6.5. 16% reflection for 3.5 to 1.5 instead of 0.0002% per layer for 3.5 to 3.49 (200 sub-layers) at 0 degrees for example.

\[ R = \frac{n_1 - n_2}{n_1 + n_2}^2, \quad \theta_i = \theta_t = 0 \]

Throughout this chapter, we are using 200 sub-layers for all further investigations, the difference the number of layers makes for the double and averaged layers is negligible. We have compared directly and achieved identical results; as there are no further changes in the refractive index and hence negligible reflection at the boundaries, we can keep the number of sub-layers constant (200) for all simulations.

6.3. **Size variance in nanoparticle samples**

Section 6.2 demonstrated the convergence of the model for graded media and multiple layers, where we show that after 200 sub-layers the change in the peak position and extinction are negligible. Here we discuss another approximation used within the model and how it affects the modelling results.
Frisvad et al. [126] showed that an effective radius can be used as a suitable approximation for Mie calculations, which is the basis of the model, as described in Chapter 5. In Section 5.2.2 we discussed how we can add a particle size distribution to our calculations and here we show through experimental results that a log normal distribution is a good approximation. Eq. 6.1 [195], where \( r_{eq} \) is the effective radius (equivalent spheres), \( V \) is the volume, and \( A \) is the surface area. This is used to find the equivalent sphere size that we can use within the Mie calculations, described in Chapter 5.

\[
\frac{r_{eq}}{V} = 3 \frac{V}{A}
\]

Using Z-Contrast mode on a Scanning Transmission Electron Microscope (STEM), we can image the nanoparticles. Then using ImageJ (software), we can find the boundaries of the nanoparticles and hence find the effective radius; this calculation is based on the circumference of the particle, where the volume would be approximately given by Eq. 6.2, where \( c \) is the circumference, or outline, of the spherical object.

\[
V \approx \frac{4}{3} \pi \left( \frac{c}{2\pi} \right)^3
\]

Figure 6.6 (a) shows the approximate effective radius of the 146 nanoparticles that were analysed. The nanoparticles were Citrate-stabilised Ag nanoparticles (50 nm), dispersed with a concentration of 0.1mM in aqueous solution and Toluene (NANOCS). We found that the nanoparticles had an average effective radius of 23 nm (46 nm diameter, compared with the quoted 50 nm), we also found quite a large size distribution (46±4 nm) and that it follows a log normal distribution of the particle size. Figure 6.6 (c) shows a typical Z-contrast image of a nanoparticle group that we used in the analysis.

To see what effect a size distribution may have on the results, we modelled a distribution of nanoparticles with a radius of 50 nm and standard deviation of 0.1 nm, 1 nm and 10 nm. Figure 6.6 (b) shows the results from the model, where we can see larger changes in the quadrupole resonance (~ 460 – 500 nm) than in the dipolar resonance (~ 400 nm). This suggests that the particle size distribution will have more of an effect on the extinction efficiency and resonance peak positions as the particles get larger (> 50 nm diameter for silver), where multipolar resonances start to occur. When multipolar effects occur (quadrupole, octupole, etc.) the nanoparticles will start to forward scatter [87], which can be used to trap light in solar cells, improving the efficiency [79].

In this section, we have shown that the particle size distribution can be approximated with the use of a log normal distribution via experimental methods (STEM, Z-contrast imaging). We
previously verified the use of this method in Section 5.4.1, which also took into consideration the standard deviation of the average particle sizes.

![Histogram](A) ![Extinction Efficiency](B) ![Scanning Transmission Electron Microscopy](C)

**Figure 6.6 (top left)** A histogram of the effective radii of the Ag nanoparticles measured from a (bottom) Z-contrast scanning transmission electron microscopy example image of the nanoparticles. (top right) Shows how changes in the standard deviation affects the extinction efficiency of the particles, broadening and closing of the dipolar (shift) and quadrupolar resonance peaks for a 50 nm radius particle.

6.4. Multiple and Hybrid Coatings Results

In Section 6.1 applications, material configurations and structures were discussed and we introduced four different structures that we will consider in more depth. TiO$_2$ Anatase and SiO$_2$ would also be further investigated due to their common use in photovoltaic applications. In this section, we explore the implications of the different structures using this material system in different configurations.

We start by looking at specific examples, where we first fix the core particle size and look at the effects from increasing the coating size, then we look at the opposite, where we change the core particle size and fix the coating size. We will compare what happens in both cases before looking at 3-D analysis (varying both core particle and coating sizes) by looking at the plasmon resonance peak position and extinction (scattering and absorption) intensity.
Generally, as the overall size of the particles increases, the resonant peak position will red-shift (for particles < 50 nm, or dipole interactions only). We can use additional or hybrid coatings to control the resonant peak position. Figure 6.7 demonstrates the case where we have a fixed core size and increase the coating size. We explore the four different configurations (double, averaged, and linear and exponentially graded coatings, as shown in Figure 6.4). The results shown in Figure 6.7 have been calculated for silver nanoparticles with a radius of 25±1 nm radius, and coating sizes between 5 nm and 40 nm as shown in the legend. We note that, with a very thin coating (5 nm), the peak positions between the different types of coatings are similar (~ 470 - 480 nm). As the overall size of the nanoparticle increases, resulting from the introduction of additional layer(s), the resonant peak position red-shifts by varying amounts. For example, the double layered (Figure 6.7 (b)) coating has a plasmon peak position of ~ 470 nm for a 5 nm coating, which red-shifts to ~ 650 nm for a 40 nm coating. Whereas for the exponentially graded media (Figure 6.7 (d)), the peak starts at ~ 470 nm (5 nm coating) and shifts to only ~ 550 nm for a 40 nm coating. This is a substantial difference (100 nm) between the same materials, but different configurations.

From Figure 6.7 (b) and (c), it is apparent that the difference between having a linearly graded, and a double layered coating is very small, with the plasmon peak positions only ~30 nm apart for a 40 nm coating. However, we do note a reduction in the extinction efficiency for the double layered approach compared to the linear one (3.5 compared with 4).

Figure 6.7 (e) and (f) show what happens to the peak positions and to the extinction efficiency as the particle size increases, where all the methods follow the same patterns. As the particle size (coating) increases, the peak position also increases, and the extinction efficiency at the plasmon peak position decreases. The exponential method has the smallest change in the peak position, and suffers from a larger drop in the extinction efficiency as the particle size increases. The double coated method shows the largest change in the resonant peak position, and the second lowest extinction efficiency. Whereas the linearly graded method has a similar peak shift than the double coating method, but has the highest extinction efficiency as the particle sizes increase. Note that the line shape between the methods does not vary between methods.

The results for when the coating size is varied have been presented for a fixed size core silver particle (Figure 6.7). Figure 6.8 (a) – (f) demonstrates the effects of keeping a fixed coating size of 30 nm but varying the core silver particle size from (5±1 nm to 40±1 nm core radius). This would be representative of a practical case, where there will always be some variation in the size of the nanoparticles [130]. It is apparent that the results for the four configurations in this case are substantially different, and the predictable patterns observed in Figure 6.7 no longer hold true.
Figure 6.7 Ag Nanoparticle core with 25 nm radius and varying the size of the coating layer, which is the TiO$_2$:SiO$_2$ graded material we are investigating. The thickness of the coating is varied from 5 nm to 40 nm in steps of 5 nm. (a) – (d) the Extinction Efficiency over wavelength, which demonstrates the plasmon resonance peak between 450 nm and 650 nm for the (a) Averaged Coating, (b) Double Coating, (c) Linearly Graded and (d) Exponentially Graded. The resulting peak positions and intensities for each thickness are shown in (e) and (f) respectively. In all the configuration, except the exponentially graded case, there is an apparent red shift of > 100 nm. Also, as the coating size increases, the peak intensity of the extinction reduces.
Firstly, the plasmon peak position for the 5 nm core particle radius is different for each configuration. This is because the coating size is 30 nm, where the plasmon peak has shifted by different amounts in each configuration (see Figure 6.7 for more details). Secondly, we observe that, as the overall size of the particles increases, the resonant peak position blue-shifts first before the expected red-shifting. This is unusual and we will investigate the probable causes here.

Interestingly, the arithmetically-averaged configuration never exhibits this behaviour and red-shifts in all cases. This would suggest that this phenomenon is due to having more than one coating – or in the case of linearly and graded coatings, the variation in the optical properties within the layer.

The arithmetically-averaged configuration of the layer leads to a total red shift of ~ 100 nm (Figure 6.8 (e) and Figure 6.7 (e)), which is comparable to what was found when fixing the core particle size and changing the coating size (Figure 6.7). Although, where in Figure 6.7 (f) the extinction efficiency decreases as the particle size increases, in Figure 6.8 (f) we see that, as the core particle size increases, the extinction efficiency does too, saturating towards larger particles sizes (> 100 nm diameter, where multipolar effects come into action).

The situation that exhibited the largest blue-shift in the peak position is the exponentially graded configuration (Figure 6.8 (c)), which starts at ~ 510 nm resonant peak position for a 5 nm radius core particle size, and shifts to ~ 470 nm for a particle with a 15 nm radius, before red-shifting to ~ 540 nm with a 40 nm core particle radius. This effect has been previously observed experimentally by Peng et al. [173] in much smaller particles with small functional coatings. They observed that, as the core particle size increased from 1 – 12 nm diameter, the functional coating (OAm - oleylamine) caused the resonant peak position to shift from 440 nm to ~400 nm before red-shifting with increasing particle size. During their theoretical calculations, they were able to simulate the blue-shift by using a Drude model [173] but by assuming a lower electron density at the surface of the Ag nanoparticle. They were unable to correctly reproduce the red-shift after the blue-shift as the particle size increase. This does, however, imply that adding a third material into the system is the cause of the blue shift, which means that this would never occur if the coating is treated as a single/averaged coating system.

In both the linearly graded and double coated examples, we find that the blue-shift seen in the exponentially graded layer does occur, but by a smaller amount (~ 20 nm instead of 40 nm in the exponential case).
A constant coating thickness of 30 nm. The thickness of the core particle size is varied from 5 nm to 40 nm in steps of 5 nm. (a) – (d) the Extinction Efficiency over wavelength, which demonstrates the plasmon resonance peak between 450 nm and 650 nm for the (a) Averaged Coating, (b) Double Coating, (c) Linearly Graded and (d) Exponentially Graded. The resulting peak positions and intensities for each thickness are shown in (e) and (f) respectively. In this case, with the increasing core particle size, we observe a blue-shift in the plasmon resonance in all the configurations, except for the averaged case. This effect is most pronounced in the exponentially graded case, where a blue-shift of ~20 nm has occurred.
There are subtle differences in the line shape as the total particle sizes increase above 100 nm, when multipolar effects start to appear, where the averaged method seems to show more defined peaks compared to that of the double layered approach. This suggests that, as we add additional layers, the contribution from the multipolar peaks will decrease. The extinction efficiency between the different methods follows the same pattern at the same particle sizes, where it saturates towards larger particle sizes (multipolar effects, > 100 nm total particle size).

To investigate this phenomenon further, to understand the extent of the plasmon resonance shift with each of the material configurations, we adapted the model to create colour maps of the peak positions (Figure 6.9 and Figure 6.10), when we change both the size of the core radius and the coating layer thickness. The model simulates iteratively through the range of possible combinations of core and shell thicknesses. An algorithm to fit the final extinction efficiency spectra and find the dipole resonance peak position is utilised, which outputs in a format that can be displayed as an interpolated colour map. Figure 6.9 (a) – (d) show the resonant peak positions (z-axis) when varying the core radius (y-axis) and the shell thickness (x-axis) for silver core particles with a TiO$_2$ to SiO$_2$ coating. Figure 6.10 (a) – (d) shows the same parameters as Figure 6.9, but with a reversed order for the coating materials (SiO$_2$ to TiO$_2$ Anatase). This allows us to compare multiple configurations together and visually display the configurations where the blue-shift effect can be seen.

We would expect that the arithmetically-averaged configuration would not give different results when reversing the order of the materials due to the way that it is calculated ($\frac{(n_1 + n_2)}{2}$). All the others we would expect to see differences in the resonant peak positions between methods.
Figure 6.9 The peak extinction (dipole) efficiency wavelength (colour bar) for Ag NPs with TiO$_2$ Anatase and SiO$_2$ coatings in different configurations (averaged (a), double (b), exponentially graded (c), and linear (d), see Figure 6.3 in Section 6.1 for more details of the configurations). In the double, exponentially and linearly graded examples (b)-(d) the TiO$_2$ Anatase is closest to the core particle and the SiO$_2$ closest to the surface of the outer-shell (Ag@TiO$_2$:SiO$_2$). The core radius size represents the size of the central Ag NP radius and the shell radius represents the total radius of all the sub-layers making up the coating around the Ag NP (TiO$_2$:SiO$_2$). In the double, exponentially and linearly graded case (b)-(d), a blue shift is apparent with increasing core particle size, which is not apparent in the averaged case (a).

As we have seen in the previous results (Figure 6.7 and Figure 6.8) both the Linear configuration and the Double layered approach exhibit very similar patterns (Figure 6.9 (b) and Figure 6.10 (b) for double layered, and Figure 6.9 (d) and Figure 6.10 (d) for linear), where the minimum resonance peak position (< 370 nm for double layered and ~380 nm for linearly graded) is found with a 5 nm core particle size with 25 nm coating (SiO$_2$ → TiO$_2$), which is at the limit of our simulation range in this case. The highest peak position (> 580 nm for double layered and > 600 for linearly graded) is found in the same place with the materials switched (TiO$_2$ → SiO$_2$). It is therefore apparent that the double layer and linearly-graded shell configurations around a silver core particle are not that different to each other. The similarities between the two, which can be seen in (Figure 6.4 (a)) are that the mid-point within the layer
will have the same refractive index. The primary difference is that the change in the optical properties at each of the sub-layer boundaries in the linearly graded method is very small compared to the big change in the middle of the layer for the double layered method. This could account for the changes in extinction efficiency, where we observe more loss overall in the double layered configuration than in the linearly-graded one.

Figure 6.10 The peak extinction (dipole) efficiency wavelength (colour bar) for Ag NPs with TiO$_2$ Anatase and SiO$_2$ coatings in different configurations (averaged (a), double (b), exponentially graded (c), and linear (d), see Figure 6.3 in Section 6.1 for more details of the configurations). In the double, exponentially and linearly graded examples (b)-(d) the SiO$_2$ is closest to the core particle and the TiO$_2$ Anatase closest to the surface of the outer-shell (Ag@SiO$_2$:TiO$_2$). The core radius size represents the size of the central Ag NP radius and the shell radius represents the total radius of all the sub-layers making up the coating (SiO$_2$:TiO$_2$) around the Ag NP. In all cases, in comparison to Figure 6.9 (TiO$_2$:SiO$_2$), there is no apparent blue-shift with increasing core particle size, as would be the expected behaviour in plasmonic nanoparticles.

In contrast to all the other methods, the exponentially graded method demonstrates a strong blue-shift of the resonant peak position in the TiO$_2$ → SiO$_2$ materials configuration as the core particle size increases, which agrees with previous results (Figure 6.8 (c)). This effect does not appear in the case of SiO$_2$ → TiO$_2$, which suggests that it is also dependent on the material configuration, and the way that it changes at each boundary. It would also suggest that, the larger the difference in the complex refractive index is between the materials used in the
coated layer, the more the peak will blue-shift in this configuration. This agrees with the observations of Peng et al. [173], where our model is capable of explaining both the initial blue-shift, and then the following red-shift; as the particle size increases.

Figure 6.11 (a – inset) The points that have been plot in (a – main), which have been taken from Figure 6.9 (c), demonstrating the blue shift seen with a 25 nm coating and varying core particle size. (b) The refractive index change throughout the 25 nm layer, where all methods start and end with the same refractive index, with the exception of the averages treatment. (c) The extinction efficiency, which corresponds to the peak intensity at the positions given in (a – inset). In this exponentially graded case, we can see the extent of the blue-shift (< 30 nm) as the particle size increases, for a particle coating size of 25 nm.

The peak intensities (extinction efficiencies), shown in Figure 6.11 (c), for any of the four configurations follow the same pattern, within the range of interest. As the core particle size increases, the extinction efficiency also increases, whereas as the shell increases, the extinction efficiency decreases. With the same total particle size, it is possible to achieve both the minimum and maximum extinction efficiencies. The point where the extinction efficiency is minimum (5 nm core radius and 25 nm coating layer) is also the same place where we have seen the lowest and highest resonant peak positions for the double and linear methods.
In organic photovoltaics (OPVs), the layers of the device are very small (10 - 200 nm) and for this reason we need to keep the total nanoparticle size well below the device thickness. Another useful property for photovoltaic applications is the ability to tune the resonant peak position. Different active material blends absorb in different parts of the solar spectrum, hence, to further improve the efficiency, plasmon resonance tuning can be utilised. The resonance should be tuned to the parts of the spectrum where there is room for the most improvement. This can then lead to improved device efficiencies through light scattering, improved transport properties, increased charge dissociation and/or charge mobility’s. We have shown how this model can be used to design bespoke nanoparticles for specific applications such as OPV.

6.5. Summary

In Chapter 5, an all-inclusive plasmonic model was demonstrated, capable of simulating particle distributions and multiple layers in absorbing surrounding media. In this chapter, we applied the model to investigate different material configurations (Averaged, Double, Linear and Exponential) where we demonstrated the tunability of the plasmon resonance and how we can use the model as a tool for tunability. The can be further utilised to optimise existing structures, or even reverse engineer to find coating thicknesses etc. depending on the application.

We chose to study the material system consisting of Ag (core) and TiO$_2$ Anatase/SiO$_2$ coatings in different configurations. In a specific configuration, namely exponentially-graded with TiO$_2$ closest to the core material, a blue-shift was apparent when the particle size increased. This has been previously seen in much smaller particles (< 10 nm) [31] experimentally. However, we have shown that, under relatively strict conditions for particle and coating size distributions, this can also occur in much larger nanoparticles (> 30 nm). Interestingly, this was most pronounced in the exponentially-graded configuration, and both Linear and Double layered demonstrated the same effect to a smaller degree. This did not, however, appear in the Averaged layer case, which leads us to believe that this only occurs due to the introduction of a third material with different optical properties. We showed that reversing the conditions also did not replicate the blue-shift (SiO$_2$ closest to the core), which suggests that it is very sensitive the change in the refractive index between each stage of the particle (core/shell/atmosphere).

With the same material system, we demonstrated that depending on the configuration, coating size, and core particle size, we can tune the particle resonance over a large range ( > 200 nm), from < 370 nm in a double layered configuration, and > 600 nm in the linearly graded configuration. This coincidently covers most of the visible spectrum (400 - 700 nm), making it an exceptional candidate for solar cell applications, and other wavelength dependent applications.
Chapter 7

7. Conclusions and Future Work

7.1. Conclusions

This work has been focused on developing physical models as a basis to enable optical simulation of complete Organic Solar Cell (OSC) devices including nanoparticles. In the literature review (Chapter 2) we discussed the implications of including nanoparticles in OSCs (Section 2.2.4), showing that on average you can obtain a +0.44% improvement (compared with +1.28% for DSSCs). To maximise the efficiency improvement, we look at how we can effectively model nanoparticles in OSCs, using the Transfer Matrix Method (TMM) for the modelling of multi-layered structures, and Mie Theory for the simulation of nanoparticles. Chapter 3 described the optical model developed, based on the TMM. The TMM calculates the reflection and transmission at each boundary, and the absorption through coherent, partially coherent, and incoherent layers. The model that was presented in Chapter 3 is extremely flexible, allowing N number of layers, with any optical properties. This would allow for the simulation of more complex systems, such as binary and ternary OSCs. One of the main advantages of using this method, over other methods such as the Finite-Different Time-Domain (FDTD) method is that it is an analytical solution. This leads to reduced computing resource requirements, which enables many simulations to be ran in a short space of time. One use for such a simulation is device optimisation, which we have demonstrated in Chapter 4 to design semi-transparent OSCs with specific colours, for decorative window applications.

The optical model (Chapter 3) can simulate a multi-layered stack of complex materials, with independent interface and surface roughness, over a range of wavelengths and incident angles. Some of the outputs of the model are the absorption, transmission and reflection spectra, which can be directly compared to UV-Vis spectra. Comparisons between experimental and modelling results have been presented in Chapter 3, where we verified the accuracy of the model. This lead to us being able to predict UV-Vis results from fabricated semi-transparent OSCs (Chapter 4). Other outputs included: electric and magnetic field maps, power dissipation, exciton generation rates, and residual absorption plots, which have all played a role in understanding optical optimisation in OSCs.

To completely verify the model, a comparison was made between an experimental device based on a PCDTBT:PC_{70}BM active layer and the simulation. AFM results were used to obtain the layer thicknesses and surface roughness parameters, and the optical properties for each
Conclusions

of the materials were obtained from the literature (Appendix E). The simulation results agreed well with the experimental results, where we put the differences in the spectra down to differences in the optical properties between the literature and the materials used for the experimental device; as can be seen in Appendix E, there are large differences in the $n$ and $k$ values between authors for the same material system. One way to overcome these differences is to obtain the optical properties of the materials that have been specifically used using a method such as Ellipsometry. However, for an approximation of the resulting spectra, the model is demonstrably accurate.

Chapter 4 was focused on demonstrating the use of the model in the optimisation of OSCs, including a study on the optimal active layer thickness of a P3HT:ICBA based device. The total power dissipation within the active layer is subject to the interference between the incident light and the reflections from the interfaces and top contact. This leads to both constructive and destructive interferences, and when you plot the total power dissipation over device thickness it reveals peaks where the constructive interference within the active layer is at its maximum. In this case the optimal layer thickness was found to be between 220 nm and 230 nm, which was demonstrated by a peak Power Conversion Efficiency (PCE) by Kutsarov et al. [58], for their large area devices.

When the size of the layers is smaller than the wavelength of light, phase (and therefore coherent interference) effects play an important role. Optimal OSCs have layer thicknesses that maximise the constructive interference in the active layer; where it can be converted to excitons. As you change the Electron Transport Layer (ETL) thickness, the spacing between the active layer and the top contact changes. This affects the total absorption within the active layer. Chapter 4 provided a study on this so-called optical spacing effects using a PTB7:PCBM active layer with a TiO$_2$ ETL. It was demonstrated that optical spacing effects appear to have the biggest effect in thinner active layers. This is because of there is a higher proportion of the incident light reflected into the active layer from the top contact. However, the optimal ETL thicknesses in this case were between 100 nm and 200 nm (Chapter 4, and Appendix H). In OSCs, interfacial layers are there to match energy levels, and aid in the charge collection process, and thicknesses in the order of 100 nm are almost never used, especially in high performing devices. A relationship was also drawn between the separation between the start of the active layer and the start of the contact, which consistently appeared to be 200 nm at the optimal point.

Chapter 4 also demonstrated how an approximate colour of the devices can be calculated from apparent optical spectra. This approximation was compared to an experimental device, where it was found that the colour can be obtained from optical spectra. This was then utilised within the simulation and optimisation process, where a preferred colour can be defined.
During this work, it was found that material shadowing effects can occur in the case that an absorbing material is used as the Hole Transport Layer, in standard configuration (ETL in inverted configuration). This was visible over some wavelengths where the overall absorption in the active layer decreased in the ultra-violet/violet region, when using specific materials (for example, TiO$_2$, and MoO$_3$, Chapter 4).

In Chapter 4, two study cases were presented. The first utilised a PBDTTT-C-T active layer, with a Ag/ITO contact, where the ITO functions as an index matching material between the Ag and Air, reducing the reflection from the contact. The input parameters included: the material configuration; target transmissivity (30 – 40%); target colour (green); and highest power dissipation possible within the active layer. The second concentrated on a PCDTBT:PCBM active layer. The input parameters included: material configuration, target transmissivity value (40 - 50%), target colour (red), and highest power dissipation possible within the active layer. In both cases, the target parameters worked, where the first provided a ‘green’ colour, with a peak in the transmission around 540 nm. The second has a transmission peak above 600 nm. In both cases a 10 nm thick layer of Ag was found to be optimal, providing good transmissivity and highest power dissipation within the active layer.

An investigation into how the colour, and the transmission, reflection, and absorption, are affected by change in incident angle was conducted. The absorption is at its maximum, and reflection at its minimum, when the light is normal to the surface of the device. The opposite case is found when the light approaches 90° from a normal; as would be expected. What was particularly interesting, is the absorption within the device between 0° and 70° remains relatively unchanged (~40% → ~34%). This demonstrates that the performance of the devices will remain consistent over a wide range of incident angles. It was also found that the colour of the devices remains unchanged throughout.

The information provided from the studies on the optimisation of semi-transparent device fed directly into the experimental work. A device utilising a PCDTBT:PCBM active layer, and a ultra-thin Ag top contact (~10 nm) was fabricated (Chapter 4). The biggest challenge associated with the device fabrication was obtaining a uniform layer of Ag (~10 nm). A device with an average of 20% transmissivity, utilising the ultra-thin Ag contact, was fabricated. This device showed a PCE of 4.46%, where a lower fill-factor and short-circuit currents were expected due to the thin Ag layer as the top-contact. However, the thickness of the Ag in this case was ~23 nm, which was made to be thicker to obtain a uniform coating. Further development of fabrication of thin-film Ag needs to be conducted before realising a uniform 10 nm thick contact, which was found to be optimal from the device modelling studies presented in Chapter 4. Once the fabrication techniques have been developed further, it would be possible to fully realise the devices simulated in Chapter 4.
One method to further improve device performance; from short-circuit current to targeted optical absorption within the active layer, is to add plasmonic nanoparticles into the device. One of the drawbacks of including metallic nanoparticles into OSCs is the increased non-radiative recombination at the surface. For this reason, coatings (usually metal oxides) are used, which insulate the metallic nanoparticles from the excitons, which in turn drastically reduces exciton quenching [79]. This was the inspiration leading to the plasmonic model developed in Chapter 5.

The plasmonic model was based on Mie theory, and took into consideration: particle size distributions; absorbing surrounding media; and multiple and graded coatings. In the literature, only a single layer coating had been previously considered by authors. In Chapter 5 a recursive method was implemented to allow the boundary conditions to be extended to include N number of coatings around the nanoparticles. This allowed the simulation of multiple and graded coatings, such as that demonstrated in Chapter 6. The simulation was also optimised to use as much computing resource as it needed to run the simulation; this was based on optimising some of the parameters (such as the logarithmic derivative – Appendix B), and using the size-parameter to estimate the maximum number of iterations needed to obtain an accurate answer. This opened the door to other types of simulation, with data points requiring different geometries; such as the investigations shown in Chapter 6.

To verify the recursive elements of the model work, the results from the simulation have been directly compared to experimental results from literature. What was evident from this type of flexible modelling is the number of different application areas (plasmon resonance tuning; cancer treatments; and contrasting agents, to name a few). An example of this was provided in Chapter 5, where a nanoparticle system, aimed at cancer drug deliver, was simulated; providing the same plasmon resonance peak positions as the authors provided in their paper [176]. This was using standard refractive indices for the materials found within literature, and/or suppliers, such as Sigma Aldrich etc.

An interesting example, that would be difficult to simulate using FDTD or FEM methods, is the idea of having hybrid material systems, where two or more materials are mixed together to form one coating. In the case presented in Chapter 6, it was discussed that the distribution of the materials within such a hybrid system may change depending on the fabrication processes. This could create scenarios where the materials will be graded throughout a single layer. This was the basis of the study presented in Chapter 6, where a hybrid system of SiO$_2$ and TiO$_2$ around a Ag metallic core has been simulated. The different treatments (averaged, double layered, linearly graded, and exponentially graded) of the coating layer lead to different results for each method. The recursive method, dealing with graded coatings, was found to converge to an answer (Appendix F) with an increasing number of steps. This was attributed
to the interface reflections, where in a few-layered system with a large change in refractive index, would lead to higher reflection as each interface. Hence, the more layers that were simulated – minimising the change in refractive index at each interface – lead to increased accuracy of the result. The optimal number of sub-layers to simulate was found to be ~200, where no visible changes between 200 and 1000 sub-layers can be seen.

During this investigation, in the case of the exponentially coated scenario, as the nanoparticle size increases, a plasmonic resonance blue-shift can be seen (Chapter 6). Typically, a red-shift is seen with increasing nanoparticle size; due to retardation effects (Chapter 2) [86]. This was attributed to having the higher refractive index of the two (TiO₂) closest to the surface of the particle; as we did not see the same result in the other configuration. It was also suggested that the rate of change from TiO₂ → SiO₂ contributed to this; as the same phenomena was captures to a lesser degree in the double and linearly coated scenarios.

The result from the study of the hybrid coating using SiO₂ and TiO₂ demonstrates that the ability to tune the plasmon resonance is increased when you factor in the material configuration. An example would just be the presented results for double coated results, where a resonance peak of 370 nm and 580 nm can be achieved using the same materials. In the case of a 5 nm Ag particle with a layer of SiO₂ (10 nm) and a layer of TiO₂ (10 nm) can provide a resonance peak at ~370 nm, and just by switching the TiO₂ with the SiO₂, with the same sizes, a plasmon resonance peak of > 580 nm can be achieved.

This concludes the main results achieved throughout this work. We have demonstrated two tools: The first is capable of optically modelling a N-layered system of any materials, which has been developed into an efficient optimisation tool. The second is a model based on Mie theory capable of modelling N coatings around a core particle, with any non-magnetic materials, with particle size distributions also taken into considerations. Both models have been developed to simulate nanoparticles in OSCs, however, throughout the work we have also discussed other topical areas that the models can be applied to.

7.2. Future Work – Mie in the Transfer Matrix Method

The two models developed throughout the work (Chapter 3 and Chapter 5) have some common ground, which suggests that they can be combined to create a fully integrated plasmonic OSC model. Here we discuss our initial ideas and future work required to realise this.

Nanoparticles embedded into a layer of a device will change the optical properties of the layer. The absorption within the layer will increase; from the extinction of light induced by the
nanoparticles. This extinction can be translated into scattering and absorption of the incident light.

\[ S_1(\theta) = \sum_{n=1}^{\infty} \frac{2n + 1}{n(n + 1)} \left[ a_n \pi_n(\cos(\theta)) + b_n \tau_n(\cos(\theta)) \right] \]  \hspace{1cm} \text{Eq. 7.1}  

\[ S_2(\theta) = \sum_{n=1}^{\infty} \frac{2n + 1}{n(n + 1)} \left[ b_n \pi_n(\cos(\theta)) + a_n \tau_n(\cos(\theta)) \right] \]  \hspace{1cm} \text{Eq. 7.2}  

Using the Mie scattering parameters from Chapter 5 (\( S_1 \), Eq. 5.28 and \( S_2 \), Eq. 5.29), it is possible to calculate the scattered intensity (\( I(\theta) \), Eq. 5.31) at any angle (\( \theta \)) and distance (\( r \)) away from the particle (demonstrated in Figure 7.1). Where \( i_1(\theta) = |S_1(\theta)|^2 \) and \( i_2(\theta) = |S_2(\theta)|^2 \).

\[ I(\theta) = \frac{1}{2} \left( i_1(\theta) + i_2(\theta) \right) \frac{1}{k^2 r^2} I_0 \]  \hspace{1cm} \text{Eq. 7.3}  

**Figure 7.1** A schematic diagram of a point at the interface at an angle of \( \theta \) from the normal and distance (\( r \)) from the centre of the nanoparticle.

This would allow us to formulate the total scattered intensity at the interface from a scattered particle, and the average phase and angle of the scattering pattern. From this information, it would be possible to calculate the total transmission, reflection, and absorption at the two interfaces; as shown in Figure 7.2. This requires us to make some assumptions, such as anything scattered after the critical angle will be absorbed within the layer. Also, assuming a normal angle for the incident light, and equidistance between the particle and both the interfaces, and a symmetrical scattering pattern (dipolar), the equations and computational resource required for this would be dramatically reduced.

Working on the equations from the TMM at the interface (Chapter 3), we can then calculate the effective reflection, transmission and absorption of the layer (associated \( l_{jk} \) matrices and the \( L_j \) matrix, Chapter 3), assuming a partially coherent layer and including/relating the phase and angle distributions by adapting either the Fresnel method, or the random phase method; intended to incorporate surface roughness into the TMM (given in Chapter 3).
In both cases (TMM and Mie Model), they assume non-magnetic media. Accounting for the permeabilities of the materials would allow for more flexibility within the modelling, allowing the simulation of how magnetic and non-magnetic nano-materials interact.

**Figure 7.2 A schematic diagram showing the scattering (Blue) from a nanoparticle and demonstrating some of the paths the scattered intensities may take, where \( \theta_c \) is the critical angle for total internal reflection, T (Green) is the transmitted intensity, R (Purple) is the reflected intensity and A (Red) is the absorbed intensity.**

The optical model discussed in this section can be integrated with electrical models, where we produce a value for the spatially distributed exciton generation rate. It is understood that the inclusion of nanoparticles into OSCs would have a direct impact on the electrical performance of the devices, and to obtain a complete picture of all participating processes the electrical mechanisms should also be modelled alongside to obtain experimentally realistic results.

### 7.3. Future Work – Interparticle Interactions and Shapes

Improvements in the Mie model that we have demonstrated in Chapter 5 and Chapter 6, including interparticle interactions and accounting for non-spherical particles, can be useful in further understanding plasmonic effects (plasmon resonance tuning, growth mechanisms, etc.).

One method for accounting for these additions, would be the use of the T-Matrix method [196]. The T-Matrix method is an extension to the generalised Lorenz-Mie formulae, which we have implemented within this work (Chapter 5).

Clusters can be simulated by taking the summation over the superposition of all scattered fields, which can also be formulised into the T-Matrix to allow for arbitrarily shaped and sized particles, in random orientations [197]. Mackowski et al. [198], [199] have shown that this method can be used to effectively calculate the overall scattering for an ensemble of spheres.

Coupling this with the model described in Chapter 5, would make a powerful analysis tool, being able to simulate any combination of particles, including different shapes, coatings,
surrounding media, size distributions, agglomerates, aggregates, and particle number densities. This would have many applications ranging from particle synthesis mechanics and plasmon resonance tuning, to MRI contrasting agents and drug delivery systems.

### 7.4. Future Work – Semi-Transparent Cells

In Chapter 4, we highlighted preliminary results from an experimental device that was created using a thin-film of Ag. The modelling work that we presented in the same chapter showed that a 10 nm Ag layer with a coating of ITO on top was the optimal scenario for higher efficiency semi-transparent solar cells. Therefore, more work and investigation into how a uniform, thin-film, of Ag (~10 nm) can be produced.

During the evaporation process, which was used to create the ultra-thin-film of Ag, small islands (aggregations) of Ag form, due to surface tension. One method that has been reported to alleviate this is the use of a nucleation/wetting layer [200],[161], which has shown to achieve ultra-thin silver films with a high uniformity. As the layer thickness decreases, and the layer becomes less uniform, defects occur causing the series resistance to increase (this is shown in experimental results from Chapter 4). The use of a thin PEI film can stop this from happening, where authors have shown that uniform films can be fabricated with a series resistance of $< 10 \, \Omega \, \text{m}^{-2}$ [161].

From our investigation in Chapter 4, we found that a layer of ITO on top of an ultra-thin layer of silver can act as an index matching material, and reduce the amount of reflection from the Ag/Air interface. It could also lead to better uniformity in the contact and reduced series resistance. More investigation into these methods and the results would be required to fully realise our optimised semi-transparent OSCs.

One thing that was highlighted in Section 3.5.2 (Random Phase Method for including surface roughness), is that it has no direct relation to the measured surface roughness and just assumes that it is a random process. By taking surface roughness measurements of the devices, with varying surface roughness, it would be possible to build a predictive model capable of adding a scaling factor to the stochastic process. This would in turn improve the approximation, and align the method with experimental results better.

The TMM also only currently considers the permittivity, and not the permeability. This limits the simulations to only non-magnetic materials. In some cases, magnetic materials may be used, and corrections to the model should be made to account for this.
Appendix A: List of Plasmonic OSC Efficiencies

Table 7.1. List of plasmonic enabled Organic Solar Cells (OSCs) including the active material that has been used, the nanostructure used, which layer it has been included in, the power conversion efficiencies (usually average of multiple devices) of their control device(s) and their result(s) after the inclusion of the nanostructures. The reference for each has been put in the last column.

<table>
<thead>
<tr>
<th>Active Material</th>
<th>Nanostructure</th>
<th>Inclusion Layer</th>
<th>Control PCE (%)</th>
<th>Result PCE (%)</th>
<th>Reference</th>
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<tr>
<td>P3HT:PCBM(^11)</td>
<td>Au NPs</td>
<td>PEDOT:PSS(^12) (HTL)</td>
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<td>4.07</td>
<td>[201]</td>
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<td>PEDOT:PSS (HTL)</td>
<td>7.25</td>
<td>8.16</td>
<td>[95]</td>
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<td>PEDOT:PSS (HTL)</td>
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<td>[129]</td>
</tr>
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<td>[129]</td>
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<td>PEDOT:PSS (HTL)</td>
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<td>3.19</td>
<td>[202]</td>
</tr>
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<td>Active</td>
<td>3.92</td>
<td>4.54</td>
<td>[213]</td>
</tr>
</tbody>
</table>

---

\(^{10}\) P3HT - Poly(3-hexylthiophene-2,5-diyl)
\(^{11}\) PC\(_{60}\)BM - [6,6]-Phenyl C\(_{60}\) butyric acid methyl ester
\(^{12}\) PEDOT:PSS – Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)
\(^{13}\) PTB7 - Poly[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]]
\(^{14}\) PCDTBT - Poly[N’-heptadecanoyl-2,7-carbazole-alt-5,5-(4’,7’-di-2-thienyl-2’,1’,3’-benzothiadiazole)],[Poly[[9-(1-octylvinyl)-9H-carbazole-2,7-diyl]-2.5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diy]-2,5-thiophenediyl]]
\(^{15}\) MEH-PPV - Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]
\(^{16}\) PBTTT-C-T - 2,6-Bis(trimethylvinyl)-4,8-bis(5-[2-(ethylhexyl)thiophen-2-yl]benzo[1,2-b :4,5-b']dithiophene]
\(^{17}\) PFSDCN - Poly[2,7-(9,9-dioctyfluorene)-alt-2,7-((4-(diphenylamino) phenyl)thiophen-2-yl)malononitrile]
\(^{18}\) P3OT - Poly[3-octyldithiophene-2,5-diyl]
\(^{19}\) Si-PCPDCTBT - Poly[2,1,3-benzothiadiazole-4,7-diyl][4,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4, 5-b']dithiophene-2,5-diyl]]
<table>
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<tr>
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<th>Device</th>
<th>V_{OC} (V)</th>
<th>JSC (mA/cm²)</th>
<th>Reference</th>
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<td>7.29</td>
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<td>5.87</td>
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<td>7.10</td>
<td>[223]</td>
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<td>2.06</td>
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<td>Ag NPS</td>
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<td>3.30</td>
<td>[224]</td>
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<tr>
<td>P3HT:PCBM</td>
<td>Ag NPs</td>
<td>Active</td>
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<tr>
<td>P3HT:PCBM</td>
<td>Ag NPs</td>
<td>MoO&lt;sub&gt;3&lt;/sub&gt; (ETL)</td>
<td>3.84</td>
<td>4.37</td>
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</tr>
<tr>
<td>PBDTTT-C-T:PCBM</td>
<td>Ag NPs</td>
<td>MoO&lt;sub&gt;3&lt;/sub&gt; (ETL)</td>
<td>7.15</td>
<td>7.94</td>
<td>[57]</td>
</tr>
<tr>
<td>P3HT:PCBM</td>
<td>Ag NPs</td>
<td>PEDOT:PSS (HTL)/Active</td>
<td>0.54</td>
<td>1.40</td>
<td>[226]</td>
</tr>
<tr>
<td>P3HT:PCBM</td>
<td>Ag@SiO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;27&lt;/sup&gt; NPs</td>
<td>PEDOT:PSS (HTL)</td>
<td>2.81</td>
<td>3.35</td>
<td>[113]</td>
</tr>
<tr>
<td>PTB7:PCBM</td>
<td>Ag@SiO&lt;sub&gt;2&lt;/sub&gt; NPs</td>
<td>Active</td>
<td>7.26</td>
<td>8.49</td>
<td>[50]</td>
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<td>PTB7:PCBM</td>
<td>Ag@SiO&lt;sub&gt;2&lt;/sub&gt; NPs</td>
<td>PEDOT:PSS (HTL)</td>
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<td>7.98</td>
<td>[50]</td>
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<td>P3HT:PCBM</td>
<td>Au@SiO&lt;sub&gt;2&lt;/sub&gt; NPs</td>
<td>HTL/Active</td>
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<td>3.80</td>
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<td>2.69</td>
<td>[94]</td>
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<tr>
<td>P3HT:PCBM</td>
<td>Au-GO</td>
<td>PEDOT:PSS (HTL)</td>
<td>3.27</td>
<td>3.55</td>
<td>[227]</td>
</tr>
</tbody>
</table>

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<sup>20</sup> IC<sub>xx</sub>BA – Indene C<sub>xx</sub> Bis Adduct
<sup>21</sup> MoO<sub>3</sub> – Molybdenum Trioxide
<sup>22</sup> CsCO<sub>3</sub> – Cesium Carbonate
<sup>23</sup> TiO<sub>2</sub> – Titanium dioxide
<sup>24</sup> ZnO – Zinc oxide
<sup>25</sup> PEDOT - Poly(3,4-ethylenedioxythiophene)
<sup>26</sup> ITO – Indium tin oxide
<sup>27</sup> SiO<sub>2</sub> – Silicon dioxide
<table>
<thead>
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<th>Composite</th>
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<th>Details</th>
<th>J. No.</th>
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<td>Au-GO</td>
<td>GO&lt;sup&gt;28&lt;/sup&gt; (HTL)</td>
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</tr>
<tr>
<td>P3HT:PCBM</td>
<td>Au-GO</td>
<td>GO (HTL)</td>
<td>3.26 3.98 [228]</td>
</tr>
<tr>
<td>P3HT:PCBM</td>
<td>Au@P3HT NPs</td>
<td>Active</td>
<td>2.66 3.65 [79]</td>
</tr>
<tr>
<td>P3HT:ICBA</td>
<td>Au@P3HT NPs</td>
<td>Active</td>
<td>5.79 7.16 [79]</td>
</tr>
<tr>
<td>PTB7:PC&lt;sub&gt;71&lt;/sub&gt;BM</td>
<td>Au@Ag@SiO&lt;sub&gt;2&lt;/sub&gt; Nanocubes</td>
<td>PEDOT:PSS (HTL)</td>
<td>7.72 8.84 [92]</td>
</tr>
<tr>
<td>PTB7:PC&lt;sub&gt;71&lt;/sub&gt;BM</td>
<td>Au@Ag@SiO&lt;sub&gt;2&lt;/sub&gt; Nanocubes</td>
<td>Active</td>
<td>7.72 9.48 [92]</td>
</tr>
<tr>
<td>PCDTBT:PCBM</td>
<td>Au@Ag Nanocubes</td>
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<td>7.78 8.74 [129]</td>
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<td>3.10 4.03 [117]</td>
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<tr>
<td>P3HT:PCBM</td>
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<td>Active</td>
<td>3.10 3.30 [117]</td>
</tr>
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<td>Ag Nanoprisms</td>
<td>Active</td>
<td>3.60 4.07 [229]</td>
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<tr>
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<td>Active</td>
<td>3.50 4.40 [230]</td>
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<tr>
<td>PCPDTBT&lt;sup&gt;29&lt;/sup&gt;:PCBM</td>
<td>Au@SiO&lt;sub&gt;2&lt;/sub&gt; Nanorods</td>
<td>Active</td>
<td>3.17 3.58 [230]</td>
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<td>P3HT:ICBA</td>
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<td>MoO&lt;sub&gt;3&lt;/sub&gt; (ETL)</td>
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<td>PEDOT:PSS (HTL)</td>
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<td>Ag Nanoplates</td>
<td>PEDOT:PSS (HTL)</td>
<td>6.10 6.40 [231]</td>
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<td>Active</td>
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<td>Al NPs</td>
<td>Active</td>
<td>5.33 5.84 [214]</td>
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<td>PCDTBT:PCBM</td>
<td>Al NPs</td>
<td>Active</td>
<td>5.48 6.00 [232]</td>
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<td>Active</td>
<td>3.16 4.09 [232]</td>
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<td>ITO</td>
<td>2.29 2.57 [233]</td>
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<td>Ag NPs and Nanoprisms</td>
<td>Active</td>
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<td>Ag NPs and Au NPs</td>
<td>PEDOT:PSS (HTL)</td>
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<td>Au NPs and Nanorods</td>
<td>PEDOT:PSS (HTL)</td>
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<td>Active</td>
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<tr>
<td>PCDTBT:PCBM</td>
<td>Au-Al NPs</td>
<td>Active</td>
<td>5.33 6.12 [214]</td>
</tr>
</tbody>
</table>

<sup>28</sup> GO – Graphene oxide
<sup>29</sup> PCPDTBT - Poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta [2,1-b;3,4-b’]dithiophene)-alt-4,7(2,1,3-benzothiadiazole)]
Table 7.2. List of plasmonic enabled Dye-Sensitised Solar Cells (DSSCs) including the active material, or in this case dye, that has been used, the nanostructure used, which layer it has been included in, the power conversion efficiencies (usually average of multiple devices) of their control device(s) and their result(s) after the inclusion of the nanostructures. The reference for each has been put in the last column.

<table>
<thead>
<tr>
<th>Active Material</th>
<th>Nanostructure</th>
<th>Inclusion Layer</th>
<th>Control PCE (%)</th>
<th>Result PCE (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z-907&lt;sup&gt;30&lt;/sup&gt;</td>
<td>2D Ag Nanodomes</td>
<td>Contact</td>
<td>3.15</td>
<td>3.87</td>
<td>[234]</td>
</tr>
<tr>
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<td>MP&lt;sup&gt;31&lt;/sup&gt;-TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.20</td>
<td>2.20</td>
<td>[192]</td>
</tr>
<tr>
<td>N3&lt;sup&gt;32&lt;/sup&gt; Dye</td>
<td>Ag@TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>MP-TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>3.10</td>
<td>4.40</td>
<td>[193]</td>
</tr>
<tr>
<td>N3 Dye</td>
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<td>MP-TiO&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>9.00</td>
<td>[193]</td>
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<tr>
<td>N-719&lt;sup&gt;33&lt;/sup&gt;</td>
<td>Ag and TiO&lt;sub&gt;2&lt;/sub&gt; Nanostructures</td>
<td>MP-TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>7.10</td>
<td>8.90</td>
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<td>5.97</td>
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<td>MP-TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>5.97</td>
<td>7.20</td>
<td>[236]</td>
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<tr>
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<td>Au@TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>MP-TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>5.97</td>
<td>7.08</td>
<td>[236]</td>
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<td>5.60</td>
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<td>2.28</td>
<td>[239]</td>
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<td>Electrolyte</td>
<td>2.81</td>
<td>3.52</td>
<td>[91]</td>
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<td>Electrolyte</td>
<td>2.81</td>
<td>4.02</td>
<td>[91]</td>
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<td>Electrolyte</td>
<td>2.81</td>
<td>5.52</td>
<td>[91]</td>
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<td>Ru-Dye</td>
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<td>5.33</td>
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<td>6.00</td>
<td>7.28</td>
<td>[81]</td>
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<td>MP-TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>6.00</td>
<td>7.38</td>
<td>[81]</td>
</tr>
</tbody>
</table>

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30 Z-907 - cis-Bis(isothiocyanato)(2, 2’ - bipyridyl - 4, 4’ - dicarboxylato)(4, 4’ - di - nonyl - 2’ - bipyridyl) ruthenium(II)
31 MP – Mesoporous
32 N3 - Ru(4,4’-dicarboxy-2,2’-bipyridine)2(NCS)2
33 N-719 – Di - tetrabutlammonium cis - bis(isothiocyanato)bis(2, 2’ – bipyridyl - 4, 4’ - dicarboxylato) ruthenium(II)
34 Ag<sub>2</sub>S – Silver sulphide
Appendix B: Logarithmic Derivatives and MATLAB

This appendix demonstrates how we have adapted the logarithmic derivatives to be able to efficiently calculate the parameters using Matlab.

To efficiently simulate and calculate some of the required functions for the Mie theory calculations, non-standard forms of some of the equations were developed. We have used Stratton's Electromagnetic Theory for the recurrence relations and functions [82]. Eq. B.1 is the first of two logarithmic derivatives \( X_n \) and \( Y_n \) that have been used in the model, where \( \psi_n(x) = xj_n(x) \), which leads us to the form of the equation given in Eq. B.2.

\[
X_n(z) = \frac{\psi'_n(z)}{\psi_n(z)} \tag{B.1}
\]
\[
X_n(z) = \frac{d}{dz} \left( \frac{zj_n(z)}{zj_n(z)} \right) \tag{B.2}
\]

Recursion is a relationship between the terms that allow the calculation using previous (or future terms in the series. Recursion in one direction maybe stable, however, in the other direction it could be unstable and diverge away from the answer [89]. This generally depends on the initial conditions, in the case of Mie parameters upwards recursion is found to be unstable, and hence the downwards recursion form for the derivative (Eq. B.3) is generally used [242].

\[
\frac{d}{dz} zj_n(z) = zj_{n-1}(z) - nj_n(z) \tag{B.3}
\]

The relation between the spherical Bessel function of the first kind and the Bessel function of the first kind is given in Eq. B.4 [82]. This relation holds true for spherical Bessel functions of the first \( j_n \) and second kind \( y_n \), and for spherical Hankel \( h_n^{(1)} \).

\[
j_n = \sqrt{\frac{\pi}{2z}}j_{n+0.5}(z) \tag{B.4}
\]

This allows the logarithmic derivative \( X_n \), Eq. B.5) to be represented in terms of standard Bessel functions (Eq. B.6). Matlab has pre-built stable functions capable of calculating the standard Bessel functions \( j_n \) and \( y_n \), which is the reason behind converting the equations and simplifying.
\[ X_n(z) = \frac{z j_{n-1}(z) - n j_n(z)}{z j_n(z)} \quad (B.5) \]

\[ = \frac{z \sqrt{\frac{\pi}{2z}} I_{n-0.5}(z) - n \sqrt{\frac{\pi}{2z}} I_{n+0.5}(z)}{z \sqrt{\frac{\pi}{2z}} I_{n+0.5}(z)} \quad (B.6) \]

To make the calculations more efficient, we simplify the logarithmic derivative shown in Eq. B.6 and obtain the form shown in Eq. B.7.

\[ X_n(z) = \frac{I_{n-0.5}(z) - (\frac{n}{z}) I_{n+0.5}(z)}{I_{n+0.5}(z)} \quad (B.7) \]

To reduce the number of calculations needed for the solution, we can group the like terms (Eq. B.8), which are also used in calculating the second logarithmic derivative (\( Y_n \)). This simplifies the equation further (Eq. B.9).

\[ A = \frac{n}{z}, \quad B = I_{n+0.5}(z) \quad (B.8) \]

\[ X_n(z) = \frac{I_{n-0.5}(z) - AB}{B} \quad (B.9) \]

This concludes the first of two logarithmic derivatives, the second utilises Hankel functions of the first kind (\( h_n^{(1)} \)), and requires a bit more simplification than \( X_n \) (Eq. B.1). The second logarithmic derivative is given in Eq. B.10, which is in the same form as the first, however using the Ricatti-Bessel function \( \zeta_n \) (Eq. B.11) instead.

\[ Y_n(z) = \frac{d}{dz} \frac{\zeta_n(z)}{\zeta_n(z)} \quad (B.10) \]

\[ \zeta_n(z) = z h_n^{(1)}(z) \quad (B.11) \]

The conversion between the Hankel function and the spherical Bessel functions is given in Eq. B.16.

\[ h_n^{(1)}(z) = j_n(z) + iy_n(z) \quad (B.12) \]

Using the relationships that we previously used for the first logarithmic derivative, applied also to the Bessel function of the second kind (\( y_n \)) we obtain the downwards recursion form of the derivative (Eq. B.13 – Eq. B.16).
\[
\frac{d}{dz} h_n^{(1)}(z) = z h_{n-1}^{(1)}(z) - n h_n^{(1)}(z) \tag{B.13}
\]

\[
\frac{d}{dz} z h_n^{(1)}(z) = z(j_{n-1}(z) + i y_{n-1}(z)) - n(j_n(z) + i y_n(z)) \tag{B.14}
\]

\[
= z \left( \frac{\pi}{2z} (j_{n-0.5}(z) + i y_{n-0.5}(z)) \right) - n \left( \frac{\pi}{2z} (j_{n+0.5}(z) + i y_{n+0.5}(z)) \right) \tag{B.15}
\]

\[
= \frac{\pi z}{2} \left[ (j_{n-0.5}(z) + i y_{n-0.5}(z)) - \left( \frac{n}{z} \right) (j_{n+0.5}(z) + i y_{n+0.5}(z)) \right] \tag{B.16}
\]

The logarithmic derivative \( Y_n \) can then be expressed in terms of standard Bessel functions (Eq. B.17).

\[
Y_n(z) = \frac{\sqrt{\pi z}}{2} \left[ (j_{n-0.5}(z) + i y_{n-0.5}(z)) - \left( \frac{n}{z} \right) (j_{n+0.5}(z) + i y_{n+0.5}(z)) \right] \tag{B.17}
\]

With an additional term for the simplification (B.18), and using the previously defined terms from Eq. B.8, the equation simplifies to Eq. B.19, where the number of required computations have been cut significantly.

\[
C = y_{n+0.5}(z) \tag{B.18}
\]

\[
Y_n(z) = \frac{(j_{n-0.5}(z) + i y_{n-0.5}(z)) - A(B + i C)}{B + i C} \tag{B.19}
\]
Appendix C: Snell’s Law

The angle of refraction with reference to the atmospheric conditions, first described by Pettersson et al. [19], which has been referenced and used by other authors [35], [97], is based on Snell’s law. The solution that is given in the paper incorrectly described the angle of refraction, here we re-derive and obtain the correct equation that has been implemented within our model.

From Snell’s law (Eq. C.1.), we can specify that the difference in angles is equal to the difference in the refractive indices, which we can rearrange to give Eq. C.2.

\[
\frac{\sin(\theta_1)}{\sin(\theta_2)} = \frac{n_2}{n_1} \quad \text{(C.1)}
\]

\[n_1 \sin(\theta_1) = n_2 \sin(\theta_2) \quad \text{(C.2)}\]

Using the trigonometric identity \(\sin^2(x) = 1 - \cos^2(x)\) we can obtain the relationship shown in Eq. C.3.

\[n_1^2(1 - \cos^2(\theta_1)) = n_2^2(1 - \cos^2(\theta_2)) \quad \text{(C.3)}\]

If we generalise this here, and use the atmospheric refractive index \((\eta_0)\) and the angle of incidence \((\theta_0)\), in relation to the refraction angle of the \(j^{th}\) layer \((\phi_j)\) with complex refractive index \((\bar{n}_j)\), we obtain in the same form.

\[\eta_0^2(1 - \cos^2(\theta_0)) = \bar{n}_j^2(1 - \cos^2(\phi_j)) \quad \text{(C.4)}\]

We require the equation to be in the form \(\bar{n}_j \cos(\phi_j) = f(\bar{n}_j, \theta_0, \eta_0)\), the resulting equation, which has been implemented, is given in Eq. C.5.

\[\bar{n}_j \cos(\phi_j) = \sqrt{\bar{n}_j^2 - \eta_0^2 \sin^2(\theta_0)} \quad \text{(C.5)}\]
Appendix D: E-Field Correction (Jung et al)

Jung et al. [136] described the electric field propagating through a layer as shown in Eq. D.1, and then give the parameters for the backwards and forward propagating parts (Eq. D.2 and Eq. D.3 respectfully).

\[ \mathbf{E}_j(z) = \left[ t_j^+ e^{i\beta_j z} + t_j^- e^{-i\beta_j z} \right] \mathbf{E}_0^+ \]  \hspace{1cm} (D.1)

\[ t_j^+ = \frac{t_j}{1 - r_j^+ r_j'' e^{-2i\beta_j d_j}} \]  \hspace{1cm} (D.2)

\[ t_j^- = \frac{t_j^+ r_j''}{1 - r_j^+ r_j'' e^{-2i\beta_j d_j}} \]  \hspace{1cm} (D.3)

By expanding Eq. D.1, using Eq.’s. D.2 and D.3 we obtain a general expression for the electric field as a function of the Fresnel complex reflection and transmission coefficients used in the partial system described in Chapter 3. Eq. D.4 shows the resultant calculation, where it is apparent that it does not describe what was intended.

\[ \mathbf{E}_j(z) = \frac{t_j' e^{i\beta_j (z+d_j)} + t_j'' e^{i\beta_j (d_j-z)}}{e^{i\beta_j d_j} - t_j^+ r_j'' e^{-i\beta_j d_j}} \mathbf{E}_0^+ \]  \hspace{1cm} (D.4)

This equation tries to specify the Electric field (Eq. D.4) through a layer, with the use of a description outside of the layer bounds (set by \( d_j \), which is the thickness of the layer). Therefore, we need a set of equations that brings us in to describe the propagation in both forward and backward directions so we can look at interference effects. We know that to achieve this we need to equation to be in the form \( X_1 e^{-iy_1 (d-z)} + X_2 e^{iy_2 (d-z)} \) and hence, we re-define \( t_j^+ \) and \( t_j^- \).

\[ t_j^+ = \frac{t_j'}{1 - r_j^+ r_j'' e^{2i\beta_j d_j}} \]  \hspace{1cm} (D.5)

\[ t_j^- = \frac{t_j'' e^{-i\beta_j d_j}}{1 - r_j^+ r_j'' e^{2i\beta_j d_j}} \]  \hspace{1cm} (D.6)

\[ \mathbf{E}_j(z) = \frac{t_j' e^{-i\beta_j (d_j-z)} + t_j'' e^{i\beta_j (d_j-z)}}{e^{-i\beta_j d_j} - t_j^+ r_j'' e^{i\beta_j d_j}} \mathbf{E}_0^+ \]  \hspace{1cm} (D.7)
Appendix E: Material Complex Refractive Indices

### Aluminium (Al)

- (Betancur, 2013)
- (Centurioni, 2005)
- (Jiang, 2011)
- (McPeak, 2015)
- (Nam, 2010)
- (Rakic, 1998)
- (Woollam, 2000)

### Bathocuproine (BCP)

- (Betancur, 2013)
**Glass (BK7)**

- Refractive Index
  - [Sopra, 2008]

- Extinction Coefficient
  - [Sopra, 2015]

**C60**

- Refractive Index
  - [Betancur, 2013]

- Extinction Coefficient
  - [Betancur, 2013]
Gold (Au)

(Betancur, 2013)
(Johnson, 1972)
(McPeak, 2015)
(Rakic, 1998)

Indium Tin Oxide (ITO)

(Betancur, 2013)
(Centurioni, 2005)
(Konig, 2014)
(Mariano, 2014)
(Nam, 2010)
(Shen, 2012)
(Shen, 2014)
(Sopra, 2015)
(Stabinger, 2005)
(Woollam, 2000)
Effective Medium – Glass/ITO (ITO-Glass EMA)

(König, 2014)

Li et al. [252]
Doped Lanthanum-Zirconium-Oxide (LZO)

(MoO$_3$)
Poly(3-hexylthiophene-2,5-diyl) (P3HT)

(Betancur, 2013)

Poly(3-hexylthiophene-2,5-diyl): Idene-60-bisadduct (P3HT:IC$_{60}$BA)

(Betancur, 2013)
(Chen, 2014)
(Mariano, 2014)
(Shen, 2014)
(Zhou, 2012)

[148]
[149]
[148]
[248]
[250]
[253]
Poly(3-hexylthiophene-2,5-diyl): Phenyl-C61-butyric acid methyl ester (P3HT:PC60BM)

2,6-Bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b’]dithiophene : Phenyl-C71-butyric acid methyl ester (PBDTTT-C-T:PC70BM)
Phenyl-C61-butyric acid methyl ester (PC$_{60}$BM)

Poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]:Phenyl-C61-butyric acid methyl ester (PCDTBT:PC$_{60}$BM)

(Betancur, 2013)

(Schmiedova, 2015)

(Quiles, 2015)

[149]

[255]

[5]
Poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)]:Phenyl-C71-butyric acid methyl ester (PCDTBT:PC$_{70}$BM)

(Schmiedova, 2015)  
(Guerrero, 2013)  
(Quiles, 2015)  
(Xerxes, 2011)

Poly[(4,8-bis-(2-ethylhexyloxy)benzo(1,2-b:4,5-b′)dithiophene)-2,6-diyl-alt-(4-(2-ethylhexanoyl)thieno[3,4-b]thiophene-2,6-diyl)]:Phenyl-C71-butyric acid methyl ester (PBDTTT-C:PC$_{70}$BM)

(Zhou, 2012)
Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS)

(Nam, 2010)  
(Stark, 2015)

Poly [(9,9-bis(3’-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN)

(He, 2012)  

[147]  
[256]  
[59]
Poly((4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl]{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl}): Phenyl-C61-butyric acid methyl ester (PTB7:PC_{60}BM)

RefRACTive INDEX

Extinction Coefficient

Wavelength(nm)

(Quiles, 2015)

[5]

Poly((4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl]{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]): Phenyl-C71-butyric acid methyl ester (PTB7:PC_{70}BM)

RefRACTive INDEX

Extinction Coefficient

Wavelength(nm)

(Betancur, 2013)

(Guerrero, 2013)

(Betancur, 2013)

(Guerrero, 2013)

[149]

[144]
Silver (Ag)

(Babar, 2015)  
(Betancur, 2013)  
(Johnson, 1972)  
(McPeak, 2015)  
(Rakic, 1998)

Tandem Materials - [148]

(LBG-PC<sub>70</sub>BM)  
(PTB-PC<sub>70</sub>BM)
Titanium Dioxide (TiO$_2$) 

(Woollam, 2000) 

Tungsten Trioxide (WO$_3$) 

(Shen, 2014)
Zinc Oxide (ZnO)

(Betancur, 2013)  
(Sun, 1999)  

[149]  
[258]
Appendix F: Mie Model Convergence Results

This appendix demonstrates the convergence of the recursive Mie theory, shown in Chapter 5. It also demonstrates how the time linearly scales with the number of sub-layers. Figure F.1. (a) shows how the linearly graded solution changes as you increase the number of sub-layers.

Figure F.1 demonstrates convergence with increasing number of sub-layers, where the change in the peak position decreases as the number of layers gets larger. Timings show a linear increase with the number of sub-layers (N).

The spacing between each of the peak positions in Figure F.1. (a) decreases as the number of sub-layers increases. This is demonstrated better by Figure F.2, which shows that as the number of sub-layers increases beyond ~200, the resonant peak position, and extinction efficiency does not change significantly. It also demonstrates convergent behaviour.

The timings (Figure F.1. (b)) shows the timings of the model with 0, 50, 100 and 100 layers, over 5 simulations. This has been run on a standard laptop, demonstrating also that the model can be used on any device. It is important to note that these timings are representative of modelling nanoparticles under visible light, where the particle sizes are comparable to the wavelength (50 nm vs. 400 – 750 nm). In the case that the wavelength is much smaller than particle size, the number of required iterations within the Mie calculations (based on the size parameters) increases significantly. Hence, the simulation times will also increase.
Figure F.2 peak position (black) and extinction efficiency (b) with increasing the number of sub-layers. This demonstrates convergent behaviour, where the optimum between simulation speed and accuracy of the result is around 200 sub-layers. This same pattern is seen in all small particle cases (<100nm).

To demonstrate how this affects the answer, Figure F.3. (a) shows a graph of the real-part refractive index, and how it changes with increasing number of iterations. This accompanies by Figure F.3. (b) leads us to believe that the convergent behaviour is due to the change of the optical properties as each interface. This has been described in Chapter 6.

Figure F.3 Exponential gradient for TiO2 Anatase to SiO2 real part refractive index, 25 nm is the end of the core Ag nanoparticle. As the number of sub-layers increase the change in both the peak position and efficiency converge to a more accurate answer. (a) shows the refractive index profile over space, (b) gives the extinction efficiency with the same colour key as (a) for comparison. Note that as the number of layers increases the ‘smoothness’ of the refractive index profile also increases leading to less reflection and refraction at each of the layers; as would be the case in graded media and a limitation of some of the Effective Medium Approximations.
Appendix G: **NanoTech France 2016** (Presentation)

Energy Harvesting with Decorative Colour Specific Windows


**Slide 1: Introduction** – *Demonstrate how we can optimise colour specific cells to also obtain the maximum power conversion efficiency.*

**Introduction**

Organic Solar Cells

**An ideal OSC:**

- Flexible
- Efficient (>13.2% Currently highest achieved\(^1\))
- Lightweight
- Solution processed (Reduced Costs)

**Drawbacks:**

- Low efficiencies (High recombination rates)
- Small device areas (Currently mm scale)
- Stability (Hours lifetime)

\(^1\)Heliatek sets new Organic Photovoltaic world record efficiency of 13.2%, Feb. 2016

**Slide 2: Introduction** – *Describing what an ideal Organic Solar Cell (OSC) is, and where the drawbacks are. Also, mentioned that the world record efficiency is currently 13.2% as of February 2016.*
Slide 3: We describe the work we are currently doing, including: Modelling of multi-layered structures such as shown on the slide. How we are developing a plasmonic model for coated nanoparticles, and how we hope to end up with a model capable of modelling nanoparticles in OSCs. We show a standard structure solar cell and when the cathode gets thinner, transmission through the device can be achieved.

Slide 4: A high level description of the Transfer Matrix Method for simulation of OSCs. We obtain reflection and transmission at each interface and coherent interference within the layers leading to absorption. The model takes in the optical properties (refractive indices), the layer thicknesses and the interface/surface roughness. Then we can use the model for N-layered devices and obtain the optical response.
Slide 5: Demonstration slide of how we can achieve different colour cells by changing the material system and layer thicknesses. Aiming for specific transparencies and RGB values.

Slide 6: Demonstration of an experimental semi-transparent solar cell with its corresponding layer thicknesses. The estimated colour from the model is like the colour within the working device area (centre of the device).
Slide 7: UV-Vis spectra compared with modelling spectra from the device, demonstrating that the model can accurately predict the realistic optical spectra, and hence colour.

Differences in the spectra could be due to changes in the refractive index (from literature)
Layer thickness accuracy in measurements (only approximate thicknesses and SR values were used)
If all of the information was obtained experimentally it would be identical.

Material system determines base colour, that can be tuned by ETL and other peripheral layer thicknesses.

Possibly underestimating absorption within glass near UV, and absorption by Ag in NIR regime.

Slide 8: The differences in the spectra could be due to differences in the optical properties of what we have used for the modelling (from literature) compared with the materials used when creating the device. The layer thickness accuracy measurements and surface roughness could also lead to differences in the spectra.
Appendix H: Optical Spacer Effects (ZnO Results)

In Section 4.2 we demonstrated optical spacing effects in Organic Solar Cells (OSCs) using a PTB7:PC70BM active layer and a TiO2 electron transport layer (ETL). In this appendix, we present additional results utilising a different ETL and active layer.

Figure H.1. (a) Device Structure, (b) integrated power dissipation of the active layer for different active (legend), and electron transport layer thicknesses. The crosses represent the line colour in figures (c) – (f). (c) reflection, (d) absorption, (e) transmissivity, and (f) active layer absorption from devices.
The device was constructed out of Glass (700 μm)/ ITO (100 nm)/ PEDOT:PSS (40 nm)/ PCDTBT:PCBM (10, 50, 150, and 250 nm)/ ZnO (10 – 300 nm)/ Aluminium (100 nm). The optical properties used can be found in Appendix E. The absorption peaks change, and are dependent on the thickness of both the active layer and the ETL. To explore this further, Figure H.2. shows the crosses in Figure H.1. and how the absorption is distributed. In the maxima case (yellow cross, Figure H.2. (c)). The absorption for this combination is optimised to give the larger amount of absorption within the active layer. This is the case when compared to (b) and (d) from Figure H.2, however, the device itself does not look to be as optimised as the TiO₂ case, which could be solved by changing the ITO and HTL layer thicknesses.

![Figure H.2](image)

**Figure H.2. The power dissipation through the device over wavelength for active layer thickness of 100 nm and an ETL thickness of (a) 10 nm, (b) 60 nm, (c) 170 nm, and (d) 250 nm.**

The other case, where we look at the maxima of each active layer thickness is shown in Figure H.3, where we start to see patterns arising in the absorption peaks when the ETL thickness is optimised. This is confirmed by Figure H.4. The exception to this is when the active layer thickness is 120 nm, it appears to be relatively flat throughout. This, like the case with TiO₂, suggests that the active layer is becoming thick enough to absorb most of the incident light on a first pass. Hence, reflections, and contributions thereof, from the back contact have minimal effect.
Figure H.3. (a) Device Structure, (b) integrated power dissipation of the active layer for different active (legend), and electron transport layer thicknesses. The crosses represent the line colour in figures (c) – (f). (c) reflection, (d) absorption, (e) transmissivity, and (f) active layer absorption from devices.
Figure H.4. The power dissipation through the device over wavelength for active layer thicknesses (and ETL thicknesses): (a) 60 nm (160 nm), (b) 80 nm (150 nm), (c) 100 nm (150 nm), and (d) 120 nm (90 nm).
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