

Optimisation of Luminescent Downshifting Layers for Large-scale PV Systems Integration

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Abstract

This research project aims to enhance Photovoltaic (PV) technology's power conversion efficiency by adding a Luminescent Downshifting Layer (LDS). An LDS increases the solar spectrum absorption range of a PV cell, enabling better integration into residential and commercial buildings. The LDS layer enhances photon interaction with the PV cell, which increases power conversion efficiency.

The project focused on fabricating an LDS layer for silicon PV cells to boost their interaction with the solar spectrum. Subsequently, these LDS-PV cells were integrated into different systems, thus improving overall efficiency. The aesthetic appeal of LDS layers, available in various colours, can increase their desirability for building façades without compromising building functions.

Luminescent dyes of different concentrations and thicknesses were tested and optimised in LDS layers, transparent polymers doped with luminescent dye applied to solar cells using a spin coating technique. These optimised LDS layers increased the solar cell power conversion efficiency. As part of the larger EU project IDEAS, these LDS-layered PV cells were integrated into a Compound Parabolic Concentrator (CPC) system and tested under actual weather conditions in Ferrara, Italy, and County Mayo, Ireland. The LDS layer, integrated into a CPC system, produced over 100 W during peak exposure compared to 60 W from a commercial PV panel. These LDS-layered systems demonstrated integration into a completely renewable energy system, including heat pump-powered underfloor heating and AI-controlled operation unit.

Simulations identified optimal luminescent dyes and their concentrations for the LDS layer tailored to specific PV cells. Lumogen Violet was most suitable for enhancing silicon solar cell efficiency. Due to supply issues, methyl orange from Sigma Aldrich was used, showing potential efficiency enhancement as a 20 μm thick LDS layer. This layer expanded the wavelength range for PV system interaction with the light spectrum.

The LDS's viability was also assessed for different PV devices, including silicon, a-si, and CdTe, showing broad applicability across various PV technologies. After successful LDS applications to PV cells, Plasmonic LDS(pLDS) layers that is, LDS layers with metal nanoparticle enhancement, were fabricated and tested. The pLDS layers experienced lower power output, prompting further reassessment for development.

COVID Impact:

COVID-19 had an impact across all areas of life, especially within this research. From mid-March until mid-June, during the first full lockdown in Ireland, there was no access to Trinity College or the laboratories within the premises. Only remote working from homes was allowed.

Once there was a reopening from lockdown, there was restricted access to laboratories for limited personnel. Many of these restrictions remained in place while writing this report. A maximum of 1 person was allowed within the laboratory during the allotted time. 2 slots were available per day for 3 hours each, with an hour of cleaning between different people. As a large part of this research project was experimental-based, it required a large amount of on-hand fabrication and testing. The limited time allowed within the lab and on-campus greatly hindered the development pace of the project.

There were also long delays when ordering and receiving more materials required for the continued research of the LDS layers. As some materials would be supplied from outside of Ireland, the delays reached weeks at a time in some instances. The knock-on effect led to the slower fabrication and testing of new and different LDS layers.

Once back in the laboratory, time constraints became the main difficulty. As stated in this report, the mixing time of a solution batch can take upwards of 2 hours or more, which can account for the allotted slot for that day. The second slot can be used for layer making, and then drying is needed. However, this process could happen over several days because the laboratory is shared between multiple people.

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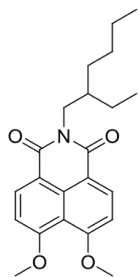
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List of Acronyms

GHG	Greenhouse Gases
LDS	Luminescent Downshifting
PV	Photovoltaic
IDEAS	Integration Designs for Increased Efficiencies in Advanced Climatically Tuneable Renewable Energy Systems (EU-funded project)
CPC	Compound Parabolic Concentrator
PMMA	Polymethyl methacrylate
MNP	Metal Nanoparticle
AG NP	Gold Nanoparticle
Eu	Europium
RE	Rare Earth
SPR	Surface Plasmon Resonance
pLDS	Plasmonic Luminescent Downshifting Layer
PCM	Phase Change Material
LSC	Luminescent Solar Concentrators
TLBO	Teaching Learning Based Optimisation
TES	Thermal Energy Storage
Si	Silicon
GaAs	Gallium Arsenide
c- Si	Single crystalline Silicon
mc – Si	Multi crystalline Silicon
a - Si	Amorphous Silicon
CdTe	Cadmium-Telluride
CIGS	Copper-Indium-Gallium-Selenide
DSSC	Dye Sensitised Solar Cells
QD	Quantum Dots
UV	Ultraviolet
QY	Quantum Yield
FQY	Fluorescence Quantum Yield
EQE	External Quantum Efficiency
TCD	Trinity College Dublin

Nomenclature

PMMA	$C_5O_2H_8n$
Chloroform	$CHCl_3$
Silicon Oxide	SiO_2
Acetone	C_3H_6O

Methyl Orange	$C_{14}H_{14}N_3NaO_3S$
Lumogen Violet	
Lumogen Yellow	$C_{32}H_{26}N_2O_4$
Lumogen Red	$C_{72}H_{58}N_2O_8$

Chapter 1. Introduction

Where Ireland is positioned geographically at 54°N 7°W. It receives a higher diffuse solar radiation throughout the year (Met Eireann, 2010) compared to other European countries such as Spain or Greece (Photovoltaic Geographical Information System, 2020). The climate associated with the geographical position also aids the implementation of an LDS layered system as the low average temperature cools the LDS systems to prevent overheating.

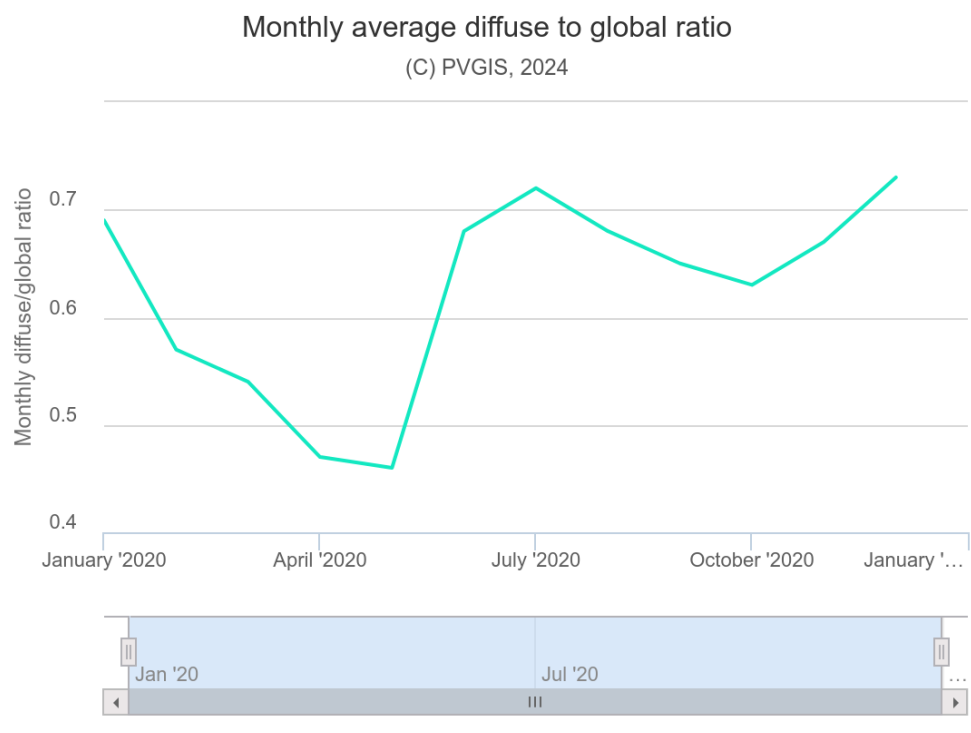


Figure 1.1 Ireland diffuse radiation (Photovoltaic Geographical Information System, 2020)

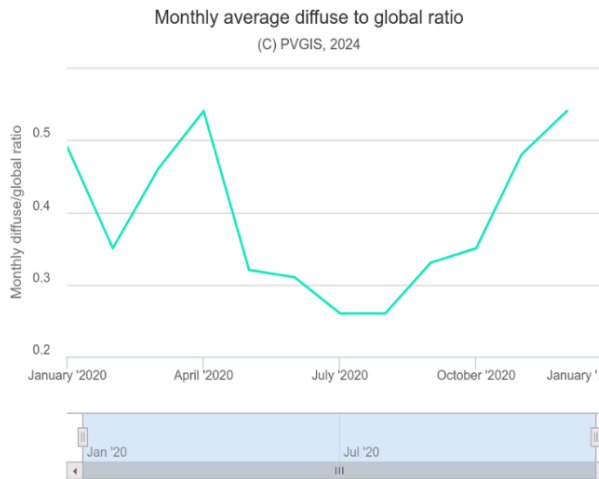


Figure 1.2 (a)



Figure 1.2 (b)

Figure 1.2 Spain (a) and Greece (b) diffuse radiation (Photovoltaic Geographical Information System, 2020)

The LDS layer can work in both direct and diffuse radiation but is more optimal in diffuse radiation (Muneer et al., 2006). This renewable source of energy is a constant passive source of energy that can easily be installed and integrated onto building roofs or facades, or both. For Ireland, the EU has three key binding targets to participate in the Paris Agreement by 2020. The first directive required a shift in the energy mix, aiming for 16% of the total energy consumed from renewable energy sources. The second directive focused on enhancing the use of renewables in transport to account for 10% of the sector's energy consumption, and the third directive using renewables to provide 12% of the energy used for heating.

Unfortunately, Ireland has not met these targets, with 11% of the total energy used coming from renewables, and the transport and heating sector's renewable contribution is 7% and 6%, respectively. (SEAI, 2020). Further targets have been outlined for 2030 (SEAI, 2020, Climate Act Plan, 2021)

- (1) CO₂ emissions to be reduced to 51%
- (2) Renewable energy sources to provide 27% of the total energy usage in Ireland.
- (3) Improve energy efficiency in the public sector from 33% in f 2020 to 50% by 2030.

To meet these objectives, it is essential for Ireland to significantly invest in renewable energy technologies. This includes solar and, as proposed in this research, the new emerging solar technologies that promise higher efficiency, lower environmental impact, and will be easy to

integrate for applications. Such investments will help transition towards a more sustainable and less carbon-intensive energy infrastructure, especially for the buildings.

This project is part of a EU project IDEAS to optimise domestic renewable energy generation by multiple sources by developing a novel building Integration control system. The project was entitled Designs for Increased Efficiency in Advanced Climatically Tuneable Renewable Energy Systems (IDEAS) with the following aims:

1. A novel solar façade element for the building integrates concentrating solar collector, luminescent layers to enhance PV efficiency and phase change material to store waste heat with a luminescent coating to enhance efficiency.
2. The optimising of heat pump technology with PV/Phase change material (PCM)
3. Novel integration and demand-side management via AI control of all renewable energy systems

This project focused on the novel solar aspect of the project. It specifically focused on optimising a luminescent downshifting layer (LDS) for the CPC system and developing a reproducible process for panel integration. The panel integration is assisted with the development and improvement that will be determined through using the Compound Parabolic Concentration (CPC) system. This PV technology application would be used to passively generate energy used by the building it is integrated into. The benefit is that the energy produced supplements the power usage of the building, reducing its demand on the established energy network. Renewable energy systems like the PV technology researched throughout this project can be applied to a commercial setting in the same vein as a domestic setting as renewable energy system for a domestic setting as they can be installed on the façade and generate power passively. The IDEAS project intends to introduce multiple system integration as a whole in both domestic and commercial settings.

1.1 Research Aim and Objectives

This aim of this PhD research is to improve the efficiency of PV technology and to further improve power output with the integration into CPC systems from the IDEAS project. With an

aim to develop and enhance the performance of solar cell technology through the implementation of an effective Luminescent Downshifting layer onto a PV device to improve its overall power output efficiency and further optimise it for other PV. Metal nanoparticles (MNPs) were incorporated into the LDS layer, which plasmonically enhanced the output of the layer in a plasmonic LDS (pLDS) layer.

These aims coincide with the IDEAS project, where the objectives focused on developing an LDS layer for a silicon PV cell in a CPC system. There are two demonstration sites for the IDEAS project in Co. Mayo, Ireland and Ferrara, Italy. These LDS layers were developed in Trinity College Dublin Ireland; the LDS layer is more effective in diffuse radiation, which in Ireland is abundant. However, the effect of the PV LDS layered system can also work in less diffuse settings such as Ferrara, Italy. Alterations can be made to adjust for the climate in which the system will be installed. The building integration includes both domestic and commercial dwellings. In domestic settings, the improvements of the LDS layered CPC systems will be used to supplement the heating of space within the building and the water system. While in the commercial dwelling will be used in the supplementing of energy for both heating and cooling of spaces within the building. This system was integrated into the building façade to achieve low/zero carbon emissions buildings through renewable energy integration This included the following aims:

1. To improve the overall efficiency of a solar cell with the application of a Luminescent Downshifting Layer. Improving the passive energy generation. The LDS is a simple layered addition without the changing of the PV structure.
2. To develop a reliable and repeatable process of LDS layer application.
3. To produce LDS layers for silicon PV technology, aligning the LDS' durability and are compatible with existing solar cell technology
4. To optimise an LDS layer to improve energy generation for PV technology, improve the integration of the PV system through CPC system integration.
5. To develop an effective fabrication method in different environments, i.e. an open laboratory setup or an inert environment.

With these aims completed, the LDS layers developed and produced can improve the passive energy generation for PV systems, while also improving the integration of PV systems into both domestic and commercial dwelling through the use of the CPC system integration. To make the most of the improved PV systems the buildings used in the IDEAS project can be modified to include insulation underfloor or within walls. While the only requirement to implement the PV system is adequate space on the outer façade. The management and maintenance of these LDS improved systems will be improved through the contribution to the IDEAS project with a full building system integration with an automated management AI system.

After the initial production and fabrication of the LDS layers were achieved, it was important to integrate the developed LDS layered PV cells into a CPC system. Once completed, the next stage objectives were as follows:

- To ensure compatibility of MNPs in a polymer layer,
- To integrate MNPs with LDS to produce a working pLDS layer
- To characterise pLDS and LDS layers.
- To use simulation software to optimise LDS layers for future and further development.

The objectives of this research can be separated into four sections. These include:

1. Development, fabrication, optimisation, and application of an LDS layer

The aim of this research was to optimise the small-scale LDS layer of 2 x 2 cm glass on a glass substrate and subsequently onto a 2 x 2 cm photovoltaic (PV) cell. Then, upscaling and eventually to a 12 x 12 cm PV cell.

2. Application and integration of LDS on various PV devices

With the LDS layer successfully applied to silicon-based PV cells, the effects of the developed LDS is to be applied to commercially available PV cells and is to test the LDS layers' effectiveness when applied to a different PV cell other than silicon. The PV technology can be integrated in both domestic and commercial settings with a façade integration using a flat based panel or a CPC system.

3. Implementation of MNP into pLDS layers

After the successful implementation of LDS layers into a functioning CPC system, the next developmental step is to add metal nanoparticles (MNP) to improve the effectiveness of further layers. The LDS layer polymer solution which consisted of 0.2 wt% of luminescent dye is used as a reference layer to attempt and develop the pLDS.

In this development, MNPs compatibility and stability in the PMMA polymer were developed. This needed to be established using the same materials as the LDS polymer. This was used as a preliminary production and the basis for integrating an MNP into an LDS layer.

When a repeatable method of combining both aspects was achieved, the fabrication and testing of pLDS was completed. A comparison with an LDS of the same luminescent material and bare PV cells was carried out.

4. Modelling to optimise LDS & pLDS

Finally, the implementation and use of a computer simulation program, which was developed within the SEAG research group, was used to aid in the determination of which luminescent species could be used with a si PV cell, while also determining which luminescent species should be used by matching both absorption and emission spectra with the desired stoke shift in wavelength. It aided in the development and adaption of the LDS layer onto different PV devices, as their requirements all differ from one another in terms of interaction with the solar spectrum.

1.2 Contribution to Knowledge

This research has demonstrated that.

- An LDS layer can manipulate the solar spectrum that benefits the solar cell underneath it. Moreover, the combination of the layered PV cells housed in a CPC system improves power conversion efficiency that can be deployed to achieve a renewable energy-efficient home. As part of the IDEAS project, the commercial demo site in Ferrara, Italy, required a power output 100 W per system. There was found to be an increase in power conversion efficiency, showing an improvement from 60 W to 100W, comparing LDS layered CPC systems to commercially

available PV systems during peak solar radiation interaction achieved at the installation site in Ferrara.

- The methodology used in the application of LDS layers has been developed across different types of PV cells, such as Si, a-si and CdTe. It has also been developed for different sized PV cells, from a small scale of 2 x 2cm to 12.5 x 12.5cm PV cells. With the adjusted development of a larger size LDS in the 12.5 x 12.5cm.
- The addition of using an inert environment in the production of the layer mixture improved layer quality when applied and the half-life of the mixture for use over time, compared to a short window of usage before polymerisation would occur. This has led to the improvement of the quality of the LDS layer before, during and after the application process.
- This inert environment implementation has streamlined the production process to create a reliable supply chain of LDS polymer stock solutions. This process proved invaluable, as the scale in which this research has taken place had not been attempted before. This process has shown the improvement made in the repeatability and consistency of the LDS layer application. Allowing for more frequent production of LDS-layered PV cells.
- A computer simulation was used to reduce the time required in selecting the luminescent species that complements the silicon (Si) PV underneath. This has also been useful as a validation tool when determining the concentration of dyes for the LDS cells used in the CPC systems for the IDEAS project.
- The addition of MNPs showed the difficulty of combining the two materials, luminescent species and MNP from commercially available sources. This also demonstrated the compatibility of the LDS layer to host MNP particles successfully within the PMMA polymer. The premade materials came with different parent solutions, i.e., water-soluble into a chemical compound.

- The viability of use for an LDS layered PV cell system for a domestic setting and how impactful the process may be in the long term when compared to the development process

1.3 Thesis Layout

This thesis report is divided into a total of 8 chapters.

Chapter 1 is an introduction to the thesis and sets out the aims and objectives of the research undertaken, highlighting the contribution to knowledge and thesis layout.

Chapter 2 describes the literature reviewed leading to the work being conducted and the reasoning behind its use. Topics such as renewable energy usage, PV technology and how it has progressed, and the development of LDS layers to date are discussed as a background to the research topic. This chapter shows the gaps and areas for improvement of PV and how this research has intended to implement improvements.

Chapter 3 details the different research methodologies and techniques used throughout the work undertaken. This chapter presents the tools used to develop the LDS layer fabrication process that has improved throughout this thesis.

Chapter 4 highlights the outcomes of the initial fabrication and characterisation of the LDS layer used on si PV cells. The upscaling from a 2 x 2cm to a 12.5 x 12.5cm PV and the issues associated with the application and integration of the LDS layered PV cells are found and addressed in this chapter. Leading to the improvement and optimisation of the development of the LDS layer.

Chapter 5 discusses the use of computer simulations and their benefits and uses for developing an LDS layer. The desired thickness and luminescent dye concentration were determined and validated experimentally using this method.

Chapter 6 details the implementation of the LDS layer used in various PV technologies and its further development of the LDS layer with the integration of metal nanoparticles. The process and application of the LDS layer onto various PV devices is demonstrated in this chapter. The initial development of a polymer based layer with the addition of MNPs is also achieved and shown in this chapter. This process is using the recipe of the LDS initially without the luminescent material involved.

Chapter 7 discusses the effects of pLDS integration and its comparison to LDS layered and non-layered systems. The upscaling of the commercially available pLDS is also shown in this chapter. The viability of which is also assessed in comparison to both a LDS layered system and a system of PV cells with no addition.

Chapter 8 details the conclusions of the research undertaken during this PhD and the future work to be continued. This chapter highlights the work undertaken throughout this thesis, touching on the key aspects which demonstrates contribution to knowledge from this work. These chapters are followed by the reference section and appendices, which includes all the referenced work acknowledged throughout this thesis, and all the data sets that were not directly mentioned in this work.

Chapter 2. Literature Review

2.1 Introduction

This chapter presents a review of the research which has been published in the area of solar and Luminescent devices. The chapter is arranged into the following subsections:

- Policies for implementation of renewable energy resources
- The energy demand that has encouraged the development and usage of renewable energy sources.
- The development of an up-to-date PV technology and where it is today.
- How LDS layers can be used to improve PV cells and the aspects that influence the effectiveness of those layers
- The project in which this thesis is involved and the part that LDS layered cells play within

The findings of the review identified knowledge gaps which paved the way for the development of this research, which integrates a luminescent downshifting (LDS) layer with a photovoltaic (PV) cell, leading to further enhancements using metal nanoparticles (MNP)

2.2 Ireland's Policy and their Influence

The "Climate Action Plan 2021" for Ireland outlined several ambitious targets for renewable energy, aiming to significantly reduce carbon emissions and enhance sustainability across various sectors. Key renewable energy targets outlined in the plan include:

Electricity Generation: The plan aims to generate 70% of Ireland's electricity from renewable sources by 2030.

Transport Sector: The plan includes targets to increase the number of electric vehicles (EVs) on Irish roads. By 2030, the goal is to have approximately 945,000 electric vehicles, including cars and vans.

Heating and Cooling: The Climate Action Plan also outlines targets for renewable energy in heating, aiming to install 600,000 heat pumps in new and existing buildings by 2030. This move is part of the effort to decrease the heating sector's reliance on oil and gas, thereby reducing emissions and increasing energy efficiency.

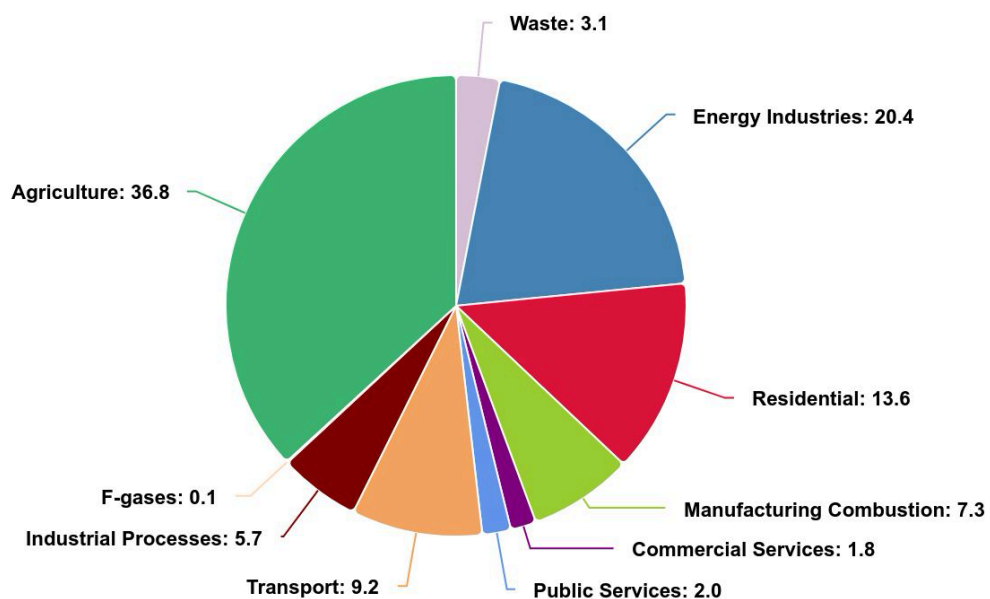
These targets are part of Ireland's broader commitment to align with the European Union's Green Deal and to achieve net-zero carbon emissions by 2050.

The Paris Agreement, signed by 196 parties in Paris in December 2015, aims to reduce the use and reliance on fossil fuels (Paris Agreement, 2020). For Ireland to reduce its CO₂ emissions per the Paris Agreement, we must reduce our energy consumption while improving energy efficiency and transitioning to low-carbon or carbon-neutral energy resources (SEAI, 2021).

The Irish targets have been readjusted and aimed towards 2030. There are now three areas in focus: (SEAI,2020)

- (1) CO₂ emissions to be reduced to 40% of 1990 levels.
- (2) Renewable energy sources provide 27% of the total energy usage in Ireland.
- (3) 27% improvement in energy efficiency.

Greenhouse gas emissions share by sector 1990



Highcharts.com

Figure 2.1 Greenhouse gas emissions for Ireland 1990 (SEAI energy balance, 2024)

Greenhouse gas emissions share by sector in 2023

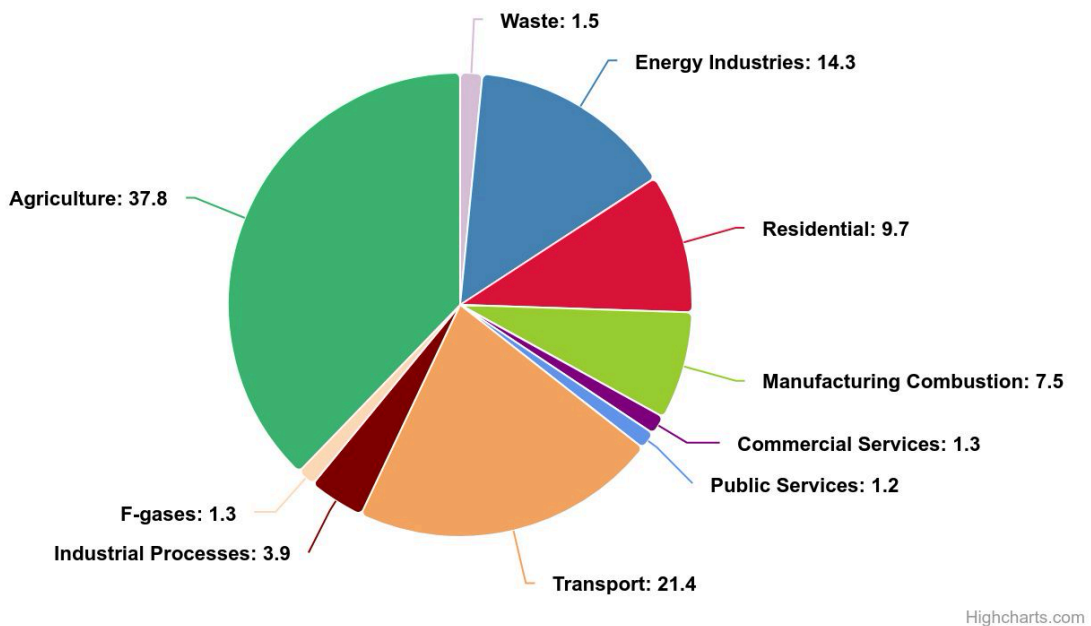


Figure 2.2 Greenhouse gas Emissions for Ireland 2023 (SEAI energy balance, 2024)

Figures 2.1 & 2.2 shows the greenhouse gas emissions in Ireland by sector from 1990 & 2023 respectively, with Ireland's effort sharing regulation emissions annual limit for 2023 is 40.52 Mt CO₂eq. Ireland's provisional 2023 greenhouse gas ESR emissions are 42.79 Mt CO₂eq, this is 2.27 Mt CO₂eq more than the annual limit for 2023 (SEAI energy balance, 2024)

Ireland has a Climate Action Plan to aid in achieving the overarching goals by 2030, which includes (SEAI,2020)

- A target of 75% reduction in emissions by 2030 through the facilitation of large-scale renewable energy sources to decarbonise the power sector.
- Improved energy efficiency of existing structures and zero emissions for new builds which will reduce emissions by 45% from commercial buildings and 40% from residential dwellings.
- Reduce or avoid the need for private travel, encourage public transport, and improve facilities for walking, cycling, and energy-efficient vehicles to achieve a 50% reduction in emissions from the transport sector.

2.3 Energy Demand

Access to different sources of energy has influenced the development of human civilizations over the last centuries. With the human population exceeding 7.5 billion, energy demands have increased exponentially for many countries around the world.

Ireland's total energy usage compared to another European country like Italy shows a vast total energy usage difference. As seen in figures 2.3 and 2.4, respectively (IEA, 2023) Italy is compared here as this country is used as a demo site for the IDEAS project while still be geographically close as part of central Europe compared to Ireland in western Europe. For Ireland, the top three contributors are Transport (32%), Residential (27%) and Industry (20%). While the top three for Italy are Transport (30%), Residential (26%) and Industry (25%). In terms of renewable energy sources in solar technology, Italy has an installed capacity of 22.56 TWh (Sunergy works, 2022) while Ireland has 1GWh of solar energy connected to the electricity grid. (RTE, 2024). The consumption for both countries is shown in Figures 2.3 & 2.4 respectively.

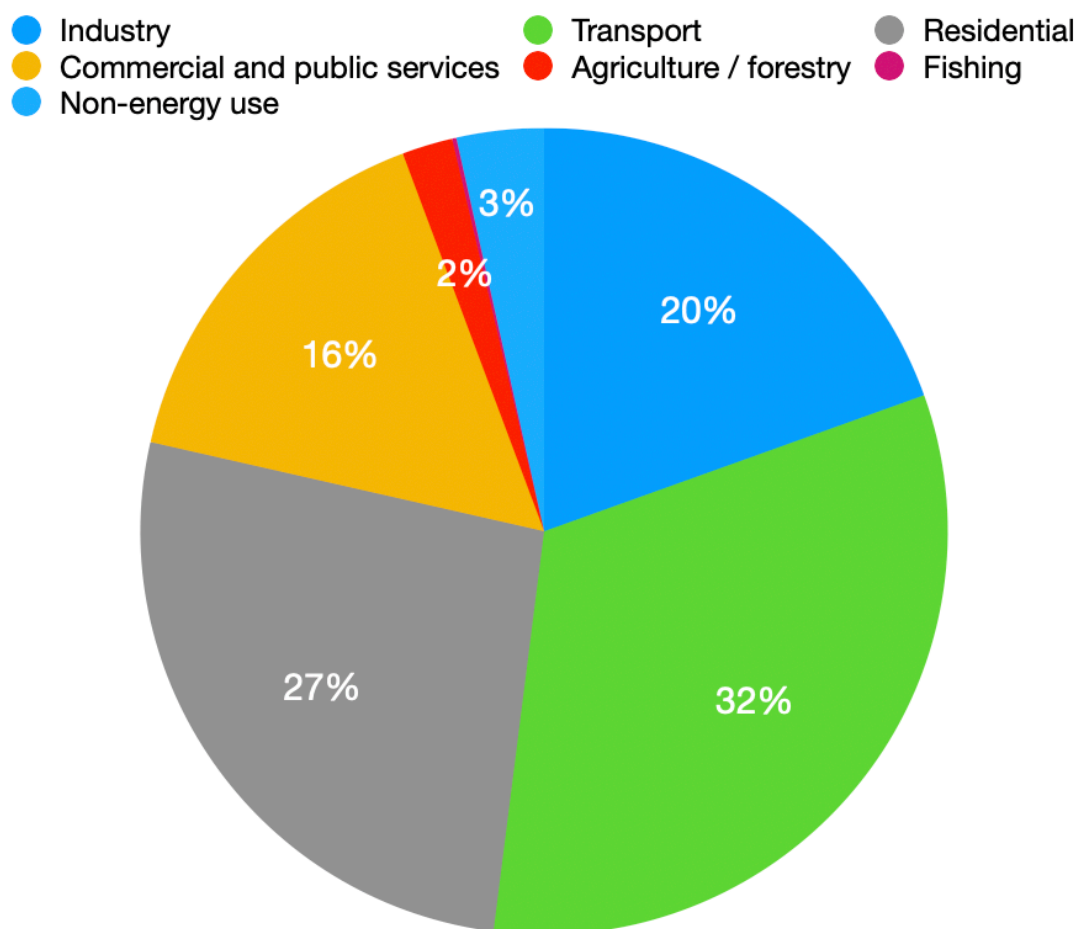


Figure 2.3 Ireland total energy usage 2000 – 2021 (IEA, 2023)

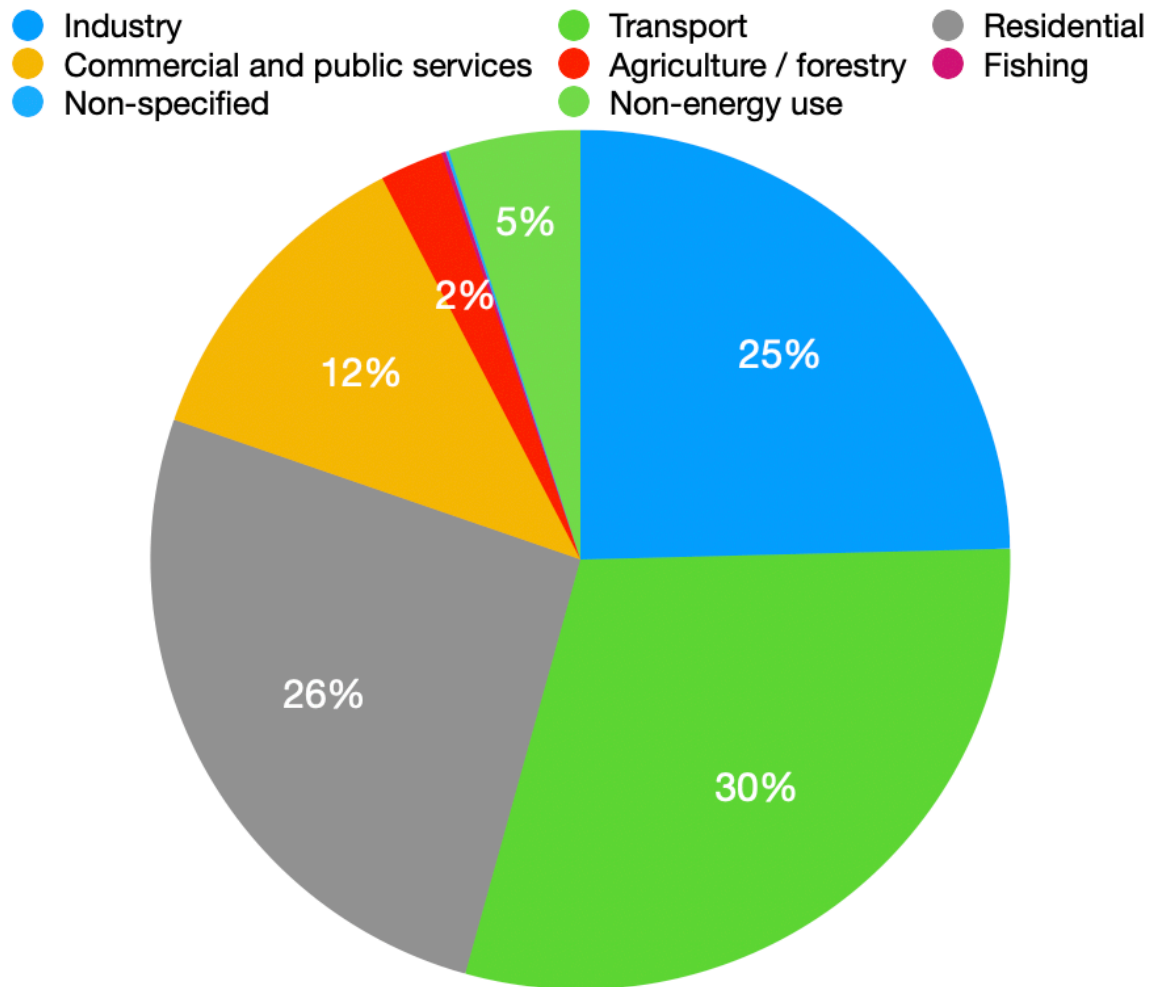


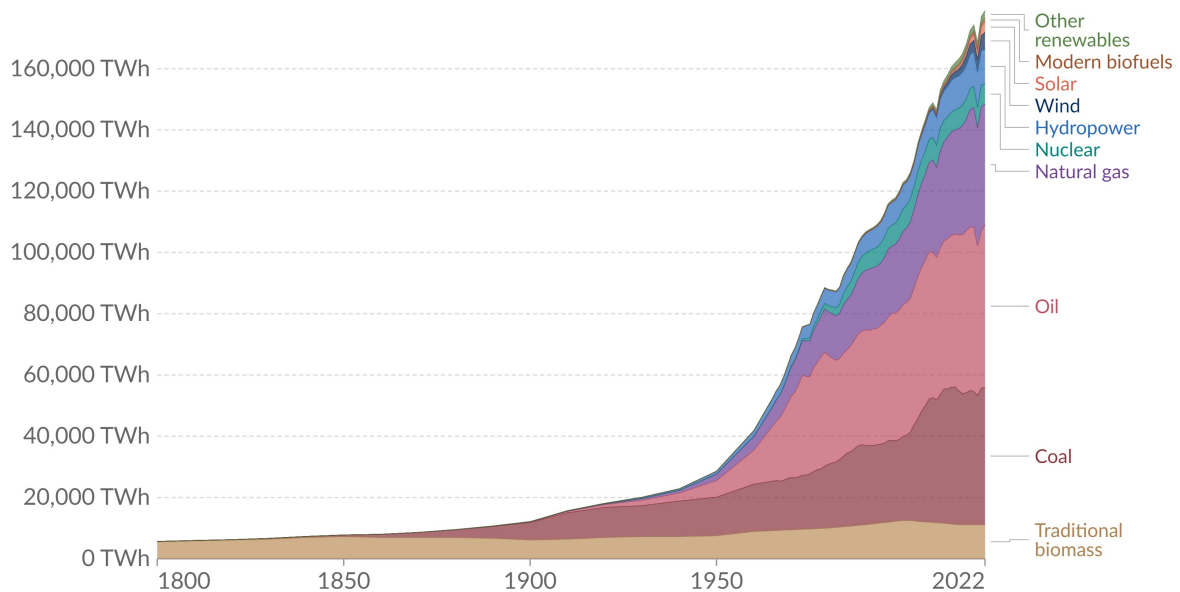
Figure 2.4 Italy total energy usage from 2000 -2021 (IEA, 2023)

From 1980, when energy consumption was at 88 million GWh, it significantly increased to 176 million GWh by 2021 (as shown in Figure 2.5) and is projected to reach 250 million GWh by 2050. (Smil, 2023) Fossil fuel reserves trend towards an unsustainable level, where the required fossil fuel needed is larger than the available fossil fuels. Fossil fuels use also have a high environmental impact due to high CO₂ emissions (Raj & Singh, 2012). Their associated greenhouse gas emissions (GHG) are typically 469g CO₂eq/kWh at the lower emission level and 1001g CO₂eq/kWh at the upper end of emission levels, depending on the fossil source and energy conversion process.

Global primary energy consumption by source



Primary energy is calculated based on the 'substitution method' which takes account of the inefficiencies in fossil fuel production by converting non-fossil energy into the energy inputs required if they had the same conversion losses as fossil fuels.



Data source: Energy Institute Statistical Review of World Energy (2023); Vaclav Smil (2017)
OurWorldInData.org/energy/ | CC BY

Figure 2.5 Trend of global energy consumption (Smil, 2023)

This increase in consumption has predominately been attributed to fossil fuels, however, the renewable energy contribution has grown, as of 2022 Ireland uses 36.8% of its total energy usage in electricity (SEAI, 2023). As seen in Figure 2.5 in 2022 there was a usage of 20,000 TWh from renewable sources (Smil, 2023). From Figure 2.5, the demand for reliable, sustainable, low-cost, and large energy source supply has grown along with population growth in many countries (Kadoshin et al,2000). Currently, 88 % of this energy comes from fossil fuels such as coal, oil, and natural gas. (Smil, 2023).

Figures 2.6 and 2.7 show the energy production for renewable energy sources in Italy and Ireland from 2000 – 2022, respectively. Italy having 286,674 GWh of total energy production in 2022, with 33% coming from renewable sources (IEA, 2024), 10% of which is from solar PV as seen in figure 2.6. Ireland's total energy production from 2022 was 33,926 GWh with 38.2% coming from renewable energy sources (IEA, 2024), only 0.3% of which came from solar PV sources as seen in figure 2.7. With both countries within 6% of each other of total energy production coming from renewables, there is a large scope in which implementation of solar

PV in Ireland can further increase renewable energy contribution to the total energy production in the country.

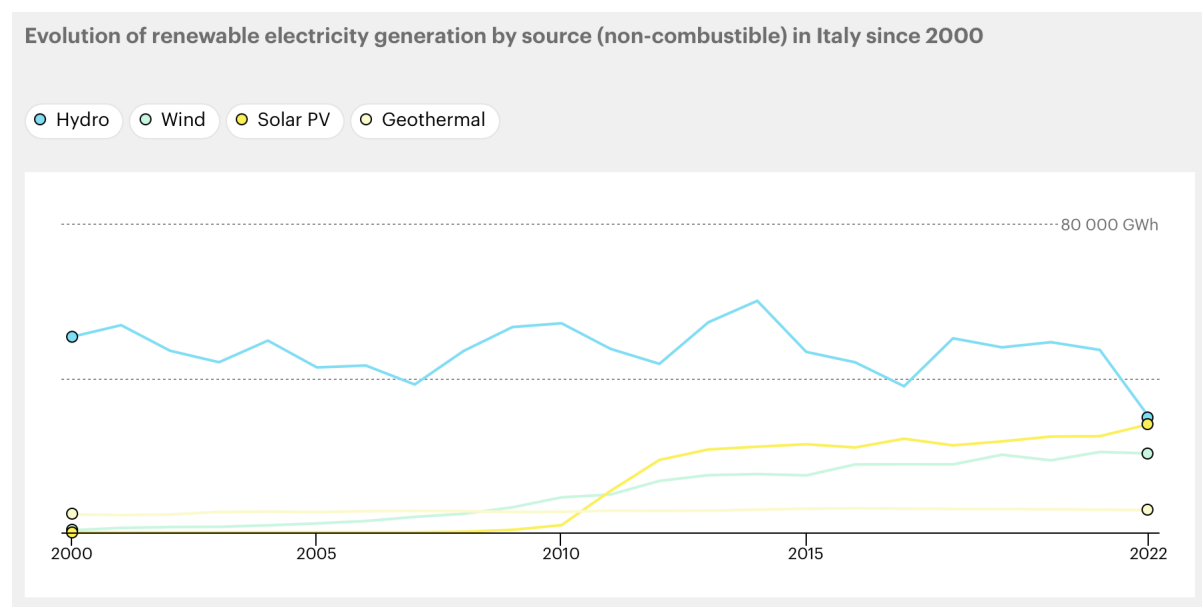


Figure 2.6 Renewable energy generation for Italy 2000 – 2022 (IEA, 2024)

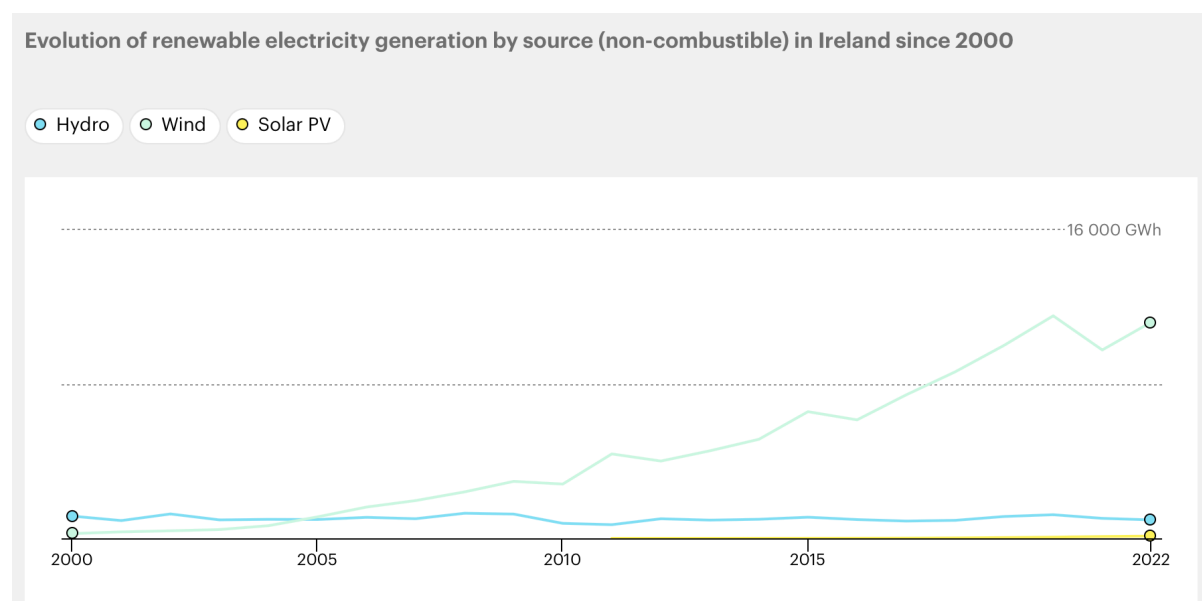


Figure 2.7 Renewable energy generation for Ireland 2000 – 2022 (IEA, 2024)

Ireland's energy consumption has decreased from 5.7 MJ in 2000 (IEA, 2023) to 5.2 MJ in 2021. This has been achieved through the implementation of policies such as the Climate Action Plan, as described in section 2.2.

In Ireland in 2021, the average energy consumption per household was 20,424 kWh, with the energy split 75% from direct fuel (non-electric) and 25% through electricity. In 2017, the average consumption was 14,810 kWh. This is an increase of 5,614kWh (27.48% increase). (SEAI, 2021)

Renewable energy technologies are considered carbon neutral or have minimum carbon emissions at the point of generation. (SEAI 2020) For Ireland, these renewable sources include wind power produced using wind turbines both on land and offshore. As of 2020, offshore pipeline projects have increased to 23 total projects, providing 36% of the electricity demand (IEA WIND TCP, 2020). A milestone was also achieved with wind energy generation passing over 10TWh in total produced in Ireland (IEA, 2020). Hydroelectricity through hydroelectric dams in rivers such as Ardnacrusha (producing over 86 MW) is also available. As of the most recent report from the SEAI in 2021, Wind energy produces 32.5 % of Ireland's gross final energy consumption and hydropower contributes 2.3 %. (EPA, 2020) For heat usage, biomass contributes 2.4% in Ireland, while solar thermal contributes 0.3% to Ireland's gross final heat consumption. Also, the use of renewable energy offsets the amount of CO₂ that is produced. A total of 7Mt CO₂ was avoided due to using renewable energies. (Irish Gov, 2023)

Solar is also a growing renewable technology in Ireland, roof -top installations on buildings and larger solar farms such as Ballymacarney Solar Farm (County Meath) with a capacity of 200MW (Ballmacarney Solar Project, 2022). There has been a steadily growing installation of solar energy generation PV systems in Ireland. As of June 2023 (ISEA, 2023), 680 MW had been installed, with some sites greater than 5 MWh, such as solar farms, producing 349 MWh of the share and microgeneration (such as domestic dwellings) producing 208 MWh.

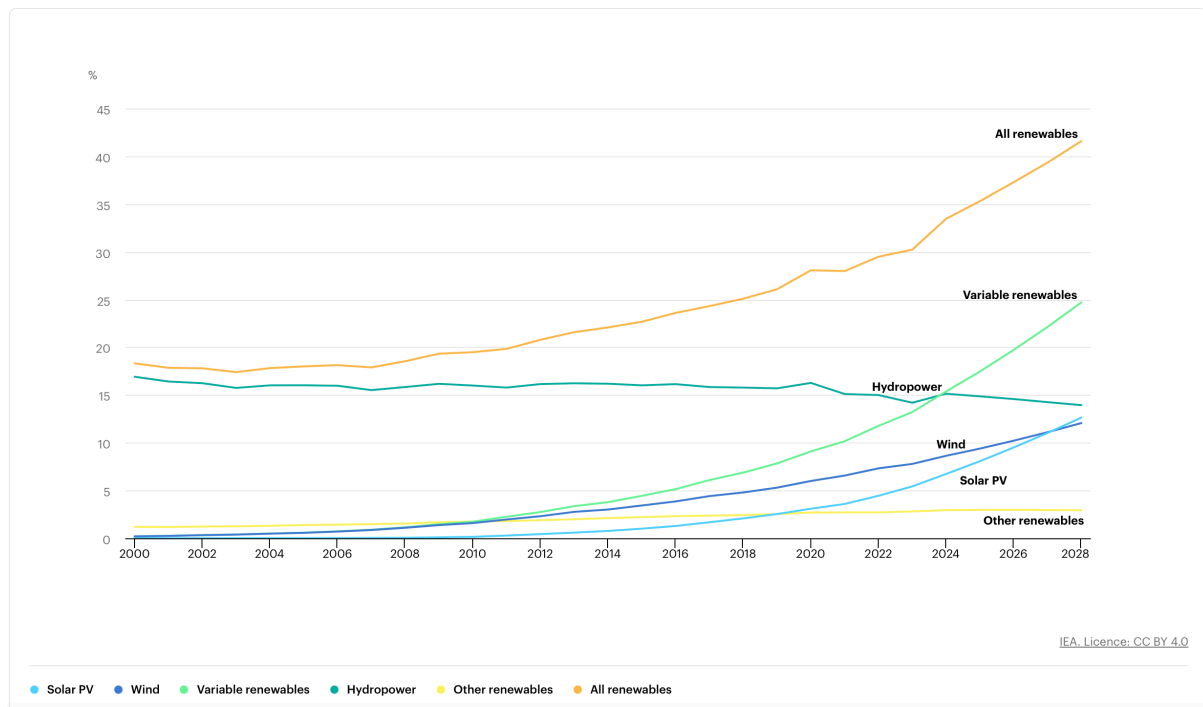


Figure 2.8 Historical energy consumption by fuel in Ireland from 2000-2023 and forecasted consumption to 2028 (IEA, 2023)

Figure 2.8 illustrates the trend of energy consumption by renewables for Ireland from 2000, projected to 2028.

2.4 The IDEAS Project

This PhD research is part of a large EU-funded IDEAS project with 14 partners from academia and industry, coordinated by Trinity College Dublin from fields such as engineering, computer modelling, chemistry, social integration, and public awareness. The IDEAS project aimed to create an innovative building-integrated renewable energy system, and new solar panels were one section of this project. Figure 2.9 demonstrates the different aspects of the IDEAS project when applied to one of the demo sites; in this case, it is in the UNIFEA, Ferrara, Italy. The solar aspect of the IDEAS project is highlighted, and the LDS-layered PV cells are encased in the CPC system.

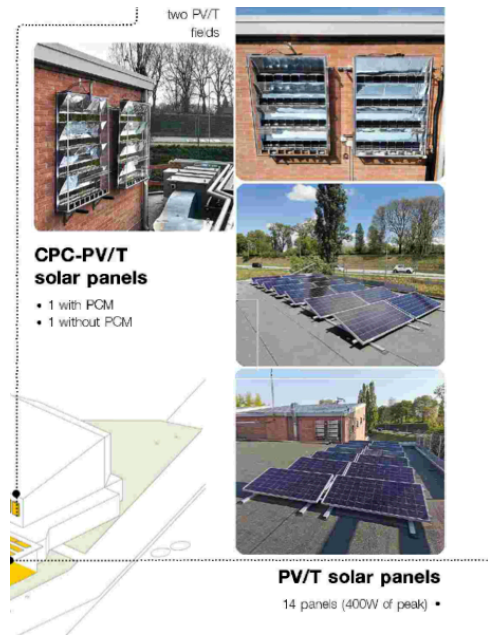


Figure 2.9 Image IDEAS CPC LDS layered system used at the demo site, Ferrara, Italy

The LDS technologies developed in this PhD research were integrated with a compound parabolic concentration (CPC) system. The placement of the CPC/ LDS panels on the façade presents an innovative technological solution for solar building integration as part of Work Package 1. This work package developed the CPC/LDS system, and while this research focused on the LDS development, it is essential to understand the CPC and the unique conditions created for an LDS within a CPC system. The CPC design and fabrication formed part of another PhD project (Ortega, 2022). The IDEAS project required an LDS layer for the PV devices being installed within a CPC system. From this the research for this thesis separated into research milestones such as the fabrication and upscaling of LDS, improving the LDS layer fabrication process, implementation of MNPs into a polymer layer and the eventual integration into a plasmonic LDS layer. Within these milestones computer simulation and system fabrication and assessment also occurred. For the first demo site there was 400 W power requirement. This could be achieved through the development of 3 LDS CPC systems producing 100W per system. This requires 32 LDS PV cells per system, making a total of 144 PV cells to be layered with the LDS layer.

The CPC's design and functionality significantly influenced the efficiency and effectiveness of the LDS layer in this novel solar façade application. Understanding the CPC is integral to the overall study of LDS-enhanced solar energy systems. The integration of these CPC LDS systems that can produce 100W per system introduces a wider demographic of sectors for renewable

energy sources. The industrial/ commercial sector becomes a more viable area as the larger energy production can supplement usage for water heating or special heating. Thus, reducing the reliance of fossil fuel generated energy. This is focused on the demo site based in Ferrara, Italy. As previously mentioned, for this to be achieved, it requires 4 CPC LDS layered systems to provide 400 W to the desired site. This large-scale LDS layer application will display how LDS layered PV cells will manage integration into a system, how the application of the LDS layer holds up on a larger PV cell, in terms of uniformity and enhancement and reliability in integration into a larger renewable energy system.

2.4.1 CPC

These systems are non-imaging-type concentrating collectors, where incident solar radiation, after reflection from the reflector, is focused on the smaller area, usually a solar cell, and does not produce an image of the light source.

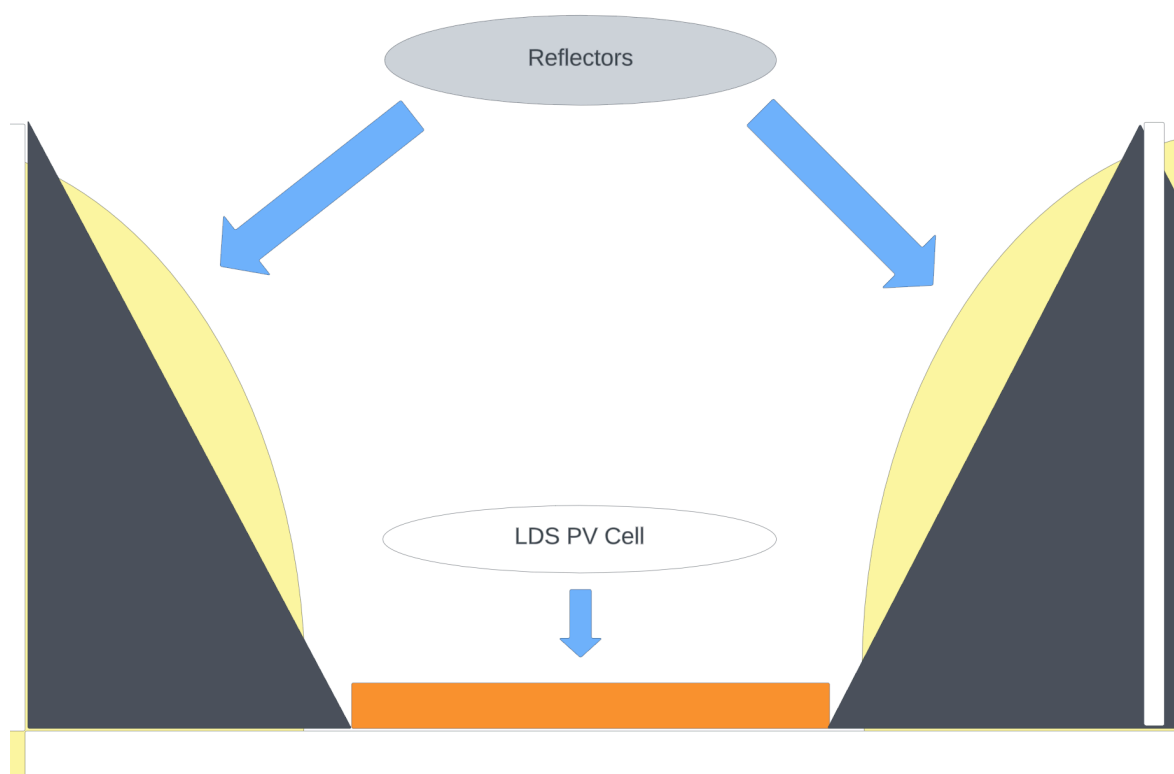


Figure 2.10 Example of reflectors within CPC system, with LDS layered cell.

Compound parabolic concentrators (CPCs) focus radiation from the aperture onto the receiver, as shown in Figure 2.8 (Ortega & McCormack, 2023). Furthermore, these concentrators can effectively collect the incoming beam and diffuse radiation at the absorber

surface (Ortega & McCormack, 2023). This functionality can substantially enhance solar cell performance, resulting in a notable increase in electric power generation per unit area of a photovoltaic (PV) installation [Ortega & McCormack, 2023]. The schematic diagram of a CPC is shown in Figure 2.9, and it consists of two different parabolas (A and B), the axes of which are inclined at an angle $\pm \theta$ concerning the optical axis. (Welford & Winston, 1978) From these CPC LDS systems, 100W is the expected and desired output for the IDEAS project, this power demand will rely heavily on the LDS layered PV cells working effectively.

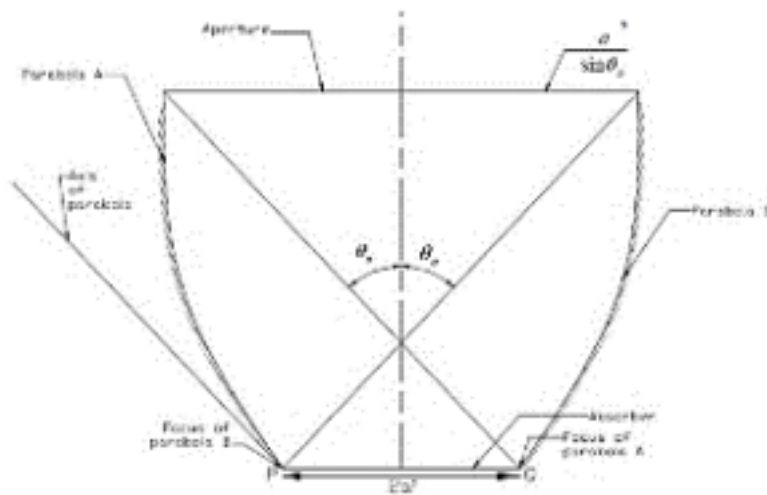


Figure 2.11 CPC structure (Welford & Winston, 1978)

2.4.2 PV Thermal

In addition to the CPC system and the LDS layered cells, some IDEAS systems had a PV thermal (PVT) energy storage system applied to the back of the system plate. Phase change materials (PCM) improved the system's overall efficiency. PCM can provide cooling for PV cells, and when applied to a CPC system, it can be used for energy storage for short-term daily usage. It can store energy by using the difference in the latent heat during the transitioning phase. This is due to the heating and cooling cycle of the day and would vary depending on the seasonal temperature changes. The energy stored in the PCM can be used to heat water in this novel PVT system.

2.5 Weakness in Photovoltaic Technologies

Photovoltaic technology is the main method of solar energy generation, producing voltage and current when exposed to sunlight. Silicon solar cells are made of two different semiconductors, a p-type and n-type semiconductor which are connected through a p-n junction. When sunlight is absorbed, electrons are excited and move from the positive p-type, and holes move to the negative n-type, creating an electric field. This causes positively and negatively charged particles to move in different directions (Boyle, 2004). These semiconductors can be made of various materials; two of the most common are silicon (Si) or gallium arsenide (GaAs). (NREL, 2023)

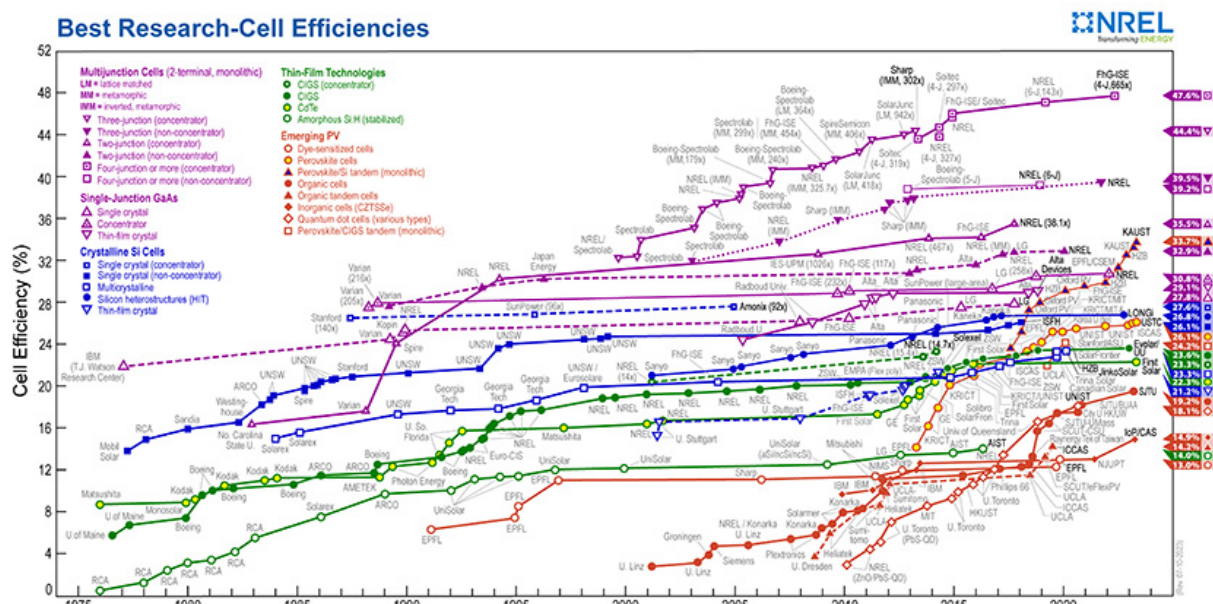


Figure 2.12 PV cell efficiency to date (NREL, 2023)

The first silicon semiconductor photovoltaic cell, with an efficiency of 6%, was fabricated in 1954 at Bell Lab (Boyle, 2004). Since then, efficiency has been constantly improved with the discovery of different types of photovoltaic cells, as presented in Figure 2.12. First-generation PV cells utilise silicon (Si) wafers or crystalline Si for single crystalline (c-Si) and multi-crystalline Si (mc-Si) contribute approximately 90% of today's PV market. With an upper limit for commercial PV cells at 24% (Blakers et al., 2014, Boyle, 2004). Second-generation PV reduces materials by developing thin-film PV while aiming to maintain the efficiencies

achieved in first-generation PV. It consists of amorphous Si (a-Si), Cadmium Telluride (CdTe), and Copper Indium Gallium Selenide (CIGS). The highest efficiency reached for this generation is 23.3% at 14.7 sun concentration for a CIGS concentrator solar cell (ITRPV, 2017).

In 2017, an efficiency of 22.9% was achieved for a CIS cell (ITRPV, 2017), which is different from Figure 2.12. For CdTe PV cells, First Solar attained an efficiency of 22.1% in 2016 (Solar Frontier, 2017). Third-generation PV cells are multijunction cells and single-junction GaAs cells, where the highest efficiency has been reached. This was by four-junction cells at 46% in 2014, measured at a concentration of 508 suns (Fraunhofer, 2014, First Solar 2016). The highest PV multijunction cell achieved was 47.6 %, as shown in Figure 2.12 Emerging PV devices perovskite reaching 26.1% efficiency and a tandem between perovskite and si cells reaching 33.7% in 2023. (NREL, 2023).

There are also emerging PV technologies such as dye-sensitized solar cells (DSSC), perovskite cells, quantum dot (QD) cells, organic PV cells (OPV), CdTe, inorganic cells, and organic tandem cells. For most solar cell technologies, the primary energy loss mechanisms affecting efficiencies are due to the short wavelength photons not being absorbed efficiently by the PV cell (Oxford PV, 2018). The optical response of the solar cell is sharply reduced at shorter wavelengths, specifically in the UV range. Different active and passive approaches have been explored to improve the optical response in the UV range. One of them is shifting the solar spectrum to the range where solar cells are more efficient, which is a passive approach.

2.6 Types of Solar Devices Used

The specifications of the four different types of PV cells used are compared in Table 2.1, demonstrating the difference in outputs and efficiency. Table 2.2 shows the different ranges in which the PV cells operate effectively. Figures 2.13 & 2.14 show the types of PV cells used during this research project.

Table 2.1 Table of PV cell specifications.

Solar Cells	Ppm (W)	lpm (A)	Efficiency (%)	Solar Cells
Monocrystalline si JAC M5SL 2BB	2.6-2.9	5.2– 5.4	17 – 19	Monocrystalline si JAC M5SL 2BB
Monocrystalline (bankonly) si C60 Solar Cell	3.3 – 3.4	5.8 –5.9	21.8 –22.5	Monocrystalline (bankonly) si C60 Solar Cell
a-si Am-5610	0.018	0.0046		a-si Am-5610
CdTe			12	CdTe

Solar Cells	Dimensions (cm)	Bus bar (mm)	Weight (g)	Manufacturer
Monocrystalline si JAC M5SL 2BB	12.5 x 12.5 x 2	2		JA solar (Vikocell, 2023)
Monocrystalline (bankonly) si C60 Solar Cell	12.5x12.5 x1.6	7.1		SunPower (SunPower, 2010)
a-si Am-5610	0.025x0.02x 0.018		2.2	Panasonic/Amorton (Panasonic)
CdTe	50 x 50 x 0.1		55	Antec Solar BIPV (IDEAS WP1, 2022)

Table 2.2. The spectral range of solar cells tested.

PV Type	Starting nm	Ending nm	Encapsulation
Si	400	1100	Open
CdTe	300	900	Encased
a-si	400	1100	Encased

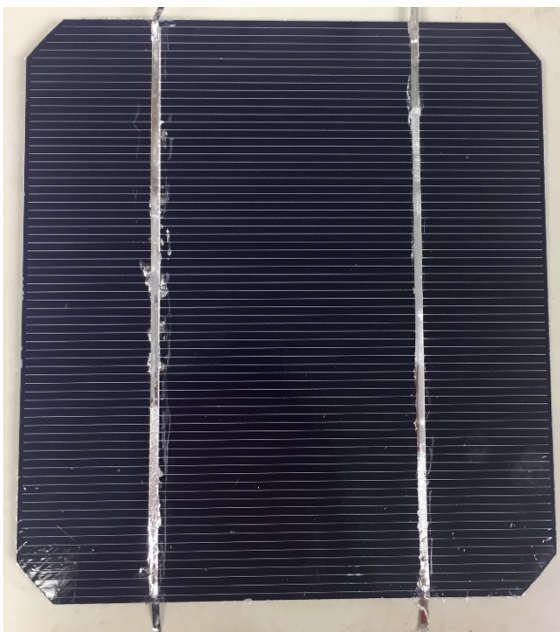


Figure 2.13 (A) Monocrystalline front back busbar. only

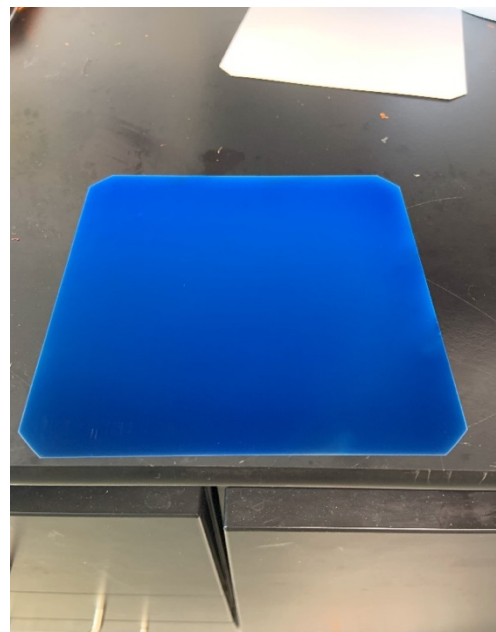


Figure 2.13 (B) Monocrystalline back busbar

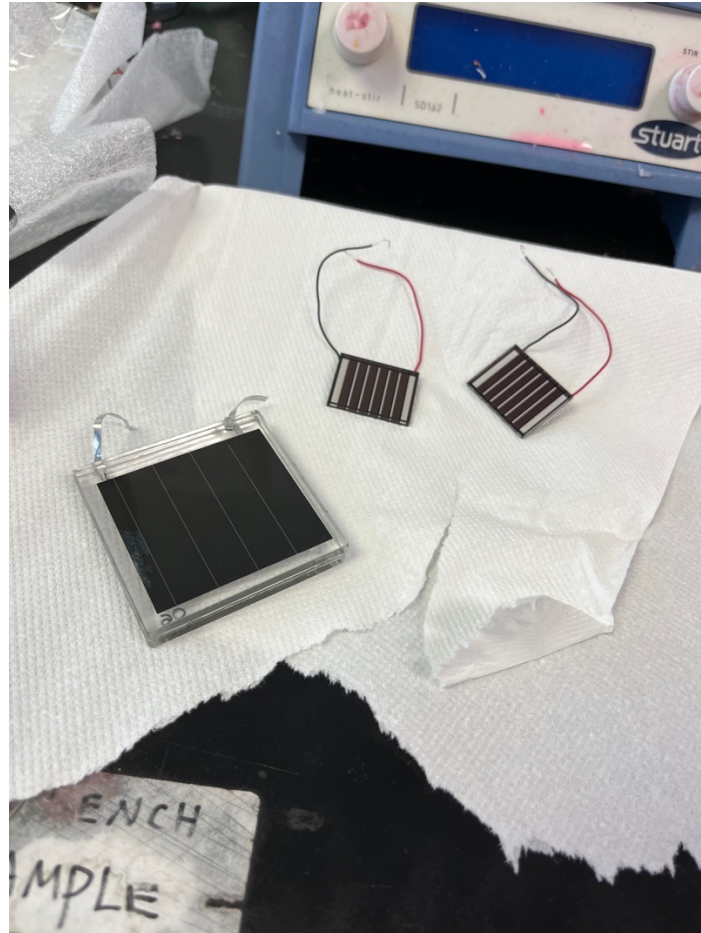


Figure 2.13 (C) CdTe (Left) and a-si (right) PV cells.

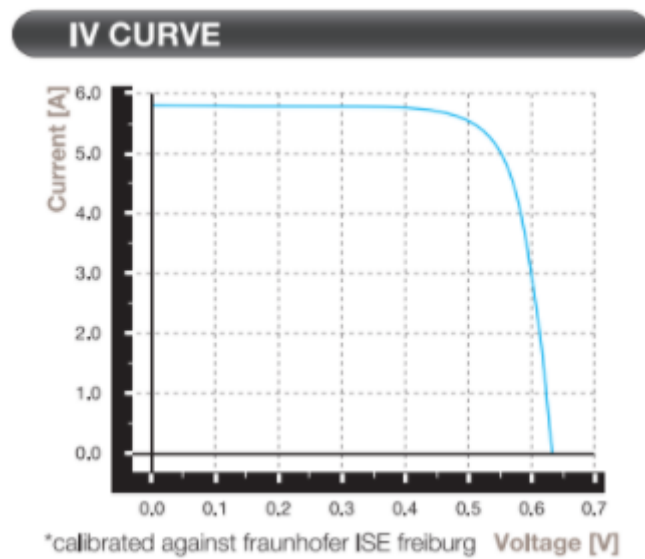


Figure 2.14 I-V Curve of a PV cell used. [IDEAS WP1, 2022]

Figure 2.14 shows the I-V curve of the PV back busbar cells used, provided by the manufacturer.

2.7 Passive Process for Solar PV Technology Improvement

There are various methods of enhancement that can be applied to PV devices to improve their efficiency and/or power output. These methods include the previously mentioned LDS layers, Luminescent Solar Concentrators (LSC), Phase Change Materials (PCM) in Thermal Energy Storage (TES) and system orientation for shadow topologies. These are the passive process since it does not change the solar cell structure and modifying basic photovoltaic principal

1. LDS: These are thin film layer materials that are applied to the surface of photovoltaic (PV) cells to enhance their performance. These layers contain luminophores, compounds that absorb high-energy photons from sunlight and re-emit them as lower-energy photons. This process converts short-wavelength, high-energy light (such as ultraviolet light) into longer-wavelength light (such as visible light) that is more efficiently used by the PV cells. LDS layers improve the overall efficiency of solar energy conversion by optimising the spectral properties of the incident light. LDS layers can be applied to various PV devices with varying success in enhancement, ranging from 3.2% on a GaAs PV device up to 19.8% on a semitransparent organic solar cell (Cho, 2023). Due to this variety of device applications and enhancement, LDS layers were proposed to be further developed in this research project.

2. LSC: is an optical waveguide made from a transparent host material doped with luminophores. This technology captures incoming solar radiation, converts it to a desired wavelength band, and concentrates the light through total internal reflection to the edges of the LSC, where a PV solar cell is attached. However, during the process of guiding solar radiation, a significant number of photons are lost due to mechanisms like re-absorption, attenuation, scattering, and escape cone losses, which reduce the optical efficiency of the device. In a review by Rafiee, there was found to be an enhancement of 20% in optical efficiency. (Rafiee et al., 2019)

3. TES: Photovoltaic-thermal (PVT) hybrid solar systems enhance electricity production by cooling the PV panel and utilising the extracted thermal energy to heat water. A mismatch often exists between power generation from renewable energy sources and demand. Thermal energy storage systems help bridge this gap between supply and demand. A PVT solar hybrid system increases electrical power output by cooling the PV panel with heat transfer fluids, thereby simultaneously generating thermal energy. The use of PVT systems through the usage of PCM has yielded improvements between 10.66% - 12%. (Ma et. al, 2019)
4. Shadow topology: Uses the shaded areas and patterns experienced on PV systems to reduce the losses due to the lack of sunlight reaching the PV system. Fixing the orientation of the PV to optimise the system potential. Using the shadow topology, there showed a 13.2% power enhancement in the systems and a reduction in a power loss of 496W (Mishra et. al, 2017)

2.8 The benefits and challenges of Luminescent Down-Shifting Layer (LDS)

Luminescent materials can alter the solar spectrum and shift the wavelength range to improve the PV power conversion efficiency (PCE) (Mckenna et al., 2017). Two different architectures have been widely explored to integrate down-shifting converters with PV cells: (i) Luminescence down-shifting layer (LDS), which is a planar design, where the down-shifting material is applied as a luminescent coating on the top surface of the PV cell (Klampafits et al. I 2009) and (ii) Luminescent Solar Concentrator (LSC), in which the luminophore is either coated on or doped within, a transparent waveguide slab, that has solar cells coupled to its edges (Debiie and Verbunt, 2012).

For improved performance, LDS materials must have a high emission efficiency, and the material emits the majority of the absorbed light photons at a separated wavelength peak, large Stoke's shift. Otherwise, the LDS material would be hindering the absorption by the device underneath. Also, the material's optical absorption band should not overlap with the absorption of the active layer in the PV cell. Thus, LDS materials absorb higher-energy photons and converts the wavelength to one closer to the PV cell's maximum external quantum efficiency (EQE).

Similarly to how the optical absorption band of the LDS material should not overlap with the absorption band of the device underneath, the absorption band and the emission band of the LDS layer should be separate. As mentioned above, this separation is referred to as a Stokes shift. A Stokes shift can occur when luminescent materials are used for down conversion by the LDS layer. This is from Stokes' Law, which states that the energy of the emitted light is lower than that of the absorbed light. Hence, the emission at longer wavelengths. The difference in energy is the Stokes' Shift. (Yusof Chan, et al, 2021)

Nonradiative relaxations are not entirely understood but occur by transferring small amounts of energy through molecular or atomic collisions. These result in the generation or transfer of heat energy but do not cause the emission of a UV or visible photon. A prevalent form of relaxation is the emission of a photon with equivalent power to the absorbed photon, (Henry, 1999)

In addition to the PCE enhancements, since LDS layers absorb higher energy photons, it is possible to select luminescent materials whose optical absorption is in the UV region of the solar spectrum. In this way, LDS converters could also impact the long-term stability of solar cells by reducing harmful UV absorption in the active layer. Whilst a UV filter could fulfil the same role, the LDS layer does not block the incident UV light but uses it for enhanced photocurrent generation (Chandra et al., 2023).

Luminescent down-shifting involves the conversion of high-energy photons to lower-energy photons that can be more efficiently absorbed by the solar cell. The LDS are placed on top of the photovoltaic material without changing the solar cell's cell architecture or electrical properties. Ideal luminescent down-shifting material should exhibit:

- A broad absorption band in the range of enhancement.
- The high absorption coefficient.
- Narrow emission band in the peak conversion efficiency region of the photoactive material.
- Good separation between absorption and emission bands.
- Low cost (Klampafits et al., 2009).
- High chemical and physical stability for long-term durability.

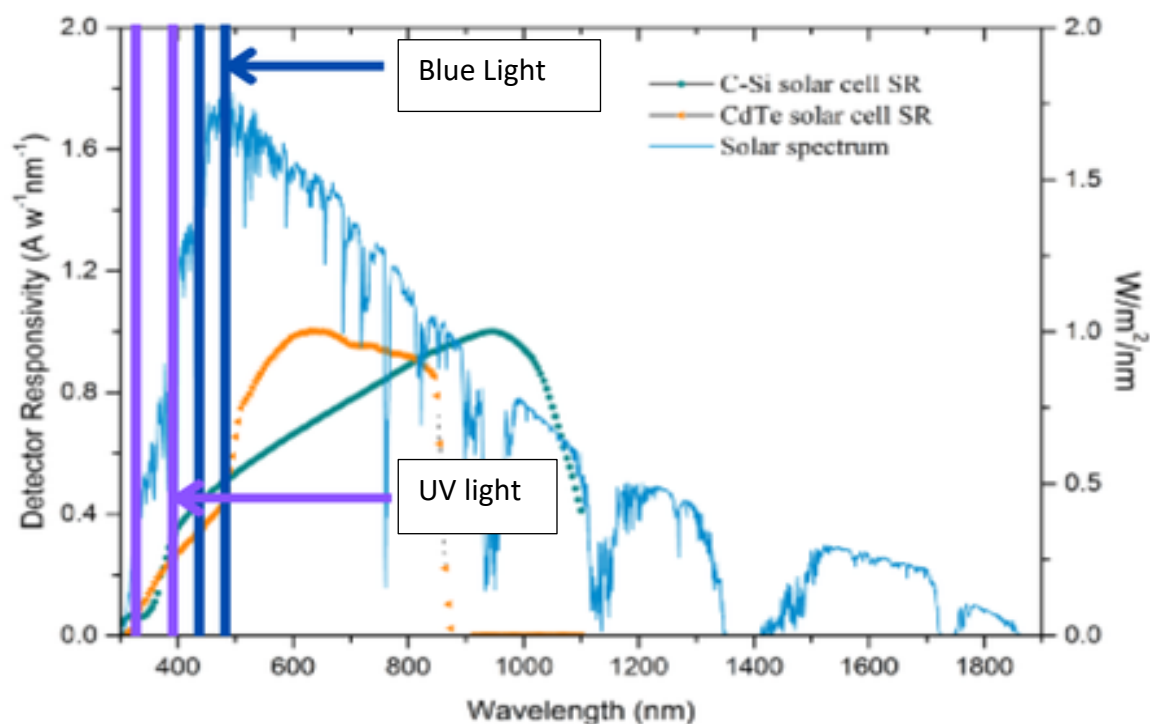


Figure 2.15 Spectral Response of c-Si and CdTe solar cells' EQE compared to the solar spectrum (Klampafits et al. 2009)

For most solar cells, the optical response of the photoactive material reduces in the lower wavelengths (blue and UV), as illustrated in Figure 2.15. Figure 2.15 shows the optical response of silicon and cadmium telluride (CdTe) solar cells concerning the AM1.5 solar spectrum. The reaction of the two PV cell types is significantly lower in short wavelength regions. Adding an extra layer on top of the photovoltaic material introduces an additional loss mechanism for the cell.

2.9 Energy Losses in LDS

While there is a high potential for increased efficiency, some optical loss mechanisms are associated with adding LDS layers. Any potential increase in efficiency needed to counter these losses arises from the spectral down-shift mechanism, resulting in an overall improvement (Klampafits et al. 2009). These losses are mainly contributed by the host material and the luminescent material (Klampafits et al. 2009):

- (1) Parasitic absorption is an optical absorption process by host material: It competes with band-to-band absorption to decrease the photocurrent because not all the photons reach the PV cell, as a fraction of them are absorbed in the LDS layer.
- (2) Emission at less than unity luminescent quantum efficiency (LQE): the ratio between the number of photons emitted and the number of photons absorbed by luminescent materials, less than unity, can lead to the loss of the total number of photons.
- (3) Reabsorption: Occurs due to partial overlapping of absorption and emission bands of luminescent species.
- (4) Escape cone/side losses: side losses occur in the LDS, like the PV. The escape cone refers to the area where photons are emitted out of the LDS following an initial interaction within the LDS layer through an angle, that is smaller than the critical angle, that is, on the top surface area of LDS layers.
- (5) Increased reflection: Usually, the host material is a polymer with a refractive index greater than 1. As the layer can change the PV's reflectance value, the reflection has increased with the refractive index.

To counter these loss mechanisms, a shift in the solar spectrum is required in the range where PV cells are more efficient. Shifting high-energy photons to lower energy or longer wavelengths is known as down-shifting (NREL, 2017). This process changes the wavelength of the incident photon before it can reach the solar cell and, therefore, can be tuned to be used with all types of solar cells. (NREL, 2017).

Figure 2.16 illustrates a schematic of an LDS, in which a layer of a luminescent material doped polymer (PMMA) on top of a PV cell. (Klampafits et al 2009)

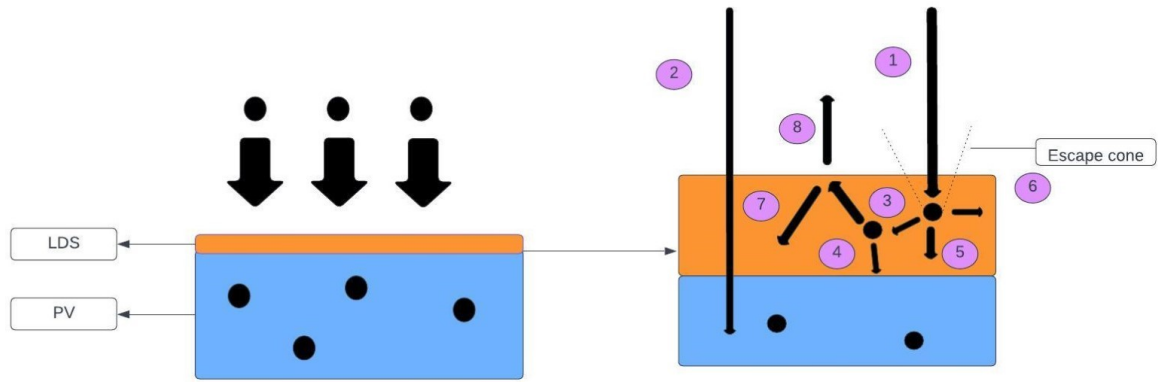


Figure 2.16 LDS Layer applied to PV (Chandra et al. , 2024)

In an LDS, incident light is absorbed by luminescent material and re-emitted at a longer wavelength. Most of the light is directly emitted to the cell or, through total internal reflection at the point where air and the LDS layer meet, is emitted into the cell, as shown in Figure 2.16. Light can also reach the PV cell by transmission, reabsorption, and re-emission, where photons interact multiple times within the LDS layer, eventually absorbed by the PV cell underneath. A portion of emitted light will be lost from the LDS layer's top surface due to the loss of the escape cone or side escape cone. Light may also be transmitted directly to the cell if not absorbed by the luminescent species.

2.10 Host Material

A polymer is used as a host material to develop an LDS layer, it must be:

- Transparent in solar spectrum wavelength range, specifically in UV and visible light with no parasitic absorption.
- Mix effectively with the luminescent material chosen, remain chemically stable when incorporated, and have high photostability, which is ideal. Still, UV-stabilizing agents can be added to improve the photostability. (Shockley & Quisser, 1961, McIntosh et al., 2009, Rothemound, 2014 Cass et al., 2022)

- Be compatible with solvent and luminescent materials to provide an optimum environment for dissolving and uniformly dispersing the luminescent species.
- Be able to endure the thermal treatment that solar cells are subjected to during their application and drying (when heated drying is used).
- Exhibit prolonged photostability over the extended periods of 20–25 years. PV manufacturers guarantee a minimum of 80% of the initial performance of their modules [Sunpower, Sharp Corporation, Sanyo Corporation].

Polymers most frequently used as host materials include polymethyl methacrylate (PMMA) or polyvinyl acetate (PVA) (Kawano et al., 1997 Matchionna et al., 2006 LeDonne et al., 2008). Polyvinyl alcohol is a polyhydroxy polymer; it is the largest synthetic, water-soluble polymer produced in the world. It is produced commercially by the hydrolysis of poly (vinyl acetate) (PVAc)(Jelinska et al, 2010). Polyvinyl alcohol has excellent film-forming, emulsifying, and adhesive properties. It is also resistant to oil, grease, and solvents. PVA is odourless, non-toxic, and has high oxygen and aroma barrier properties, (Jelinska et al, 2010)

Polymethyl methacrylate (PMMA) is most used as a host material for LDS. It is a highly transparent polymer that has proven to have long-term stability. It was tested to be stable for over 17 years in desert sunlight (Wilson & Richards, 2009). Long-term stability is essential for long-lasting applications in the real world, as devices are expected to have a lifetime of at least 20 years. PMMA exhibits high transparency in the spectrum's visible region, essential for solar applications and has a high mechanical strength. They are also compatible with organic dye molecules used in LDS fabrication. This means the luminescent dye is dispersed into the polymer solution uniformly, so once applied, the LDS layer will have an even distribution of the luminescent dye.

PMMA based layers need a reliable method of application that is repeatable and consistent. Spin coating is a commonly used method that ensures the application of thin film layers as reported in the literature (Nassier & Shinen 2022). The uniformity from the spin coating is very useful for LDS layers as the thickness of the layer is a key aspect for the layer effectiveness. This will be discussed further in section 3.3.2. It is ideal for fabricating LDS thin films via spin-coating (Nassier & Shinen, 2022, Geissler et al., 1996). More significant losses

through parasitic absorption can occur through an increased thickness LDS. Larger LDS produces a larger surface area, meaning a photon can travel further to reach the PV substrate. This increased distance also increases the probability of photon interactions within the LDS. With more interactions, there are increased chances of self-absorption within the LDS, leading to a parasitic effect from the LDS.

PMMA can have environmental impacts in the pre- and post-fabrication of an LDS layer and the eventual disposal of the material. Fortunately, if the PMMA used is fabricated correctly, it releases no pollutants into the environment (Semaltianos, 2007). If correctly separated, the polymer can be recycled mechanically or chemically in many cases. (Semaltianos, 2007)

Table 2.3 Comparison of Polymer for LDS (Regalado et al. 2020)

Characteristics	PMMA	PVB
Dissolvability	YES	YES
Luminescent material dispersion	YES	YES
Over 95% Transmittance	YES	NO

2.11 Luminescent Species

For a Luminescent species to be used, ideally, it requires characteristics (McIntosh et al., 2009, Gilligan, 2019):

- A unity luminescent quantum yield (LQY).
- A broad absorption band in the region where the EQE of the PV cell is low.
- A high absorption coefficient.
- Large Stokes shift to reduce reabsorption losses.
- A narrow emission range occurs where the EQE of the PV cell is highest.
- Low cost.
- High chemical and photostability.

Without these characteristics being met, the luminescent species could produce a negatively impactful LDS layer which causes loss' within the LDS layer and can reduce the effectiveness of the PV device underneath. For example, if the absorption band of the luminescent species is in the same wavelength range of the PV device it is applied to, the increase in absorption of other wavelength ranges is made redundant. In case of the small stoke shift between the absorption and emission band, then there can be an overlap of absorption and emission occurring at the same wavelength causing a loss in effectiveness of a potential LDS layer.

There are different types of luminescent materials, including:

- Photoluminescent materials: These materials absorb photons of light of one wavelength range and emit photons at another. These act as a passive activation addition to a polymer layer. They do not require activation and can be easily applied to PV devices.
- Ultraviolet phosphors: Absorb light in the ultraviolet region and emit light in the visible region. Some materials will convert light to a longer wavelength of ultraviolet. As a persistent luminescent material, Ultraviolet phosphors once activated can remain in an afterglow state, where they continuously work until completely discharged. This afterglow can last for a short time, only minutes or a long period up to months such, as safety signage and bioimaging. (Xiong & Peng, 2019) This lack of activation control can make it difficult to apply and enhance PV devices.
- Infrared-emitting phosphors: These are used in applications featuring electronic detection of the phosphor. It is commonly used for imaging and examination in the food industry. The range of which is in the near-infrared does not enhance the desired PV device in silicon. Silicon-based PV, as previously discussed in section 2.4, is effective between 400-1100 nm, which includes the near-infrared at 700-1400 nm. (Song et al., 2019)
- Up converters: Known as anti-Stokes phosphors. They can convert infrared wavelengths into visible light. Used in monitoring and medical imaging, working in the near-infrared to the visible light range. Used for instant image identification so long-term application with a PV device will have a negligible effect. (Strassel et al., 2021)
- Radioluminescent materials: Also known as scintillators, are very good at stopping and converting high-energy particles or beams into light. Used in radiation detection and require

an active activation process, this does not align well with an installable PV system as the system is used for passive energy generation. (Maurizio et al., 2022)

- Cathodoluminescence materials: These are excited by the impact of electrons and are cathodoluminescent. A cathode ray tube (CRT) generates these electrons. Used for the identification of impurities in materials through spectroscopy. (Bok & Schauer, 2014) Again this material is used for an instant imaging application and not a long-term passive activation required for a PV system.

Many organic dyes can exhibit relatively high absorption coefficients, close to unity LQE, and dissolve completely in polymeric matrices. Their drawbacks are narrow absorption bands and relatively small Stokes-shift, which can result in significant re-absorption losses. Several dyes can be mixed within one layer to improve their absorption bandwidth and expand their Stokes shift (Sloof et al., 2007). Their photostability over prolonged periods of UV exposure remains unreliable in some dyes, which remain amalgamated. Although significant improvements have been reported in recent years, there are already commercially available dyes that have been photostable for many years (Griffini et al., 2015).

Luminescent material introduces significant losses resulting from adding an LDS layer. A non-unity LQE gives rise to energy loss from the excited luminescent species by non-radiative relaxation (either molecular or ionic). Reabsorption losses are significant, especially for some organic dyes, when high concentrations are used (Griffini et al., 2015).

A slight stoke shift is associated with organic dyes overlapping in the absorption and emission bands.

This limits the range of the solar spectrum utilised; it, in turn, can limit the effect of a luminescent dye's ability to contribute to the effectiveness of the LDS layer on the PV cell's absorption (Griffini et al., 2015).

Another luminescent material commonly used for LDS layers are quantum dots (QDs), which are semiconductors constrained in all three dimensions, possessing optical and electronic characteristics distinct from their bulk materials. Most QDs can produce light at specific wavelengths when stimulated by light or electricity. One remarkable feature of QDs is that their optoelectronic properties rely on the nanocrystals' size and configuration. Typically,

smaller QDs (with a radius of approximately 2-3 nm) emit light at shorter wavelengths, resulting in colours like violet, blue, or green, while larger QDs (with a radius of about 5-6 nm) emit light at longer wavelengths in the yellow, orange, or red parts of the spectrum. Due to the influence of quantum confinement, QDs are stable when exposed to light, possess wide absorption ranges, emit light with narrow and symmetrical spectra, exhibit slow decay rates in their excited states, and have broad absorption capabilities. The colour of their emitted light is determined by their size and chemical composition, structure, and surface chemistry. (Ahmed, 2014, Garcia de Arquer, 2021).

Rare earth (RE) ions have been used in spectral conversion due to their abundant energy level arrangements, which enable effective photon control. The significant fluorescence lifetime duration, well-defined emission spectra, minimal long-term environmental impact harm, and exceptional resistance to photodegradation make rare earth ions promising choices for various optical applications. (Chang et al., 2019, Duan et al., 2021) One intriguing application of rare earth ions are in photovoltaic (PV) cells, where they are utilised for transforming ultraviolet (UV) and visible (Vis) light into near-infrared (NIR) light. Europium (III) (Eu) complexes have been successfully incorporated into luminescent down-shifting (LDS) layers to enhance the efficiency of copper indium gallium selenide (CIGS) and crystalline silicon (c-Si) solar cells. (Yadav et al., 2016). However, the rare-earth material particles are micro-meter in size and can increase the reflectivity of the LDS layer. (Yadav et al., 2016)

In this section, a summary of the various types of luminescent species and their various applications has been discussed in detail. The different types of luminescent materials showed that photoluminescent materials are the best match for luminescent application to PV devices such as silicon PV as that is the main PV technology used in this research. The passive activation and ease of integration of these materials are both important factors in determining an effective additive to a polymer-based solution for LDS layer fabrication. Expanding further on luminescent materials such as QD and RE as additional additives to further increase the enhancement capabilities of a photoluminescent material as part of an LDS layer.

2.12 Development of LDS Layers

2.12.1 LDS enhancement

The enhancement of photovoltaic (PV) cell efficiency through Luminescent Downshifting (LDS) layers is influenced by several factors. These include:

- Type of PV cells used.
- Optical properties of the luminescent material.
- Overall optical efficiency of the LDS layer.
- Choice of host polymers.
- Thickness of the LDS layer.

Each of these factors plays a critical role in determining how effectively the LDS layer can improve the performance of the PV cells. When a polymer-based LDS layer was applied to different Si-PV, it increased their maximum efficiency by 20.4% (mc-Si) (Gavrilute et al., 2016), 10.5% (a-Si) (Schultz et al., 2004), and 25% (c-Si) (Bergmann et al., 2002). These LDS layers complemented the PV cells underneath, as each PV cell has different interactions within the solar spectrum and require different absorption and emission bands to achieve an enhanced efficiency output. Hovel Fabricated an LDS layer combining the materials used in the two previous papers: a plasmonic LDS (pLDS) comprising silver nanoparticles and Lumogen 083, a yellow organic dye (Hovel et al., 1979). In 2005, a planar converter on CdTe contained quantum dots (QDs) in a transparent host material was that deposited on top of a mc-Si solar cell. After testing at different solar radiation intensities, an increase in power was observed, with QDs emitting at 603 nm yielding a short-circuit current increase of 6.3%, 9.6%, and 28.6% for direct, global, and diffuse irradiation, as a result of the larger blue/green content of diffuse spectra with respect to direct and global ones (Van Starkk, 2005). The next step was the introduction of the Lumogen dyes (BASF) 570, 083, 240, and 300 into PMMA and found under the illumination of AM 1.5G that there was an increase in performance of 0.37 mA/cm², which showed there was a 10% increase (Van Starkk, 2005). The first pLDS layer was produced and

tested for maximum fluorescence enhancement using QD enhanced PMMA based layer. The potential enhancement was found to reach up to 60% (Ahmed, et al. 2017).

$\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ a polymer-based layer on top of a CdTe solar cell with an efficiency increase of around 21% (Ahmed et al. 2017). For a perovskite/si cell in tandem, an LDS layer of 3 different colours was able to produce an increase of 13.1%, 11.2%, and 13.6% for the coloured dyes red ($\text{Eu}(\text{TTA})_3\text{Phen}$), green ($\text{Ir}(\text{ppy})_3$) and blue (BC_zBVi) respectively. (Bernal-Correa et al, 2023). Part of the development of PV technology with an LDS layer is the improvement of the longevity of the cell viability. UV radiation can cause cell degradation and reduce efficiency by up to 11% through exposure (Jung et al., 2023). UV exposure effectively disrupts surface passivation by changing the fixed charge density and increasing the interface defect density near the Si surface (Sinha et al., 2023). To combat this degradation (Sinha et al., 2023):

- A UV absorber material can be added to the PV module or as part of the cell design. Materials that include benzophenone in the makeup can help reduce UV degradation.
- An encapsulant, such as glass, can be used. However, photon interaction with the LDS and PV cell can be reduced if an encapsulant is used. If the glass has an anti-reflective coating designed to minimise UV radiation. For example, the addition of Ce-doped glass to minimize discolouration of ethylene-co-vinyl acetate (EVA)(Werner et al., 2014).
- An addition of an anti-reflective coating can reduce UV degradation. (Klemchuk et al, 1997).

It is important to remember that while this process can reduce and block UV radiation, it can also hinder the effectiveness of LDS layers in improving the PV cells absorption.

The use of plasmonic interaction allows the manipulation of the optical properties of luminescent materials, therefore, the increasing the optical efficiency of the LDS layer (Ahmed, 2014, Richards & Howard, 2023). Plasmonic nanoparticles such as, silver nanoparticles (Ag NP) are used as a nanostructure that is combined with a polymer (PMMA) and an inorganic dye to make a layer that is deposited onto a PV solar cell. Light interacts with MNP; it excites the surface plasmon resonance (SPR) at the surface of MNPs, it can result in a surface plasmon polariton. In this state, the electric field associated with the light is highly

amplified in a small evanescent region near the surface of the metal nanoparticles (MNPs).

There are two enhancements due to the presence of MNPs:

- an increase in the excitation rate of luminescent material
- an increase in the luminescent quantum yield (LQY).

Both are a function of the plasmonic resonance of MNPs, (Ahmed, 2017). Improvements have been made to LDS layers using the plasmonic interaction of Ag NP for Eu-doped phosphors; an improvement of 26.17% was observed, as demonstrated in Figure 2.17 (Richard & Howards, 2023).

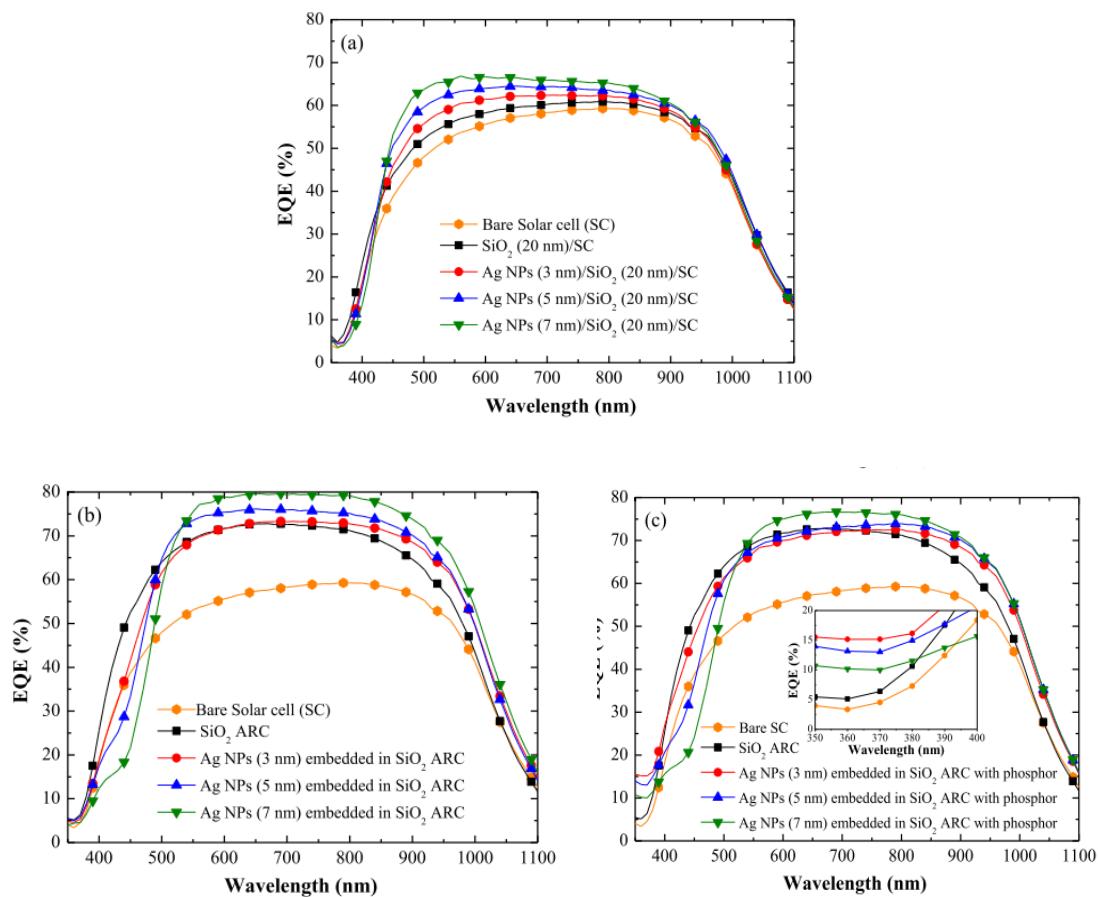


Figure 2.17 EQE responses of (a) cells with AG NPs of various diameters deposited on SiO_2 spacer layers; (b) cells with Ag Nps of various diameters embedded in SiO_2 ARC; and (c) cells with Ag NPs of various diameters embedded within SiO_2 ARC mixed with EU-doped phosphors. (Richard & Howards, 2023)

Kumar compared Ag NPs doped on the SiO₂ cells with embedded Ag NPs. Which presented an overall increase during EQE testing. (Nilesh Kumar et al., 2019).

This was replicated by Richard & Howard, who compared two doping methods: using a spacer layer and embedding doping Ag nanoparticles. They presented an overall increase of 10% in EQE testing in the range between 550-1000nm (Richard & Howards, 2023).

The integration of plasmonics into an LDS layer has dual benefits. The excitation band is produced and increased by adding an LDS layer, the addition of Ag MNPs can further broaden the bandwidth while simultaneously improving the PV cell's UV degradation resistances while being coated with YVO₄:Eu³⁺, Bi³⁺ *YVO₄: EU³⁺ Bi³⁺* with Ag MNPs (Wu et al., 2023).

The factors that can influence the potential of an LDS enhancement have been presented in this section. The added doping of PV devices with MNPs through the LDS have shown enhancement through EQE comparison. The MNP enhancement needs to be tested with LDS layer compatibility and then application. The multiple aspects affect the potential enhancement achieved by an LDS layer can lead to a long time of research spent testing in a trial-and-error method to determine the best combination of aspects that complement each other and the PV device underneath. A very important part of this testing method is modifying one singular aspect while maintaining the rest as the same throughout testing. The use of a computer simulation can reduce the time invested in the trial-and-error of repeated testing and reduce any inconsistency that may appear during the fabrication of samples.

2.12.2 LDS Modelling and Simulation

To optimise the LDS layers parameters, LDS devices are modelled in 3D using the Monte Carlo ray tracing (MCRT) algorithm, where the specification of the used materials, including different loss mechanisms such as escape cone loss, reabsorption, reflection, attenuation, and scattering, are considered in the model. Ideally, these loss mechanisms should be at 0%. However, this is not realistic as there will always be losses associated with an LDS layer, but a losses reduction close to 0% is the focus. When these losses are lower, it produces an optical efficiency output that can approach 100%. For this research, an MCRT model has been developed as an interactive software ("Ray Tracer"). The desire to have a consistent method

of potential luminescent enhancement testing pushed the development of this model. Both LSC and LDS layers can be tested using this method. Meanwhile, due to LS device development requirements, the program was designed with the ability to model and optimise both single and multi-layer LDS layers. To determine which type of layer, whether LDS or LSC is simulated, the relevant plane sensor is required to be activated. This will be discussed further in Chapter 5. Currently there is a limitation restricted to the simulation of LDS or LSC only with no MNPs being added. This aspect is still currently under development.

In the developed Ray Tracer program, solar radiation is represented by photons (rays), and the designed MCRT algorithm determines the fate of each incident ray based on the probability of different optical procedures such as reflection, absorption, scattering, attenuation, while it is travelling through LDS layer (Rafiee, 2019).

Rothemund presented a previous use of theoretical modelling to determine the potential effective EQE of an added LDS layer onto various types of PV cells (Rothemund, 2014). As mentioned in section 2.7.1, the EQE of the LDS can be a practical guide to the potential beneficial addition of the LDS layer. The model demonstrated by Lipovšek showed the possible usage of ray tracing-based models that can track the photon interaction with the LDS layer (Lipovšek et al. 2015). The model discussed in this section further evaluates a potential layer by producing the full output projection of the LDS-layered PV cell—the output, accompanied by the percentage of optical efficiency and the lost or absorbed rays.

2.13 Conclusion

This chapter has explored vital areas significant to the research of LDS layer advancement. It highlighted how policy goals related to energy use and their emissions illustrate the urgency for the accelerated development of renewable energy systems. The comparison between Ireland and Italy shows that both countries like many others have been slowly but surely accepting renewable energies in most recent years and show encouraging signs of reduced investment into fossil fuel-based fuel sources. The energy usage per sector also showed that even though the countries are not dissimilar they both need to provide stable renewable

sources in the same areas such as domestic, industrial (commercial) and travel. The introduction of the IDEAS project portrays a direct LDS layer implementation with a power output of 100W needed. From this broad implementation comes the diversification of this research project focusing on the development and improvement of the LDS layer and the eventual pLDS layer.

The progress in developing and improving PV technology continues upward, which can be further improved by adding an LDS layer. The host material being determined allows a more focused approach to the development of the LDS layer being fabricated. How the LDS layer interacts with the PV device underneath with the aspects in which losses can occur highlights the areas of focus for a usable LDS layer. The selection of luminescent material was chosen based on the most versatile option as there would be potential application across various types of PV technology, while also being able to produce an enhancement percentage that can influence the power output of PV devices currently being used. LDS materials and the latest advances in research have been presented. The addition of doping an LDS layer with MNPs can further increase the enhancement potential of the layer if the compatibility of both aspects can be achieved.

It has been found that more research is needed on the larger-scale development of LDS layer applications to be used in large PV systems. This has led to many possible avenues to explore. Along with the upscaling from small LDS layers, from 2 x 2cm to 12.5 x 12.5 cm, there are challenges, such as maintaining uniformity of the layers through the fabrication process and homogenous distribution of the luminescent dye within that polymer solution. Furthermore, incorporating metal nanoparticles to produce plasmonic enhancement and create a pLDS layer can further increase the efficiency of the solar cell. The following thesis chapters will outline the steps taken in this research to address some of these gaps in the literature.

Chapter 3. Experimental Methodologies and Techniques

3.1 Introduction

This chapter introduces the ways that best produce an LDS layer that is viable for PV cell application. The LDS layer requires a reliable fabrication method that can mix the chosen chemical solution, the powdered polymer and the luminescent material. This will require a process that can constantly mix the material. Also, the absorption and emission spectra are to be measured in both a liquid and thin film form. This will require a spectrometer and an integrating sphere to determine the sample absorption and emission spectra, respectively. The LDS layers EQE needs to be used as a comparison of the LDS layers' effectiveness when applied to a PV device. This will be used across multiple PV devices to compare LDS' effectiveness on different devices. An external quantum efficiency machine will be needed to determine this. The physical characteristics, such as the thickness of the LDS layer and the uniformity, need to be refined so that the layer can enhance efficiency and not incur losses that were described in section 2.9. The thickness effect on the LDS can be determined through the usage of the EQE machine and its resulting efficiency. Once the thickness is determined, the uniformity can be addressed directly. This requires an application process that can be repeated consistently with the least number of variables changing. Which can be achieved through methods of application. As drop casting and the use of a spin coater.

3.2 Research Tasks

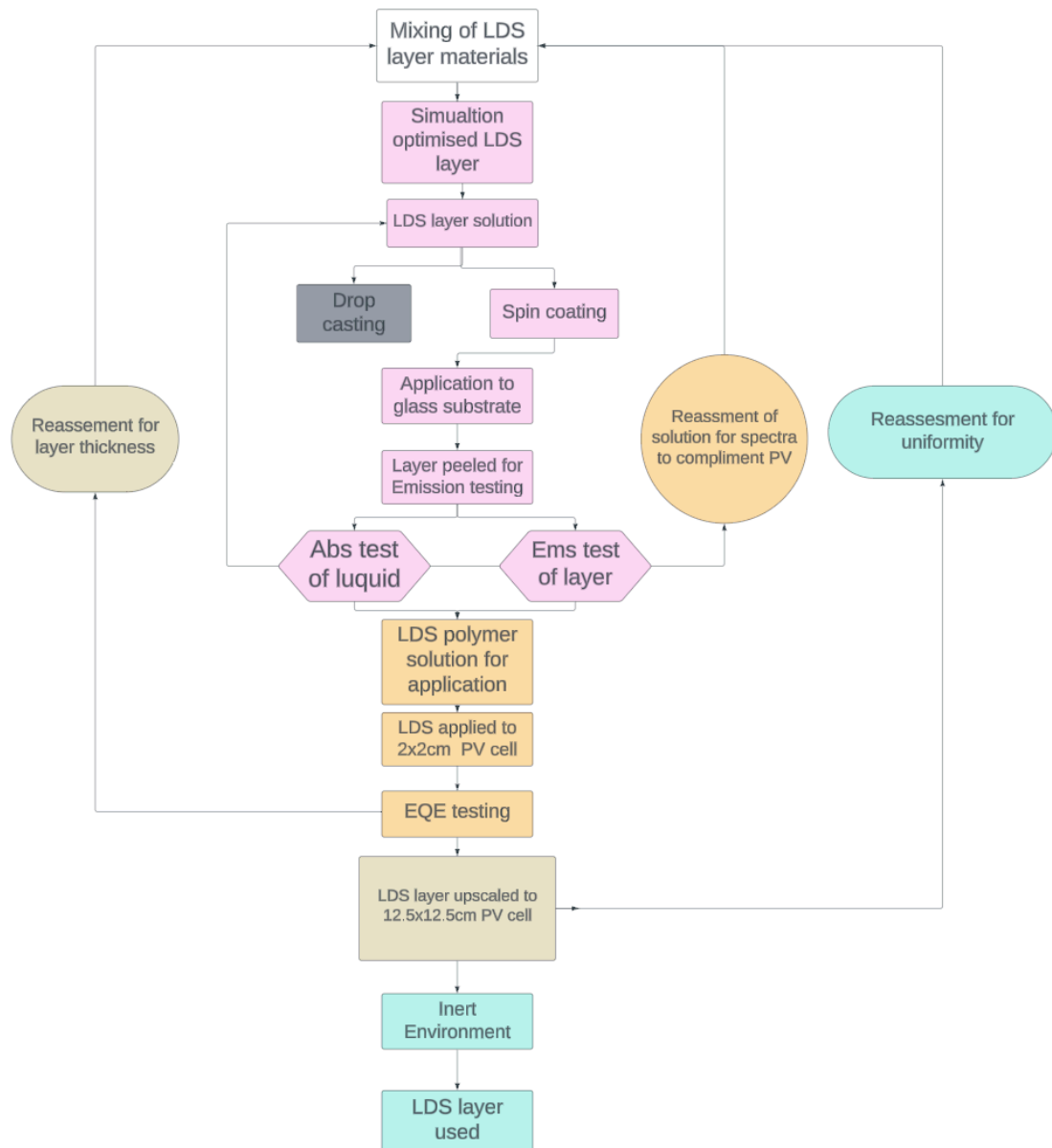


Figure 3.1 Flowchart of LDS layer fabrication process

Figure 3.1 displays the flowchart of the LDS layer fabrication process, and at which point changes or additions were made. The first task is to establish a methodology for preparing a PMMA polymer solution for coating the LDS layer, making it consistent and repeatable for multiple replication and testing.

The second task was to assess the effectiveness of the luminescent dye used in LDS layers. The objective was to find the appropriate luminescent dye and dye concentration in LDS

layers that can effectively shift UV and blue light to the spectral range where solar cells have higher efficiency.

The third task was to manufacture and integrate LDS layers for a CPC system used by the IDEAS project. 4 systems of 32 PV cells were layered with LDS layers. 166 PV cells with LDS layers were made to accommodate any extra LDS layered PV cells needed due to breakages or replacements. These layered PV cells were installed into 4 CPC systems with four rows of PV cells.

The final task was to optimise the processes to improve the quality of LDS layers based on the first aim of the research project. After the manufacturing was undertaken and completed, as stated in the second aim, the re-assessment and optimisation of the LDS layer fabrication were investigated further.

This included reassessing the environment in which the polymer solution is made and stored. To assess other suitable luminescent dyes for further benefits for an LDS layer on the PV cell. Once successfully applied to a surface such as a glass substrate or directly to a PV cell like a silicon PV cell, LDS layers can be used for various PV technologies. The layer application process remains the same; the layer's effectiveness depends on the can vary due to the PV technology since they interact with different wavelength ranges.

The LDS integrated CPC systems milestones align with the IDEAS project timelines for demonstration systems and demo sites. This added an industrial/business element to the research project, working and keeping to targets that colleagues from other institutions and industries would influence.

3.3 PMMA Polymer Solution

3.3.1 Preparation

The mixing process and layer fabrication materials that were used throughout this research work were:

- PMMA was chosen host material polymer.
- Chloroform was used as the solvent to prepare the polymer solution.

Both were selected due to their longevity and stability under prolonged exposure to high temperatures, ease of preparation of the solution, compatibility with solvents, achieving desired LDS layer thickness, and thermal polymerisation (Geissler et al.,1996, Semaltianos, 2007) (as discussed in section 2.5 and presented in table 2.1).

PMMA is available in solid and powdered forms and can easily dissolve in a chloroform solvent. Chloroform was used to improve the processability of PMMA in spin-coating by facilitating the formation of uniform, stable and high-quality coatings while also being compatible with integrating additional functional materials (Bergmann et al., 2002). Chloroform was also chosen because it does not react adversely with MNPs or affect their distribution within the polymer solution. It evaporates at room temperature, which helps dry the layers. This stability is crucial for maintaining the desired properties of the composite material, especially when the goal is to enhance the material's functionality with additives like MNPs or luminescent materials, as discussed in section 2.7.1.



Figure 3.2 Magnetic stirrer hot plate. Note the heat function was turned off.

Firstly, the ratios in which the solvent and polymer are mixed can vary the viscosity of the polymer mixture. The initial ratio for the polymer solution was 2.3:10; for every 2.3 g (13.7 wt%) of PMMA powder, 10 ml (86.3 wt%) of chloroform was added. The solution was stirred using a magnetic stirrer (as in Figure 3.2) at a temperature of 23°C at a spin speed of 500 rpm for approximately 40-60 minutes, depending on the solution being made. These conditions enabled the full dissolution of the PMMA powder into the chloroform solvent to prepare a solution. 500 rpm was used as any higher speeds would cause the solvent to be spun too quickly which would in turn, causes the powdered PMMA to conglomerate together and the dissolution to take longer. The speed used was increased to 700 rpm when more layers were needed to be made per batch. This was achieved through speed ramps of 50 rpm; as previously mentioned, if too high a speed were used, the PMMA would take longer to dissolve. This accommodated the increase in the volume of polymer solution in the batches. Stock solutions were made in batches using these ratios. These batches of stock solution were made in quantities of 30 ml chloroform as their base, with 6.9 g of PMMA.

The luminescent dye was added through two different methods:

- (1) Direct powdered form: the required amount of dye was added directly to the polymer solution as it quickly dissolved.
- (2) Dye stock solution: the dye was added to a chloroform solution at a desired concentration, i.e. 1 %wt, and then added to a polymer solution.

This was used to add a reliable concentration from the same batch of dye stock solution. However, it is essential to note that this alters the total chloroform amount in the polymer solution and changes each aspect ratio %wt, so some adjustments were required to achieve the desired layer thickness.

The direct powdered form method is used during the large-scale fabrication process to fabricate and apply an LDS or pLDS layer to a PV cell. This was due to the time requirements of the milestones related to the IDEAS project.

However, the dye stock solution was more viable when conducting more investigative methodologies, as all the testing could be linked to a single batch. Since a single batch of dye solution could be used in multiple polymer solutions, it provides a consistent LDS polymer solution to be created. As there is reduced variability in solution fabrication. Any area for variance or changes being reduced can improve the fabrication process.

3.3.2 LDS Layer Fabrication

Drop casting and spin coating are two distinct techniques for applying polymer solutions to substrates, each has specific advantages and disadvantages for fabricating polymer layers.

Drop casting: This method involves depositing a polymer mixture/solution onto a glass slide to produce a polymer layer; this layer can subsequently be detached for analysis if required. It is advantageous for evaluating the polymer layer's absorption and emission spectra and determining the concentration ratio of a polymer solution.

Spin coating: Utilising a polymer solution, spin coating achieves a uniformly dispersed polymer layer on various substrates, including glass and PV cells. This technique uses large droplets that upon impacting the substrate, spread and wet the surface due to their momentum, providing greater control compared to drop casting coating. However, the

requirement for a flat surface and the reliance on gravity and centrifugal forces for even spreading the polymer solution restricts its application to small-area films and coatings.

For the small-scale LDS layer fabrication, the polymer solution was applied using the drop cast methodology on 2 cm x 2 cm glass slides and PV cells. This was due to the fact that the smaller sized glass slides or PV cells could have an evenly uniform LDS layer applied as they could be applied using a syringe of 3ml of LDS polymer solution. The desired uniformity consisted of an even distributed layer that shared the desired thickness, which is 20 μ m. When upscaling to 12.5 cm x 12.5 cm PV cells, the ratio of PMMA at 18.7 %wt was inadequate to meet the desired physical characteristics of layer uniformity and thickness. The LDS layers were attempted to be applied using the drop cast method; however, the layer uniformity and thickness of 20 μ m could not be achieved consistently. After the drop cast method was found unreliable, a spin coater was used to deposit LDS layers. This will be discussed further in section 3.8.2. The LDS polymer solution was altered to 3.83 g of PMMA to 10 ml of chloroform, a 27.7 %wt of PMMA. For this mixture, the mixing speed was also increased to a maximum of 700 rpm for 60 minutes.

The longer the stirring period was used to completely dissolved PMMA in the solvent for homogenous solution. This was particularly important as any excess particles in the layer could lead to optical loss mechanisms, such as parasitic absorption and scattering.

These changes to the dye polymer solution to fabricate LDS layers are essential when considering the obstacles faced when upscaling from a small 2 x 2 cm layer to a 12.5 x 12.5 cm layer. In the simplest terms, a small 2 x 2 cm LDS layer area on a small 2 x 2 cm surface would have a relatively low margin for error and any imperfections or inconsistencies would also be on a small scale on the 2 x 2 cm PV cells.

However, the margin for error also increased at a larger size of 12.5 x 12.5 cm. The negative effects, such as physical defects due to lack of layer adhesion or dispersal, can also increase. Large-scale fabrication is a development from smaller scale fabrication, but both separately have a purpose in LDS layer development. The changes made between the two fabrication processes were to aid in improving the large-scale process while not reducing the effectiveness of the small-scale process, which produced a viable LDS layer.

3.4 Optical Characterisation

3.4.1 Absorbance Measurement

Absorbance measurements were performed using an Ocean Optics spectrometer containing a UV-VIS-NIR light source connected to an enclosed cuvette holder via optic fibre. This was then connected to the BLACK-Comet-SR Super Range Concave Grating Spectrometer, which measures from 220 to 1100 nm. The light source has dual lamps of deuterium and tungsten halogen, which can be individually turned on or off. It provides a range of 190 to 2500 nm. This setup was controlled by the software SpectraWiz. The integration time and number of averages can be set per sample. This data was then exported in an Excel format for analysis. This experimental setup is shown in Figure 3.3. This equipment setup was used due to the flexibility in sample size and shape testing, as the LDS layer can be tested in a physical layer as a polymer solution, and on the glass substrate. Both of these can be tested in the cuvette holder. While, an industry-used spectrometer does not have this type of flexibility to test the different sizes and shapes of samples; it has standard sample holders which can take a particular size of sample

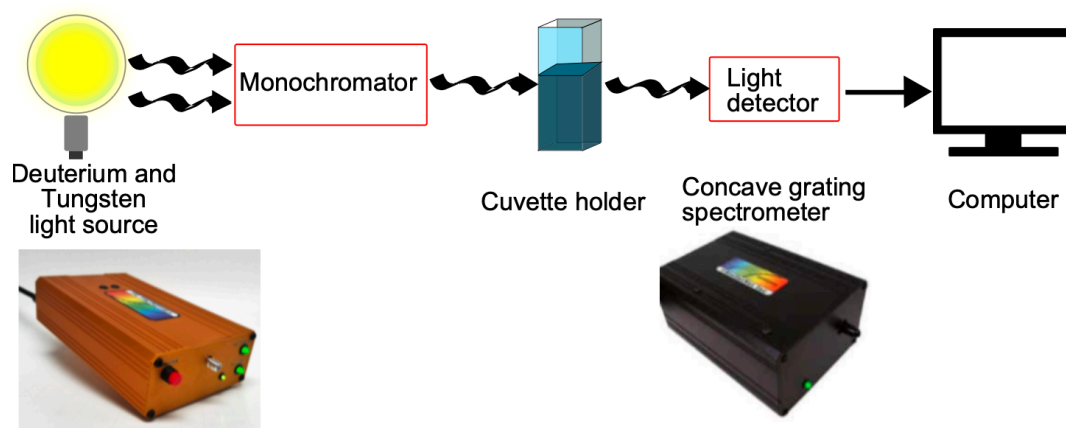


Figure 3.3 Schematic of Absorbance detection (Sethi et al., 2019)

3.4.2 Emission Detection

Emission measurements were undertaken using an integrated sphere, as illustrated in Figure 3.4. Emission measurements for the dye doping concentration optimisation and photostability tests were conducted using a AAA class oriel solar simulator light source focused on a wavelength filter, collimated to a LabSphere integrated sphere. This was connected to a BLACK-Comet-SR Super Range Concave Grating Spectrometer used in the StellarNet Inc absorbance setup. The filter used for a sample depends on the excitation wavelength needed. This setup uses the SpectraWiz software; the integration time and averages are set per sample, same as the previous absorption detection. The excitation light is collimated beam of diameter of 5 to 11 mm depending on the fibre optic used. The dye samples used in this setup were thin films held in the integrating sphere. The excitation wavelength can be chosen by changing the filter, i.e., 380nm, 405nm. This equipment setup was used to collect the total emission from the different sizes and shapes of LDS samples, including the liquid and solid film. The sample holders are designed to hold both solid film and cuvette samples. Moreover, the excitation light was supplied from a solar simulator through a customised system of filters that allows certain wavelengths to pass through. Since the solar simulator supplies the excitation light that allows the use of very deep UV light for excitation, as the solar spectrum was AM1.5G.

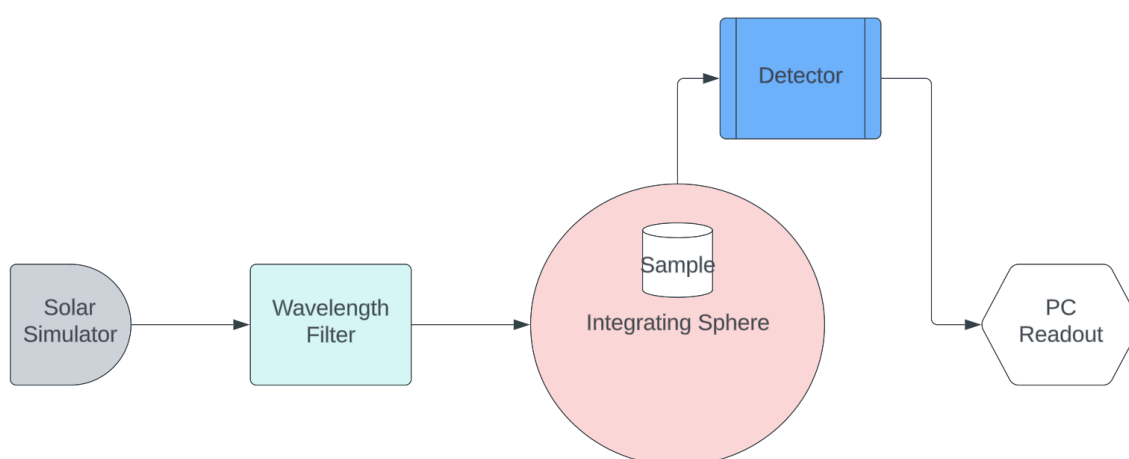


Figure 3.3 Schematic of Emission detection set-up.

3.4.3 Quantum Yield

The quantum yield is a measurement to check the efficiency of photon emission as defined by the ratio of the number of photons emitted to the number of photons absorbed by luminescent materials in the film and its intrinsic properties of luminescent materials. However, it also depends on the host medium of the luminescent materials. Therefore, measuring it for LDS layers can give the overall QY of layers. QY is normally shown as a percentage, it is an indicator of the interaction rate of downshifting of photons hitting the PV cell. This measurement indicates whether the amount of photon energy produced by the LDS layer can increase or decrease the efficiency of the PV cell or have no overall effect. The closer to 100%, the greater the enhancement achieved of a luminescent material. For example, the luminescent dye provided by Sigma Aldrich is methyl orange. It is at 70%, according to their data sheet (Sigma Aldrich).

3.5 Electrical Characterization

3.5.1 External Quantum Efficiency (EQE):

EQE is the ratio of the number of charge carriers collected by the solar cell to the number of photons of a given wavelength that is incident on the solar cell. This can be used as an indicator of how efficiently the PV cell is converting the photon's that interact with the solar cell, into electrical output. 100% EQE means the complete absorption and conversion into charge carriers at the corresponding wavelength; therefore, it can give a wavelength-dependent interaction of photons to the solar cell That helps to identify the wavelength range that requires modification or shift in the range where PV is more efficient. . It uses the bare PV cell without an LDS layer as a reference. EQE can determine the impact of LDS layers on solar spectrum modification by evaluating photon interaction with solar cells at each wavelength of the solar spectrum, whether it improves interaction, decreases the number of interactions, or has no effect. If the LDS layered PV cell produces an EQE percentage that is

greater than the initial PV cell without the LDS layer applied, then the LDS layer has enhanced the PV cells absorption. Overall, it can help to optimise the LDS layer parameters of thickness, doping concentration, and suitable luminescent dye. A schematic of the set-up is shown in Figure 3.5 (A), and the physical set-up used to determine a sample's EQE can be seen in Figure 3.5 (B).

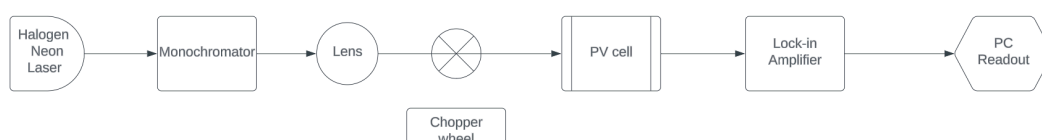


Figure 3.5 (A) Schematic of EQE experimental set-up

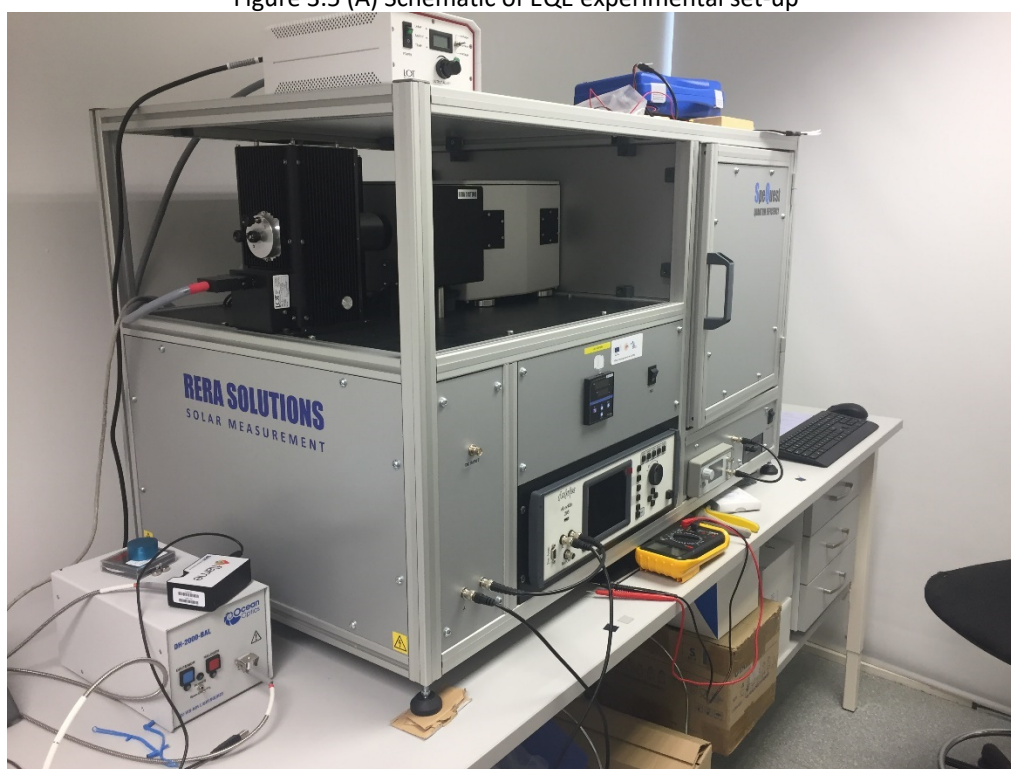


Figure 3.5 (B) Image of EQE machine

To optimise dye concentration and efficacy of the LDS layers, the ReRa Solutions SpeQuest instrument was used to measure the EQE, the schematic for which is shown in Figure 3.5 (A) and the physical set up is as shown in Figure 3.5 (B). This setup is a combination of a xenon light and halogen light source with a range of 300 to 1800 nm, an IV converter, a bias light driver, a monochromator, and a chopper. The diameter of the light spot is 4 mm, and it is directed at the centre of the cell. The system measures the photocurrent generated by the

cell at 10 nm steps. The system is initially calibrated with a silicon reference cell between 300 to 1100 nm. If a wavelength up to 1800 nm is necessary, a germanium reference cell is also calibrated between 1050 and 1800 nm. The test sample needs to be mounted under the beam of light, and the measurement commences using the Photor software.

3.5.2 Electrical Connections

Electrical soldering plays a critical role in assembling a high-performance PV module. This process is used to join different types of metals together by melting solder which is typically an alloy composed of tin and lead. A soldering iron, heated to temperatures above 315 °C is used to melt the solder. On cooling, it forms a durable electrical bond an essential process for connecting individual solar cells within a PV module. The solder station used can be seen in Figure 3.6.



Figure 3.6 Iron soldering station.

After the LDS layers were applied, the LDS layered PV cells were connected in series. Strings with different cell numbers were required to be soldered based on the novel CPC/LDS panel's specific requirements.

One panel used four strings of 11 cells soldered together in series, soldered into the panel at each end, requiring 44 cells to be connected, as shown in Figure 3.7.

After the successful fabrication and application of uniform LDS layers onto 12.5x12.5cm PV cells. The PV cells are layered, they can then be soldered and integrated into a CPC system. These systems are used in the IDEAS project. The IDEAS system used Silicon solar cells (presented in Table 2.1). One type had a front and back connection, while the other had back connections only. For the solar cell interconnection, a lead solder wire with alloy metal Sn-43Pb-14Bi (Almil Serie: KR-15) of 0.65 mm diameter was used with the soldering iron heated to 400 °C. A flux pen (ECO-WORTHY) was used to enhance the soldering process. For the solar cells with both front and back contacts, it was necessary to solder along the length of the PV cell (12.5 cm) onto the busbar, as shown in Figure 3.7. This was completed on both sides of the PV cell. For the back contact solar cells, soldering was carried out along the flux-marked paths of the dog bones interconnectors to improve the soldering efficiency.

For the front and rear busbar PV cells, a sheet of EVA glue was placed between the PV cells and the surface of the CPC system. EVA glue was used as it is flexible, which is very useful within the CPC system as the LDS layered PV cells cause an uneven surface requiring flexibility to cover. EVA also has strong bonding and quick drying while also preventing short circuit, which again benefits the LDS PV cell, making their placement more stable within the system. Once the PV cells' connections were soldered, the glue was heated using a hairdryer to stick the PV cells to the CPC. The hairdryer was used as it was able to focus a heat source onto a small area without exposing the EVA or LDS PV cells to excess heat after the glue had bonded, while also being very mobile to move around the CPC LDS system.

PV cells were initially cleaned and placed in the PV cell holders for connection, which were fabricated using a 3D printer. The back busbar PV cells were placed into individual cell holders and attached to the CPC system to reduce any extra movement of the PV cells.

As the solar cells are back in busbar contact, the complete string is faced downward on a low iron glass table. In this way, the connection can be made by looking at the back of the cells. Below the low iron glass, two 100 W halogen lamps are used to test each connection of the solar cells to identify short circuits or errors in the connections (Ortega, 2023)

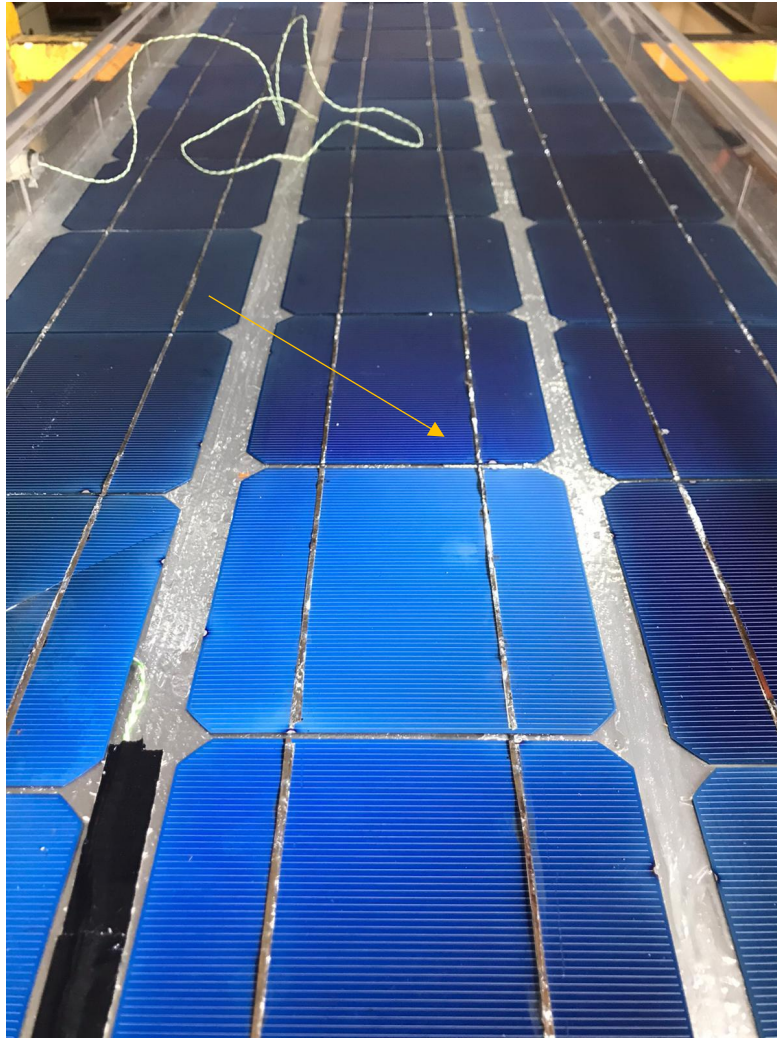


Figure 3.7 String of 11 PV cells connected in series for CPC system.

3.6 Luminescent Dye Selection

Different luminescent dyes can benefit an LDS layer in various ways as they respond to other portions of the solar spectrum; for example, a violet dye impacts the ultraviolet range around 450 nm, while a red dye will have more influence around the 650 nm range. The choice of dye is tailored to match the specific substrate, whether Si-based or CdTe PV cells, taking into consideration the cell's encapsulation, as presented in Table 2.2. Si cells are not encapsulated and allow for direct application of the LDS on the cell, unlike a-Si and CdTe cells encapsulated in glass. The concentration of the luminescent dye is crucial for the effectiveness of the LDS layer (shown later in section 4.4). Adjusting LDS layer concentrations facilitates a thorough

assessment of dye absorption and emission in solid and liquid forms. These concentrations are tested to optimise the dye that has been selected to optimise the LDS layer.

Table 3.1 Different commercial dyes tested.

Luminescent Dyes 0.02% wt	Excitation Abs wavelength nm	Emission peak wavelength nm	Availability
Lumogen Vio 1,8-naphthalimide	451	758	Limited
Methyl Orange	457	600	Readily
Lumogen Red C72 H58 N2 O8	575	612	Limited
Lumogen Ylw C32-H26-N2-O4	406	495	Limited

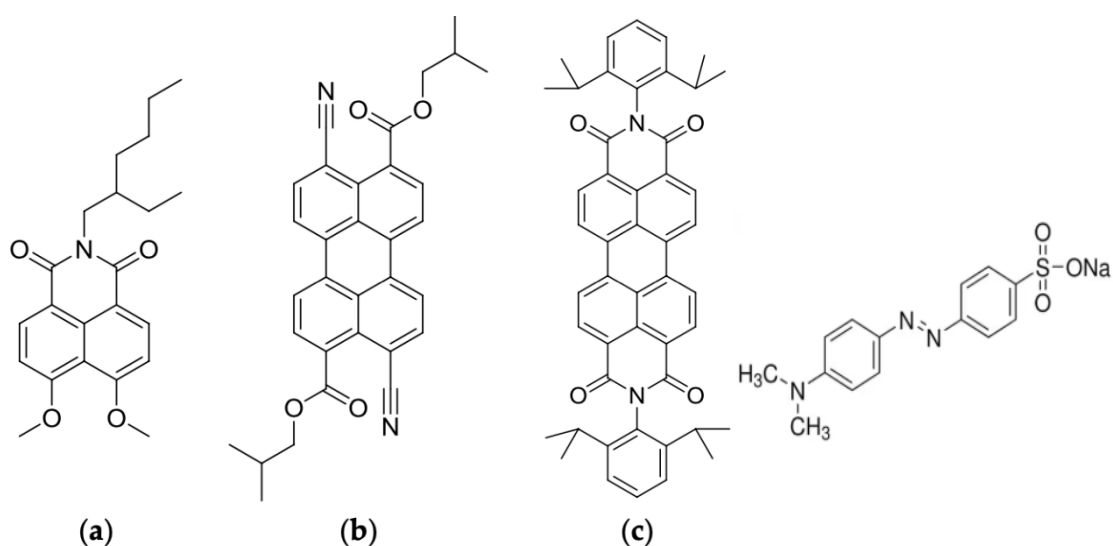


Figure 3.8 Chemical composition of: (a) Lumogen Violet 570 (b) Lumogen F Yellow 083 (c) Lumogen F Red 305 (d) Methyl Orange

Table 3.1 compares the peak excitations of the absorption and emission spectra, respectively. Figures 3.8 show the chemical composition of the luminescent dyes compared.

Another condition to consider is a dye's availability when selecting it for large-scale implementation. As shown in Table 3.1, methyl orange was readily available and had absorption and emission peaks at beneficial wavelength areas. Other dyes continued to be tested on a small scale and/or through simulation (small-scale fabrication and testing are detailed in section 4.4, and the computer simulation is detailed in Chapter 5).

Prior to selecting one or more dyes, LQY can analyse the dye's excitation wavelength, absorption, and emission spectra to identify the most efficient (where an LDS can be produced relatively easily while ensuring a high-quality layer) and effective (where an LDS enhances the power output of the PV cell) dye to use for LDS layers on the PV cells.

This evaluation acknowledges that while the luminescent dye can have a high emission peak, that peak may not align with the PV cell's optimum spectral range. Ideal absorption peaks would occur where the PV cell is relatively ineffective, with an emission peak where the PV cell is most responsive.



Figure 3.9 Image of violet dye simulation

The computer simulation, shown in Figure 3.9, was also used to assess and adjust a selection of dye concentrations and layer thickness to complement the dye selection process. Chapter 6 will expand on this.

3.7 LDS Layer Fabrication:

The desired characteristics for the LDS layer includes a:

- Thickness of 20 μm .
- The acknowledgement and strategy for managing the increasing fragility in the LDS-layered PV cell as spin coating the LDS layer causes additional stresses on the PV cell.
- The dye doping concentration of 0.02wt%.
- LDS layer even and uniform distribution on the PV cell.
- Repeatability and reliability of the fabricated LDS layer.

The optimisation characteristics associated with the LDS Layer, such as thickness, fragility, dye concentration, and uniform coverage, will be explained in more detail in the following sections.

3.7.1 Initial samples

LDS layers were applied by drop casting on 2 x 2 cm glass slides. Figure 3.10 shows an LDS layer sample removed from the slide.



Figure 3.10 Image of drop casting fabricated LDS layer.

The spin coated LDS layers were thoroughly dried in the open air at room temperature, out of direct airflow. This method ensures the layer is more straightforward to peel off without tearing or damaging it. The dryness of the LDS layer is tested wearing latex gloves and lightly placing a fingertip around the LDS layer, that confirms the stiffness of the polymer and no sticking to the latex glove. A polymer layer without the luminescent dye is used as a reference and fabricated using the same methodology described in section 3.3.2.

Measuring the absorption can be conducted on both the liquid and solid forms of the layer. However, analysing the latter in its liquid form allows for the purest absorption spectra, as

impurities such as dust or dirt may contaminate the solid LDS layer. Thus, measuring the layer in a liquid form is preferred for the most accurate and reliable initial analysis.

Emission spectrum testing requires the physical layer as the sample holder within the integrated sphere is only suitable for a 10 x 5 cm physical approximation. This size ensures that the light source can interact with the sample; if it is less than 10 x 5 cm, the light may not interact with the sample, leading to no change in the emission spectra.

Absorption and emission spectral measurements ensure the optical properties stay relatively high when moving from the liquid to the solid polymer.

However, the layer characteristics can vary when using this drop-casting method. LDS layers produced through drop casting can be evenly distributed and uniform; however, repeatedly making the desired thickness can be challenging. Therefore, the spin coating was used for the LDS layer application on PV cells. The thinnest LDS layer achieved was 10 μm . This thickness is following on from the work already completed in Hind Ahmed's work. (Ahmed, 2014). The upper limit of the LDS layer thickness usable within the computer simulation mentioned in section 3.7 is 40 μm . This will be discussed further in Chapter 5.

3.7.2 Spin Coating

This research project is connected to the larger EU IDEAS project, so large LDS layers must be made near the assembly time for the CPC system. This allows the consistency of fabrication of the LDS polymer solution that was discussed in section 3.3.1. So, the LDS layers being applied can be produced in batches that were initially fabricated at the same time. This also allows long term testing of durability of the LDS layer PV cells during usage in power production. For example, for the first four demonstration panels, 148 LDS layers were required. Therefore, a quick and reliable method was needed, and a spin coating machine was used. A spin coater (G3P-12 Systems), shown in Figure 3.11, was used to fabricate LDS layers. The spin coating speed can be programmed between 0 to 9,999 RPM, an acceleration/deceleration time of 0.1 to 25.5 seconds, and a dwell time of 0 to 999 seconds. The resulting film or layer's thickness varied depending on the solution's viscosity, the spin

RPM, the dwell time, and the evaporation rate. Following on from previous work by Glenn (Glenn et al., 2020) to spin coat 10 μm LDS layer on a 2x2cm PV cell; a 3ml LDS polymer solution spun at 750 rpm for 180 seconds. In order to produce a thicker layer, the spin speed remained the same with a change in acceleration as the catalyst for change. There was a speed ramp introduced where 500 rpm would be used first for 10 seconds then a ramp up to 1000 rpm for the remaining 170 seconds. This delay allowed for the LDS polymer to polymerise and harden slightly then spin any excess solution off. Thus, producing a 20 μm layer. To achieve thicker layers the dwell time at 500 rpm is extended by 10 seconds. Each 10 seconds was found to thicken the LDS layer by 10 μm . Once achieved for the 2x2 cm PV cell, the next step was the attempted application of an LDS layer onto a 12.5x12.5cm PV cell. The same speed, dwell times and time taken was used with a higher LDS polymer solution of 10 ml. The resulting layer produced was at the desired 20 μm . By changing these variables, different thicknesses of the LDS layers were achieved.

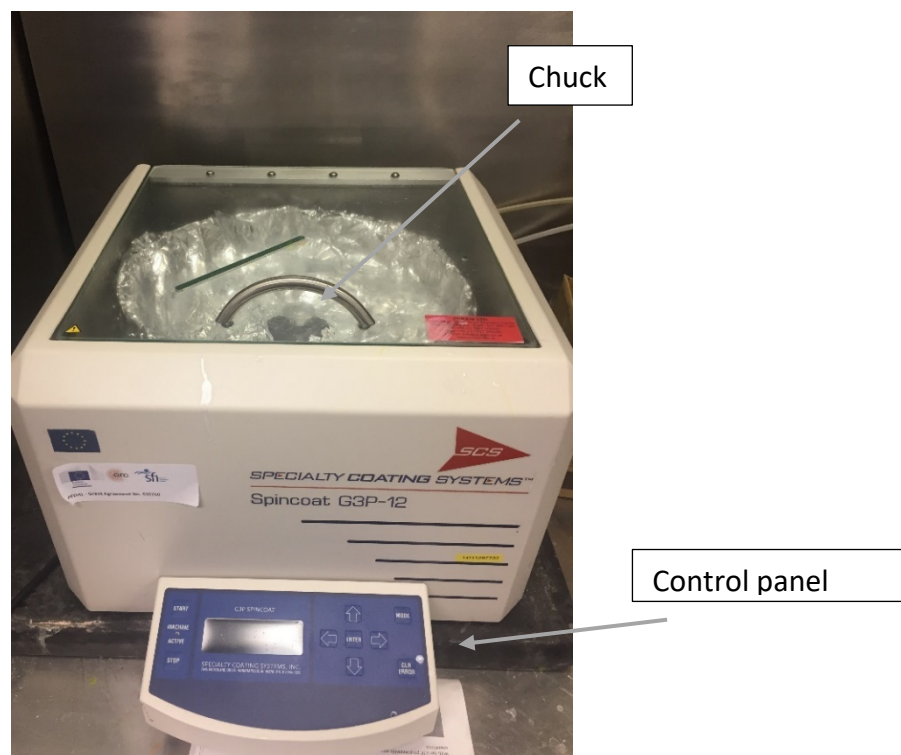


Figure 3.11 G3P-12 Spin Coater System

A PV cell was placed on the chuck and held by a vacuum. The chuck is the holder in the centre of the spin coater. It uses a vacuum tube connected underneath to create a seal between itself and the sample placed on it. The chuck can be changed to hold different PV cell sizes

and substrates. Changing the chuck size is essential as the chuck holds the sample by vacuum suction, preventing the material from being displaced. If the substrate is not secured before spinning, it can begin to spin and break. This is more important for larger-sized samples as smaller samples can fall off and be cleaned for reuse. However, larger samples are more likely to fail.

The solution was manually deposited via a pipette of varying quantities depending on the solution and the layer size required. The solution was placed into the centre of the PV cell; the chuck then began rotating and accelerating, the rotational speed causing the solution to spread outward due to the centrifugal force and coating it uniformly on the solar cell substrate. The PV cell is kept at a constant 1000 RPM. This was found to apply a consistent and usable LDS layer. The optimum RPM was determined when the applied polymer solution could be spread evenly across the desired substrate. The solution was then allowed to evaporate, and a thin film remained on the substrate, which was quickly removed from a glass slide and not easily removed from a PV cell. This is due to the PV cell being more fragile.

3.7.3 Layer Drying Methods

As PMMA thermal polymerisation at room temperature, drying is an essential process in layer fabrication. The drying processes in LDS manufacturing allow the layer to be fully adhered to, ensuring that the layer has been attached successfully, whether there are air gaps or whether peeling has occurred. Drying allows repeatable and reliable layers to be fabricated without damaging the LDS.

Open Air Drying: The definition of air-drying is to leave something in an open area at room temperature so that the surrounding atmosphere and room temperature can cause the chloroform to evaporate, which can occur at 20 °C (Pubchem, 2023). Ideally, the sample is placed out of any air-flow pathway as airflow can cause groves or dips in thicker samples (e.g. above 1 cm). Depending on the polymer mixture, the process could take 1- 3 hours. A sample fabricated from this method is shown in Figure 3.12. LDS layers produced in this figure show one of the first batches successfully applied to LDS 12.5 x 12.5 cm PV cells, demonstrating the method used to dry them. The humidity in the room remains unchanged throughout this

process and is kept at room temperature. In the laboratory, during the drying of the LDS layered PV cells, there is no excess water evaporation from other instruments.

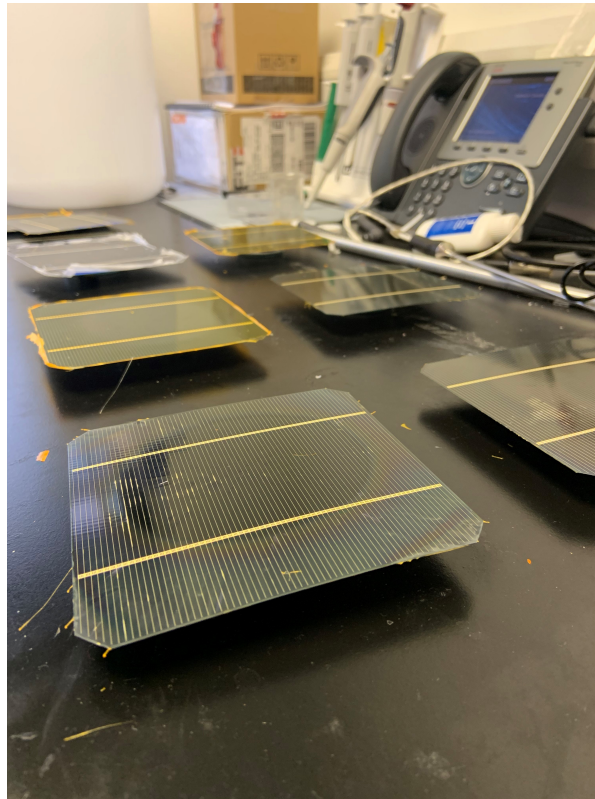


Figure 3.12 Image of open-air drying.

Thermal Drying: This is a process for dehydrating moist products based on moisture evaporation by heating (Norton et al., 2009). The heat of evaporation is transferred to the material, which is dried, either by heated hot gas or smoke fumes—by convective heat transfer or from a hot surface in contact with the material. While this drying mode is faster, if mistimed and the cell is left for too long, it can cause the layer to crack if the polymer solution is uneven. The LDS PV cells are placed on top of a metal piece to avoid any sticking of the PV cells to the oven surface. Any added extra stress to the PV cell can cause fractures. If the LDS PV cells were left over an hour in the oven, the PV cells began to crack. Since the LDS PV cells became more fragile in the spinning process, the added stress from the excess heat causes further fragility leading to fractures. As the thicker sections of the uneven layer harden, they apply more pressure on the substrate. When the substrate is a PV cell, it can cause breakage due to the fragile nature of the solar cell. This is more likely as the PV becomes more fragile directly after the layer application process in the spin coater. This is due to the vacuum holding

pressure while being held to the chuck, causing stress on the PV cell while also continuously spinning at speeds of 1000 RPM for 170 seconds.

The chloroform in the polymer solution evaporates rapidly if exposed to temperatures above room temperature (average 21 °C). So, if the polymer solution is oversaturated or undersaturated with chloroform, the layer and PV cell could be damaged or broken due to chloroform evaporation during thermal drying. An oven (as shown in Figure 3.13) is used for thermal drying.

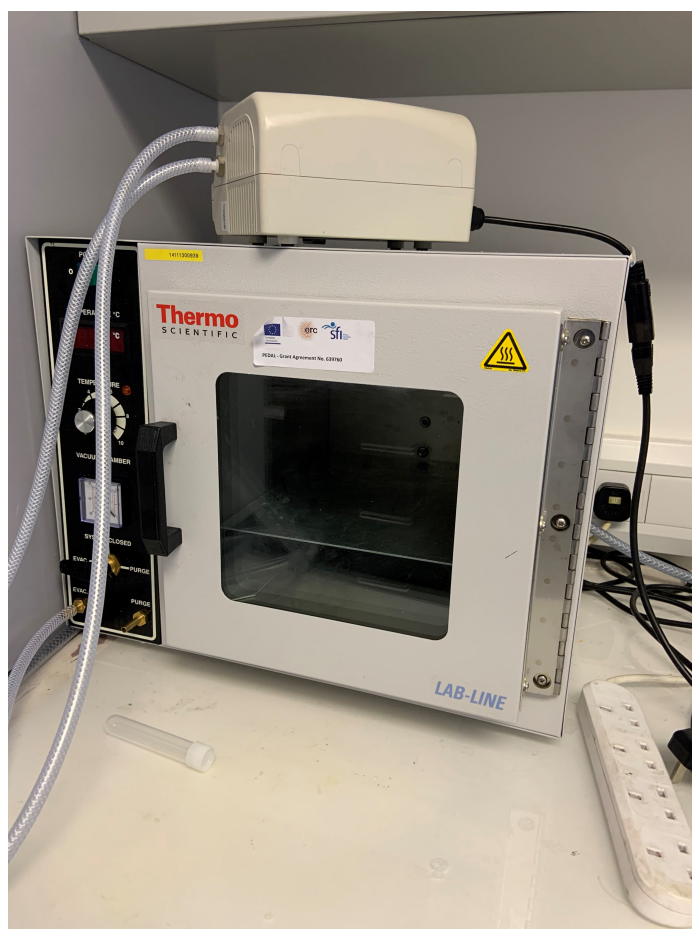


Figure 3.13 Image of oven drying.

3.7.4 Inert Environment

An inert environment is where the presence of reactive elements or compounds is minimised or eliminated. In such environments, the reactions that typically occur under normal atmospheric conditions are significantly reduced or prevented. Therefore, an additive can be applied to a solution without the risk of contamination from reactive gases in the atmosphere, such as oxygen and carbon dioxide. A nitrogen-filled glove box was used to create the inert environment, shown in Figure 3.14, and was introduced to reduce the external variables associated with the mixing process. These variables include oxygen exposure during the LDS polymer solution fabrication process, impurities such as dirt contaminating the LDS polymer solution. This environment was also used during the application process using the spin coater. The polymer solution (of PMMA and chloroform) was initially mixed in an oxygen-rich atmospheric environment under a fume hood. Instead of Oxygen (atmospheric environment), a nitrogen-rich environment was used for mixing. The nitrogen-inert climate was created by replacing atmospheric oxygen with 1 Atmospheric nitrogen pressure.

The process was determined by the standard operating procedure described in the glove box safety manual. A vacuum pump was used to pump the oxygen out of the sealed glove box, and gloves were pulled inwards. Once fully inside, the nitrogen is pumped into the box with gloves extending outwards by approximately 13 cm. This process is repeated three times to purge all the oxygen from the glove box. This inert environment can be maintained for over ten days, depending on usage. It provides fewer impurities (such as dust particles), which can contaminate the polymer solution. The enclosed and protected environment allows for a more reliable and repeatable batch-making process while improving safety measures when working with a substance like chloroform.

Using the nitrogen-inert environment for material processing minimises the experimental variables and has been shown to improve the overall quality of the LDS layer. These qualities include layer uniformity, consistency of the LDS layer thickness and the presence of any impurities. Moreover, it provides a controlled environment, ensuring consistency in using LDS stock solution for fabricating the layers

The inert environment benefits in several ways:

- It prevents the trapping of oxygen and impurities. Fewer impurities can contaminate the polymer solution, such as atmospheric dust particles and oxygen. The enclosed environment avoids the issue of oxygen being trapped in the polymer solution preparation process. This prevents the LDS layer from being damaged by air gaps in the solution and reduces the effect of air gaps when applied using the spin coater.
- The stock solution did not undergo pre-polymerisation during the mixing process, which means there is no pre-polymerisation when applying this solution to a solar cell for LDS layer coating



Figure 3.14 Image of Nitrogen Glove box in Watts lab

3.7.5 Spin Coating in Inert Atmosphere

Spin coating in an inert environment was undertaken by replacing a set of tubing on the spin coater, which is directed into open air, with tubing connected to a Nitrogen cylinder. When the spin coating process begins, a pump evacuates air out of the spin coater while the nitrogen tube fills the main compartment (this instrument is described in section 3.7.2).

The key benefit of a nitrogen-based spin coater (like the inert environment) is the prevention of oxygen-based impurities, such as air bubbles forming in the LDS during the spinning process and the reduction of pre-polymerisation.

Some disadvantages can occur when using nitrogen inert environment. The LDS layer characteristics are altered slightly, most notably by becoming much thinner (discussed in section 5.1). Also, regarding repeatability and gas usage, a higher gas flow rate is required, therefore consuming much nitrogen.

The duration that the nitrogen environment can be maintained in the glove box (figure 3.14) with a volume of 2.1 m³ can extend over several days with proper management and use. Critical practices include vacuuming before opening and ensuring the glove box is sealed off from atmospheric pressure when not in use. As a standard protocol, the inert environment of the glove box was routinely emptied and refilled every 10 – 14 days to maintain optimal conditions.

3.8 Development of Layer Refinement

Modifications were undertaken after delivering and deploying the first LDS layered cells fabricated for the novel IDEAS PV panels sent to the University of Ferrara.

Reassessing the LDS layers and the fabrication process was required, especially in terms of the overall quality of the LDS layer. This entailed evaluating the layer's purity. Purity in this context refers to the absence of contaminants that might impair the layer's functionality, such as dust, residual PMMA from the synthesis process, or MNPs that were not fully dissolved. Such impurities can adversely affect the layers' absorption (as detailed in section 2.4) by introducing optical losses.

The glove box was employed to mitigate the introduction of contaminants like dust during the material preparation stage (as outlined in section 3.8.4). This approach not only reduces impurity ingress but also enhances the overall reliability of the process. Ensuring thorough mixing of the polymer reduces premature pre-polymerisation, leading to a more homogenous polymer dissolution. This consistency is crucial for maintaining the polymer's stability over extended periods, which is very important for testing on a smaller scale. This methodological refinement ensures a uniform layer, enhancing the potential for accurate assessment and application in PV cells.

3.9 Data recording

The instrument used to record data and measure power output was a solar module analyser, as illustrated in Figure 3.16. This solar analyser was selected as it can scan the I-V curve for the PV cell in real time. It also obtains maximum power output, max current, and max voltage and can calculate a solar panel's efficiency percentage. Moreover, it is a handheld device, therefore easy to carry and do the record for outdoor testing.

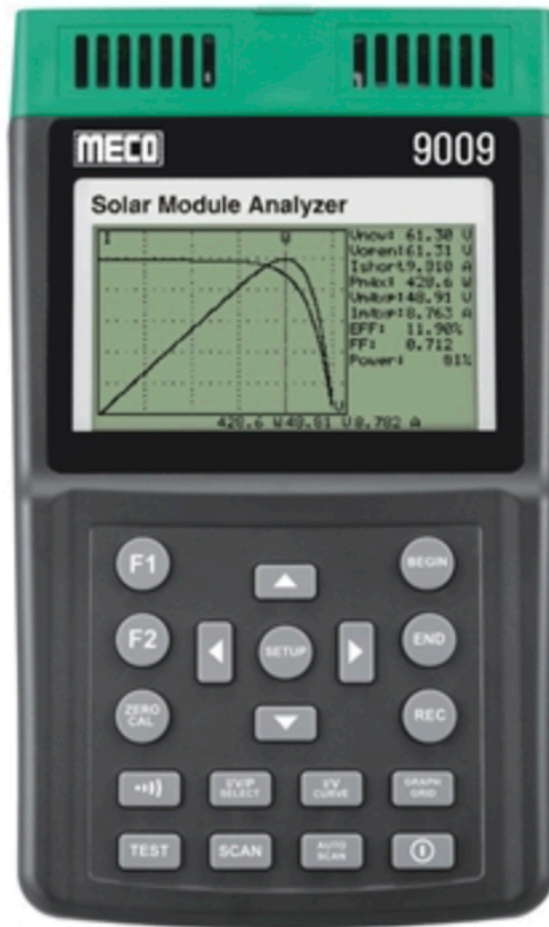


Figure 3.15 Image of solar module analyser

3.10 Conclusion

This chapter discusses the methodologies and techniques for developing and applying a functioning LDS layer to PV technology. The initial methods used for LDS production to achieve an optimum quality layer have been presented. Using a spin coater for the LDS layer application allowed for a reliable and consistent layer. This technique proved effective across a variation of sample size and LDS polymer solution concentrations. The process of selecting an appropriate drying method post-LDS application was straightforward but also reinforced the importance of maintaining factors that would influence the LDS layer's integrity.

Incorporating an inert environment significantly enhanced the quality of the LDS polymer solution's production process. Eliminating oxygen during the mixing process mitigated the risk

of premature prepolymerisation, leading to an overall improvement in the LDS layer quality. This adjustment ensured a more homogenous polymer solution for spin coating, simultaneously minimising contamination risks and improving the purity of the LDS solution.

Optimising the production environment for LDS layers involved addressing the substantial nitrogen consumption required to fabricate individual cells. The extensive nitrogen requirement (over a 2-hour period) to produce single-cell LDS layers poses a challenge to commercial scalability. Continued refinement is required for mass-producing LDS-layered systems. However, the improvement to the production quality has been significantly advantageous.

The successful application of the LDS layer to a PV cell requires:

- A consistent mixing method for the polymer solution, this will reduce any conglomeration of the polymer within the chosen solution.
- A luminescent dye that can complement the PV cell underneath the LDS layer. This can vary depending on the wavelength range desired for increased interaction.
- A clean environment to prevent impurities from contaminating the LDS polymer solution.
- A setting that can be used without oxygen to avoid prepolymerisation of the LDS polymer solution.
- The desired thickness of the LDS layer on a PV cell, the rpm speed used for the spin coater, and the dwell time used can vary the thickness of the LDS layer.
- LDS layer adhesion to the PV cell
- Uniformity, consistency, and repeatability of LDS layer fabrication
- A stable electrical connection, in this instance, soldering. This assures the LDS layered PV cells can be connected in series.

Chapter 4: LDS Layer Manufacturing and Characterisation

4.1 Introduction

This chapter presents the outcomes of the LDS layer manufacturing and the results associated with the characterisation of the layers. Using the methodologies outlined in Chapter 3, different LDS layers were fabricated for small-scale and large-scale implementations in the manufactured novel system for the IDEAS project. Figure 4.1 depicts the development pathway for an LDS layer, starting from the initial polymer stock solution in combination with the luminescent dye through to the integration of computer simulations that assess absorption & emission spectra, ultimately influencing the fabrication process of the LDS layer. This chapter also highlights the critical relationship between theoretical modelling and practical application in optimising the LDS layer production. The recipe used for the LDS layered PV cell was:

- PMMA 3.8 g (21.2 wt%)
- Chloroform 10 ml (78.6 wt%)
- Methyl Orange dye 0.00015g (0.001wt%)

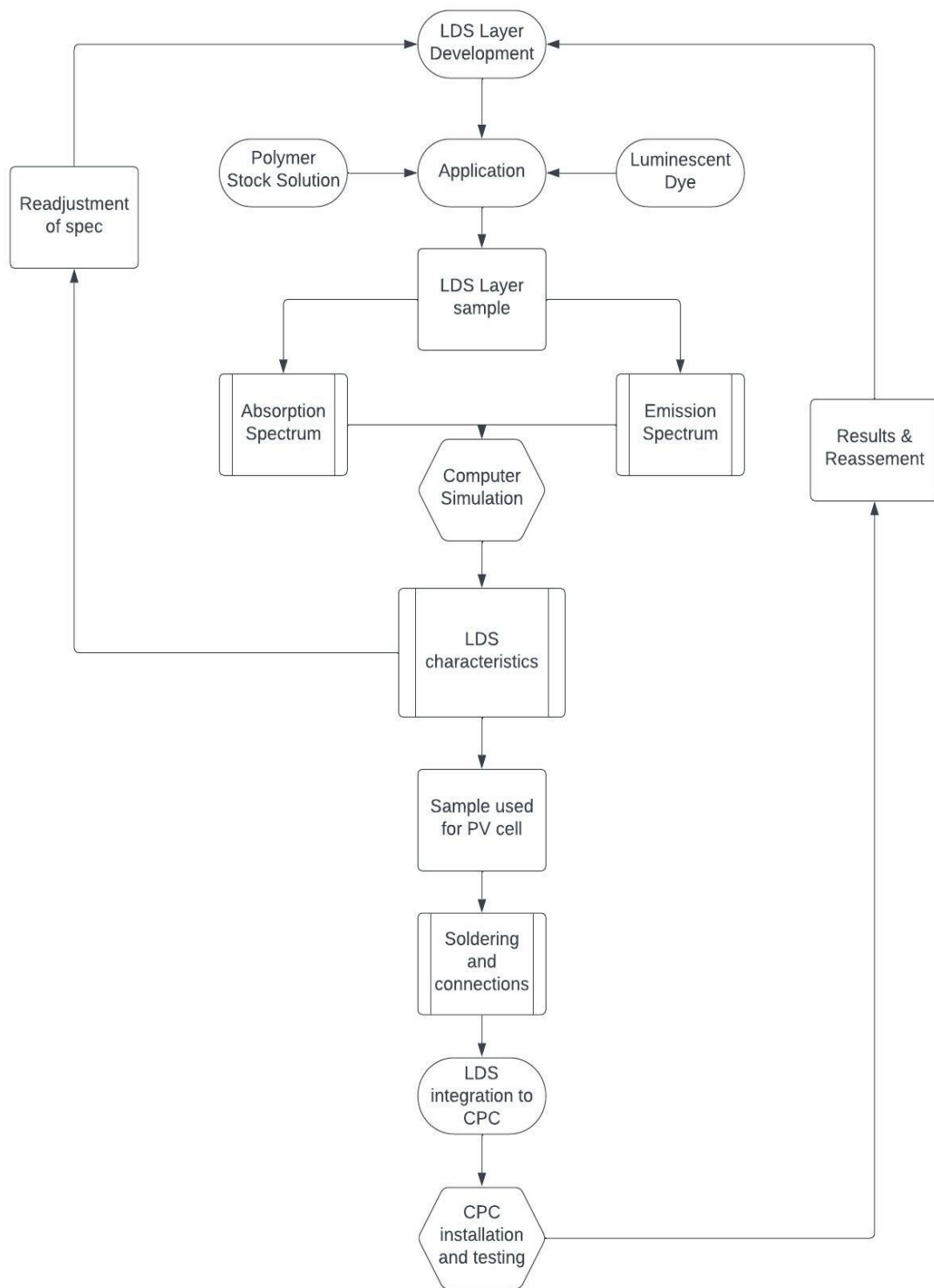


Figure 4.1 Flowchart of LDS integrated CPC system production.

4.2 Polymer

Using the methodology discussed in section 3.7, a uniform layer with an average thickness of 20 μm was achieved. As previously mentioned in section 3.8 there were different LDS layer thickness that could be achieved, the desired thickness was 20 μm , this was the average thickness of the LDS layer. This was done using a micrometer across multiple points on the LDS layer. In this research, the accepted range was between 18-22 μm . This was because the thickness of the LDS layer is one of the physical characteristics that can greatly impact the effectiveness of the LDS layer so the smaller the margin for error the better the resulting effectiveness. Sample batches of this mixture were made of 30 ml stock solution; these batches could produce three samples of LDS-layered PV cells. These 30 ml stock solutions were used for more giant PV cells and were deposited using 10 ml syringes. For each 30 ml stock solution, three separate LDS layers were spin-coated onto individual PV cells. However, issues began to arise once this solution was increased from 10 ml stock solution for 2cm x 2 cm PV cells up to 30 ml stock solution for 12.5 cm x 12.5 cm PV cells, such as varying thickness and non-uniformity of layers. The layer did not cover the cell area, and non-uniformity was clear, where areas of the layer had swirling patterns, as shown in Figure 4.2.

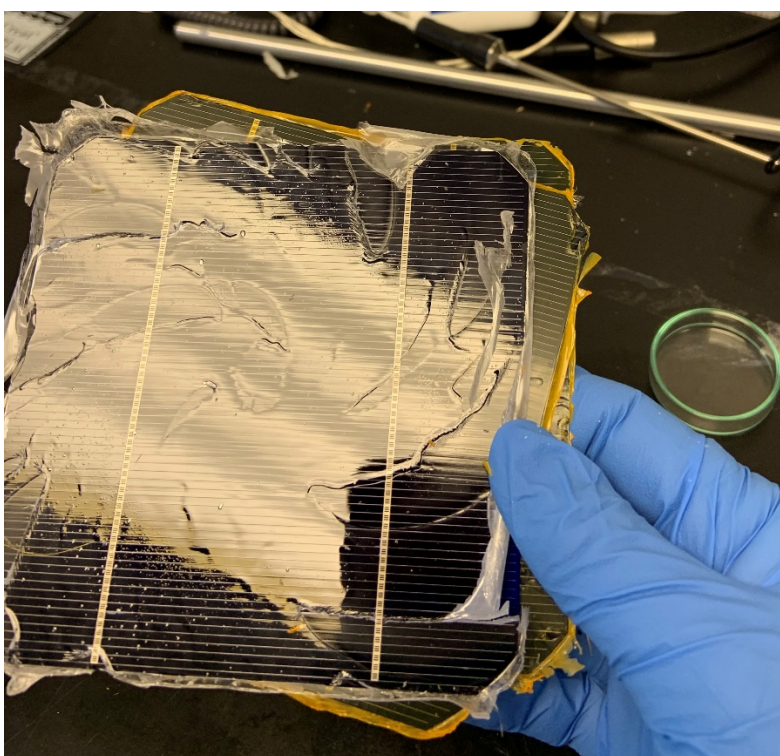


Figure 4.2 Image of PV cell with layer, illustrating swirling.

The average thickness across the cell also varied largely, from 11 μm where little mixture adhered up to 40 μm where it was applied directly onto the PV cell before spin coating. Various processes can cause non-uniformity during the application and production process, such as the polymer solution may be too viscous, PMMA may not have been fully dissolved due to the spin speed used by the stirrer being too slow, the speed used in the application of the spin-coater also being too slow, under 1000 rpm (for increased thickness) or too fast, over 1000 rpm (for reduced thickness), and also the possibility of pre-polymerisation that make polymer solution more viscous. To eliminate the issues associated with the polymer mixture process, the concentration needed to be altered, and the speed & time of mixing were also optimised (Kessentini et al., 2013). The thickness variation can be attributed to the application process of the LDS polymer solution onto the PV cells for spinning in the spin coater. When applying the LDS polymer solution using/by syringe, if pre-polymerisation occurs during the process that can cause the LDS polymer solution to harden, which can lead to a thicker layer being produced. A thinner layer can occur simultaneously during the application as if the solution is distributed and the syringe is empty but still pushed through causing a release of air. This air released spreads the LDS polymer solution in a specific area; once the spinning starts this area has less LDS polymer and the speed of rotation then causes the solution to dissipate leading to a thinner LDS layer being produced.

Polymer Concentration: In many of the test cells, the layers were spread homogeneously over the cell but they exhibited suboptimal thickness, measuring less than 20 μm . To address this, the concentration of PMMA in the solution was increased. The amount of PMMA was increased to 3.8 g (21.2 wt%) per 10 ml (78.6 wt%) of chloroform. This modification facilitated the achievement of more uniform and consistent layer thickness on the larger PV cells, thereby optimizing the functional efficacy of the applied layers.

Stirring Speed & Duration: To facilitate the dissolution of an increased amount of PMMA, the stirring speed and duration of mixing needed to be increased. Initially, a stirring speed of 500 rpm was used to dissolve the PMMA. With an increased PMMA content, this speed was gradually increased to 650 rpm. Similarly, the mixing duration was extended from the original range of 45 to 60 minutes to a minimum of 60 minutes and, where feasible, to 90 minutes.

These adjustments were critical to ensure the complete dissolution of PMMA within the chloroform and dye mixture.

After achieving a stable production of a uniform polymer layer, a dye was added to the mixing process. The dye concentration with chloroform used for layer application was 0.1 wt%. This mixture was prepared in stock solutions at 1 wt%, which were then diluted as needed. This procedure aims to prevent premature polymerisation of the polymer solution prior to its application on the PV cell.

Initially, Lumogen Violet 570 dye from BASF was selected due to its absorption and emission characteristics that complemented the spectral response of silicon solar cells. Unfortunately, this dye was discontinued by the supplier, and a replacement was required. Methyl Orange from Sigma Aldrich was selected due to the absorption peak aligning with where the si PV cell was underperforming and the emission peak aligning with where the cell had the highest efficiency. A comparative analysis of these two dyes is presented in section 4.5, highlighting their impact on the enhancement of PV cell performance.

4.3 Layer Application

The G3P-12 Systems spin coater (as described in section 3.7.2) was used for the fabrication of LDS layers. It was the most consistent and simplest way to alter the application of the LDS layer to a PV cell. Layers of 10 μm and 60 μm were applied to Si solar cells at speeds of 1000 rpm and 750 rpm for 180 seconds. The layers' thicknesses were measured at different points using a digital micrometre, and an average was calculated. This identified 20 μm as the optimal layer thickness [Neikov et al, 2019], for enhancing solar radiation absorption in the LDS layer. This procedure was initially developed for smaller 2 cm x 2 cm PV cells. To achieve similar consistency on larger 12 cm x 12 cm cells, the following parameters had to be altered:

Coating Spin Speed: The speed at which the polymer solution is applied critically influences the coverage and polymerisation rate. The desired volume of polymer solution is poured using a syringe; once the polymer solution has left the syringe, it begins to polymerise quickly. To avoid completely polymerising, it must be spun quickly. For smaller cells, a slower speed of

750 rpm provides even cell coverage and a uniform thick layer. For larger cells, the polymer will not spread out and polymerise at a speed of 750 rpm, a faster speed of 1000 rpm is required. When this speed is used for a smaller cell with a thinner layer, which is below the desired 20 μm is produced, but for a larger cell, it produces a layer of the desired thickness (20 μm) and is spread evenly.

Dwell Time & Speed Ramp: These parameters refer to the duration at which the spin coater remains at a set speed and the rate at which speed increases, respectively. Using 1000 rpm straight away can destabilise the cell on the chuck and damage the cell. By using dwell times, where the cell can build up speed in chosen intervals, the speed used in the spin-coater can be increased without the polymer prematurely polymerising or the cell breaking.

Recipe: This is the specific combination of rpm, speed steps and timing intervals used in the spin coater to produce an LDS layer and greatly impacts the quality of the polymer solution. The implementation of a nitrogen-filled glove box reduced pre polymerisation, the polymer liquid solution was less viscous (due to lack of pre-polymerisation), so speeds higher than 1000 rpm were not viable for the dispersion. The solution would be spun off the substrate, as it does need to polymerise slightly to allow adhesion. So, the optimised recipe was:

- 10 secs @ 500 rpm to spread the LDS solution to cover the substrate. This works on 2 x 2 cm and 12.5 x 12.5 cm to fully apply the LDS and allow full adhesion as long as the solution is scaled up accordingly.
- 170 secs @ 1000 rpm works on the 12.5 x 12.5 cm to fully apply the LDS and allow full adhesion.

If other speeds are used at the initial 10 secs, if faster than 500 rpm, the LDS polymer solution disperses rapidly which produces a thinner LDS layer at the end after the rest of the recipe is completed. If a longer dwell time than 10 secs is used at 500 rpm, this leads to a thicker layer being produced at the centre of the PV cell while the outer layer is thinner. This is due to the LDS polymer solution hardening when the polymer solution interacts with the oxygen rich environment.

If another speed is used during the longer duration of 170 secs, then similarly a different thickness LDS layer can be produced. If a slower speed than 1000 rpm is used a thicker layer is be fabricated. The slower rpm disturbs less of the LDS polymer solution during the spinning process. If a higher speed is used then a thinner layer is produced as the faster rpm spins more of the LDS polymer solution off the spinning PV cell.

If there is a variation of timing similar outcomes occur as previously stated. A longer dwell time at 500 rpm leads to a hardening of the LDS polymer solution which results in a thicker LDS layer. A shorter dwell time leads to a thicker LDS layer as the deposited LDS polymer solution spins off and is not distributed effectively or evenly.

4.4 Characteristics of LDS Layer

For LDS, the characteristics that have been investigated are layer thickness, quality of the layer (including impurities within and smoothness of the layer), the dye's ability to down-shift the solar spectrum (absorption, emission, and QY), and its effectiveness with solar cell by measuring EQE and Power conversion efficiency.

4.4.1 Layer Thickness

Layer thickness measurements ranged from 10 μm to 60 μm in 10 μm increments. As explained in section 2.5, any change to parameters such as layer thickness or the absorption coefficient can significantly affect the optical efficiency.

Inconsistencies in layer thickness across the cell can cause challenges to production efficiency. For example, where one-quarter of the cell has a thickness of 15 μm and another measures 35 μm , this results in non-uniform efficiency across the cell. This discrepancy can lead to increased absorption in the thicker section with lower emission and without a balance, there can be an overlap, causing a lower power output of the PV cell.

It was discovered that achieving optimized thickness in layers for larger PV cells consistently and uniformly could be best accomplished by reducing the polymer solution's viscosity by adding PMMA (Glenn et al. 2019), while ensuring sufficient time for dissolution. As the solution became thicker, the previous speed of 750 rpm needed to be increased to 1000 rpm. Using a ramp speed function on the spin coater, this was achieved without damaging the cell, and the LDS layer was applied unilaterally with an average thickness of 20 μm .

4.4.2 Layer Quality

Layer quality fundamentally pertains to the minimisation of defects within the LDS layer and the homogeneity of the LDS polymer solution during the application process. The presence of sediment of PMMA remaining in the polymer solution, can detrimentally affect the LDS layer optical properties. Refraction and reflection in the layer can increase, causing emitting photons to be refracted and scattered from the layer into the ambient environment rather than reaching the PV cell underneath.

To enhance the quality of the LDS layer, a critical initial step involves ensuring the complete dissolution of PMMA. This is best achieved by using a magnetic stirrer and incrementally increasing the speed of the stirrer by 50 rpm..

Additionally, filtration was also used to eliminate any residual PMMA particulates from the polymer solution. This procedure was conducted using a small batch of 20 ml, where complete filtration of 10 ml & 20 ml polymer solutions required 60 minutes, with constantly adding more polymer solution for filtration through the filter paper. However, this method proved unviable for larger batch volumes due to the extended time required and the potential for the polymer to solidify at the filter paper base, thereby obstructing further passage of the solution. Once removed from the magnetic stirrer and exposed to oxygen, the polymer solution begins to solidify rendering the batch unusable for further application. This emphasises the need for careful handling and processing to maintain the viability of the polymer solution for high quality LDS layer production.

4.4.3 LDS Layer Dye Selection

In the context of scaling up the manufacturing of LDS layers for the IDEAS project, two specific dyes were identified for comprehensive testing along with 6 other dyes synthesised by project partners Laboratório Nacional de Energia e Geologia (LNEG) in Portugal. The criterion for preliminary evaluation was based on the measurement of the absorption, emission, and external quantum efficiency (EQE). This metric served as a comparator for assessing absorption and emission spectra improvements. In the absence of any improvement in EQE, then further characterization of the dye was not necessary. The first dye characterised by EQE was Lumogen Violet 570 dye from BASF, as presented in Figure 4.3

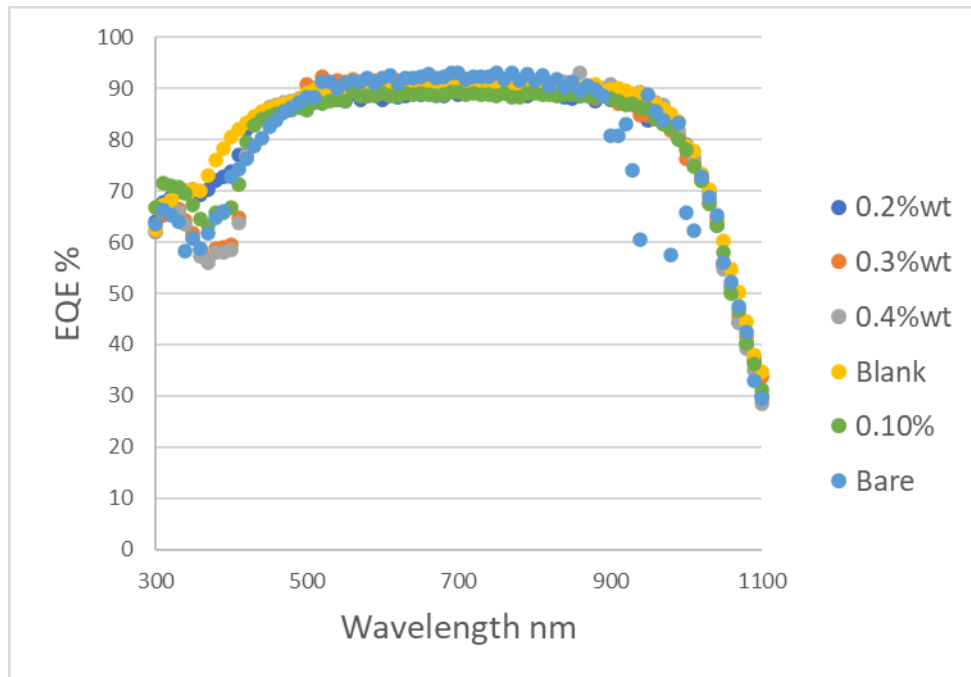


Figure 4.3 of EQE data for Violet dye (BASF) on a Si PV cell

The dyes were characterised at different concentrations (wt%) in LDS layers. The blank in Figure 4.3 is the reference and refers to a blank LDS layer with no dye, and Bare is another reference and is a PV cell with no layer applied.

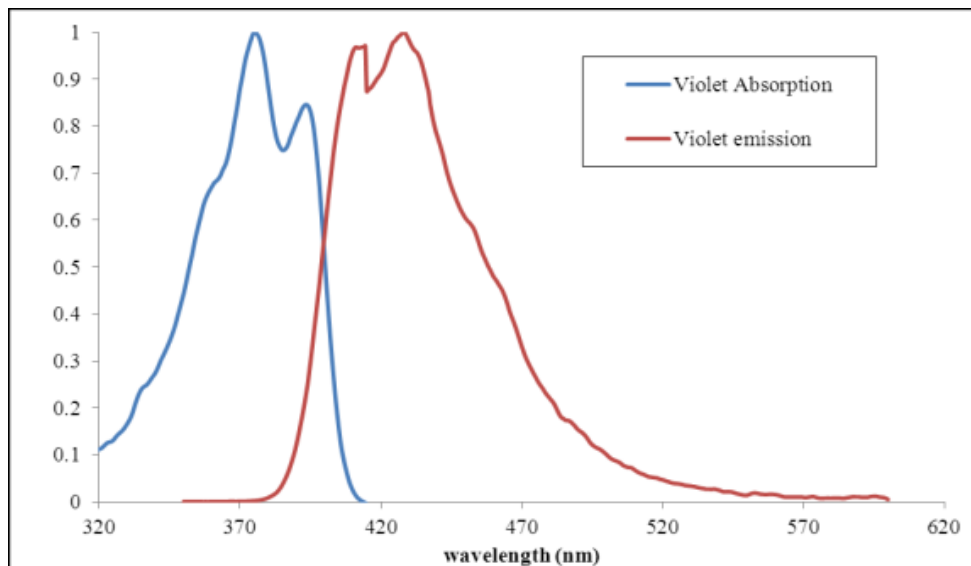


Figure 4.4 Absorption and emission of Violet 570

This dye demonstrated viability as an LDS layer to complement Si PV cells used within the project. Its effectiveness was primarily attributed to the limited stoke shift that facilitated the PV cell in absorbing light between 300 – 420 nm as shown in Figure 4.4. The dyes absorption

spectra proved advantageous falling outside the absorption range of the Si PV cell and with an emission spectrum within the Si PV cells operational range. Unfortunately, this dye was discontinued by supplier without a direct replacement.

The subsequent dye explored was Methyl Orange (4-[4-(Dimethylamino)phenylazo] benzenesulfonic acid sodium salt) from Sigma Aldrich. This commercially available dye has the advantage of being purchased in large quantities and has a relatively high quantum yield (QY) of ~ 75%. Figures 4.5 (a) and (b) and 4.6 present the absorbance and emission of Methyl Orange dye.

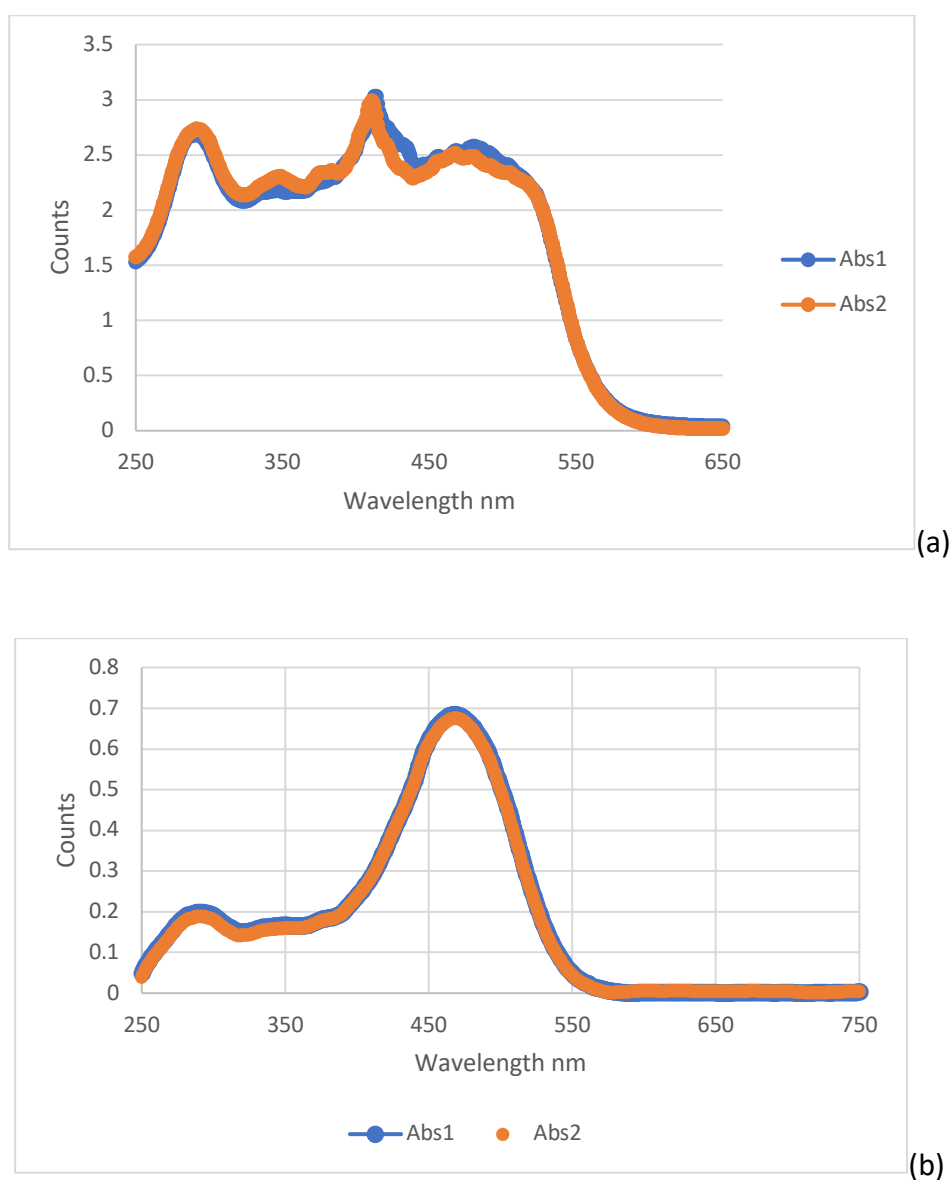


Figure. 4.5 Absorbance spectrum of orange dye used at two concentrations: (a) 0.1 wt% and (b) 0.02 wt%.

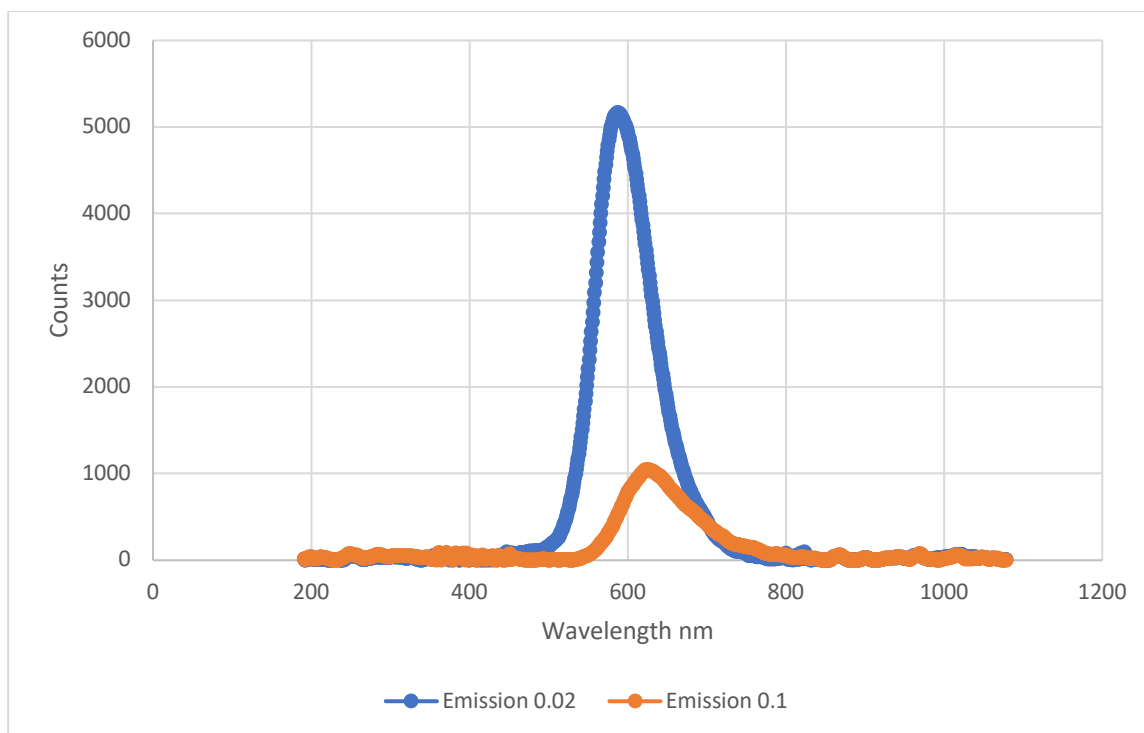


Figure 4.6 Emission Spectrum of Methyl Orange at two concentrations of 0.1 and 0.2 %wt, respectively

Figures 4.7 and 4.8 present the characterisation of the dyes synthesised by LNEG dyes (IDEAS partner) using the same experimental setup used for the methyl orange dye. Multiple dyes were characterised to determine a suitable dye for silicon PV cells in the LDS layer. The results of these dyes are shown in Figure 4.3 and discussed in later sections of this thesis.

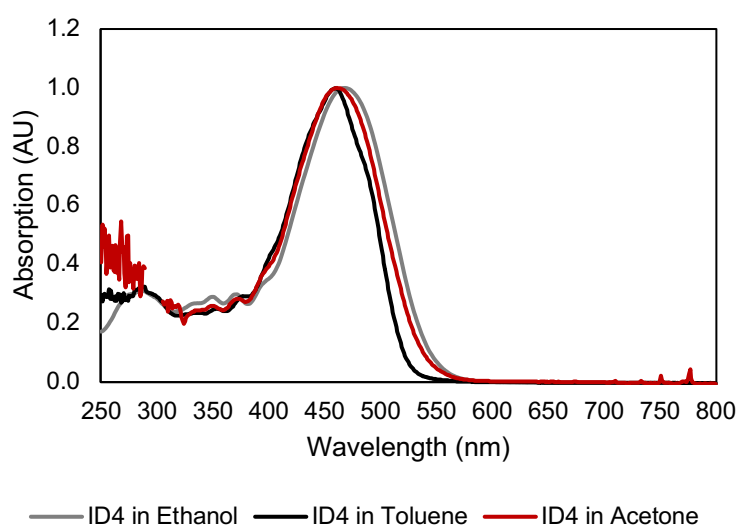


Figure 4.7 Absorption in ethanol, Toluene, and acetone

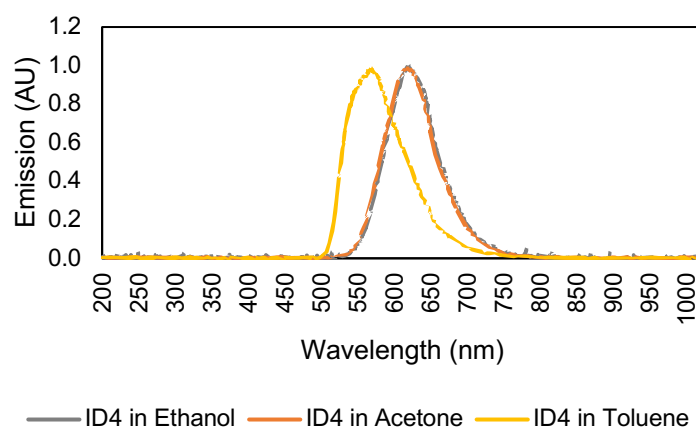


Figure 4.8 Emission of ID4 LNEG dye at 0.2%wt in ethanol, Toluene, and acetone

In the fabrication of the LDS layer, an initial dye concentration of 0.2 wt% was used. However, during the evaluation of the absorption and emission, quenching was observed. This was characterised by the dye’s complete absorption of the emitted light, leading to a decrease in emission intensity. Hence, the optical efficiency of LDS layers diminished that adversely impacting the EQE of the solar cell due to the dye concentration being too high. To mitigate this issue, a lower concentration was required (0.01 wt%) and the absorbance is shown in Figure 4.9. Further refinement led to a decrease in dye concentration to 0.001 wt% and the absorbance of the dye is shown in Figure 4.10.

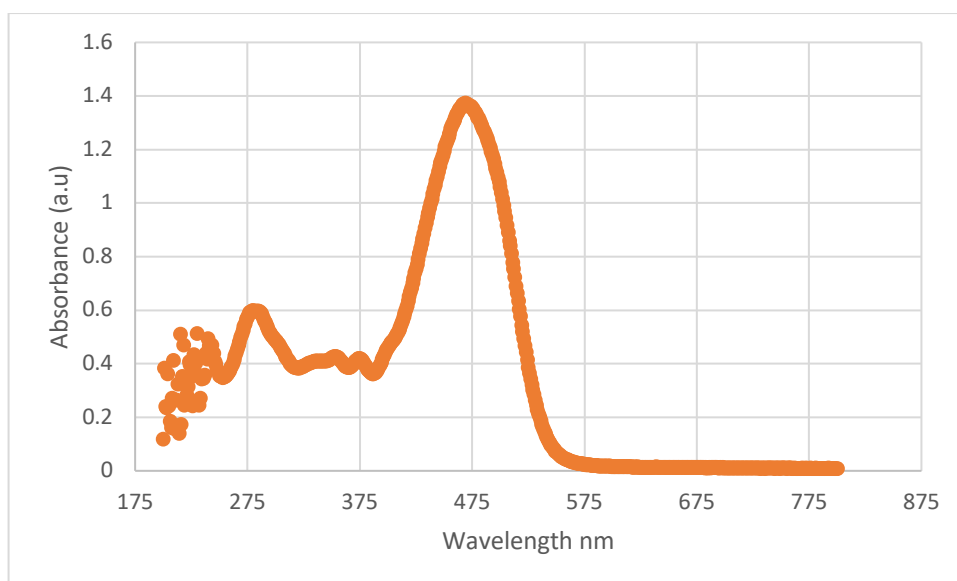


Figure 4.9 Methyl Orange 0.01wt% absorbance data from layer sample.

LNEG (IDEAS partner) provided a range of dyes in much smaller quantities for testing. These dyes were intended primarily for research and exploratory purposes rather than large scale application. However, if deemed viable there was the prospect of upscaling to a usable quantity. These dyes absorption spectra are presented in Figure 4.10, in comparison with Methyl Orange at 0.01 wt%.

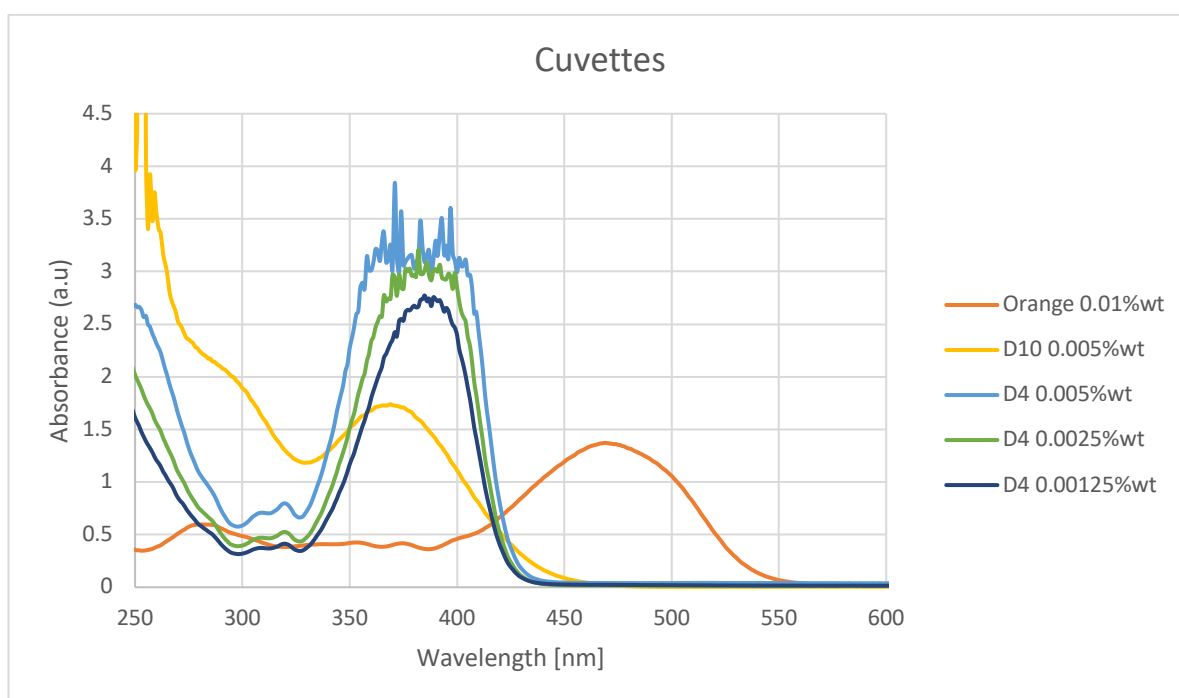


Figure 4.10 Absorption of dyes supplied by LNEG.

Each of the dyes delivered arrived in a powdered form like the already used lumogen and methyl orange dyes. The spectrometer used for the absorption measurement does not reliably measure below 300 nm. Dye D4 is light blue and has a higher peak absorption intensity of 3.7 with an absorption band between 360 – 410nm compared to the other dyes shown. However, it is important to note, the highest reliable absorbance is at 2 a.u. From the data obtained both dyes are worth investigating further. Unfortunately, the other dyes received, D1,3,7, exhibited agglomeration in their containers, rendering them insoluble in the solvent, preventing further characterisation. The remaining dyes were not characterised at the same concentrations as the other dyes, so further testing is required when a replacement of these dyes becomes available.

Dye Concentration: Using weight percentage units gives excellent accuracy when determining quantities of material required when combined with the polymer solution for an LDS layer fabrication. Preparing stock solutions of the dye in chloroform facilitates the production of larger volumes of polymer solution, optimises dye usage and minimizing potential waste. Furthermore, this approach reduces weighing errors, as the larger quantities of dye reduce the standard deviation of the instrument used to measure weight.

4.5 Fabrication of LDS Layers

In the first year of this research, as part of the IDEAS project, TCD work package was the design and implementation of designing and implementing a CPC system using LDS layered PV cells for installation at the University of Ferrara, Italy. Five systems were manufactured. . Once the LDS layered PV cells were consistently fabricated and the process was repeatable, the LDS was to be further developed by integrating plasmonics into a pLDS layered PV cell. The CPC design and manufacture was the topic of another PhD (Ortega, 2023).

The following panels were fabricated:

- 2 panels with CPC and LDS layered solar cells.
- 1 CPC panel with blank LDS polymer layers on the solar cells.
- 1 reference panel of only PV cells and
- 1 panel with no CPC.

This required 15 strings of 11 PV cells per string. 132 layers were required for 132 PV cells either with LDS, just polymer layers (blank) or without any layer. The LDS layers used were 3.8 g (21.2 wt%) of PMMA per 10 ml (78.6 wt%) of chloroform. Batches were made of 40 ml; 10 ml of the solution was applied by syringe for each LDS layer coating. The batch was mixed for 60 – 120 minutes. In some cases, where a batch from the previous day was used, it was found that the layer quality was affected as the batches began polymerising prematurely, leading to non-uniformity in thickness when applied. Sediments, such as dust, would gather on it due to the batch being exposed. The batches that were mixed and applied promptly ensured the highest quality LDS layers, characterised by uniform distribution, absence of contaminant particles, and the attainment of the desired 20 μm thickness.

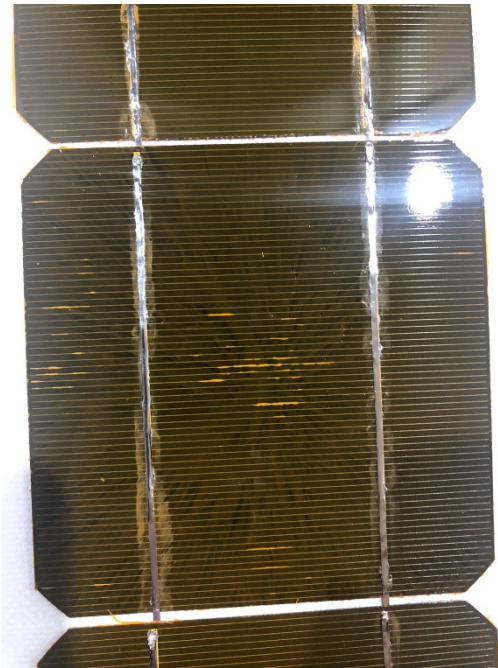


Figure4.11(A)

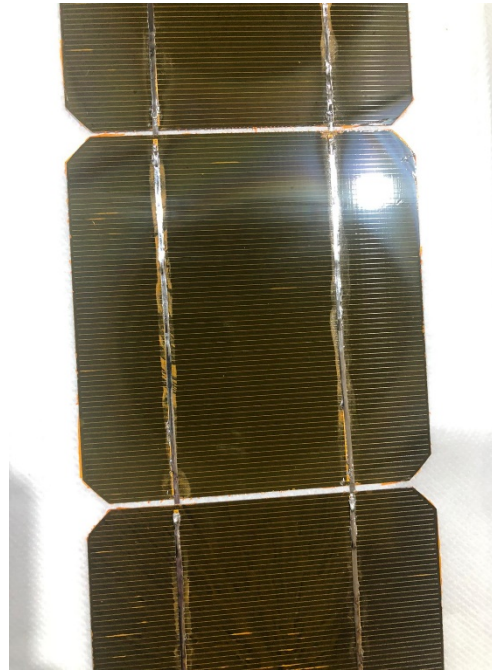


Figure 4.11 (B)

Figure 4.11 Image of layers, (A)batch left overnight (B) fresh batch.

As depicted in Figure 4.11, the difference observed in the cells is attributable to differences in the batches used for LDS layer application. In Figure 4.11 (A), the presence of numerous bright white marks is noticeable. These marks indicate the existence of large air gaps which consequently lead to the layer delamination. Conversely, Figure 4.11 (B) significantly exhibits fewer mark, indicating there was better adhesion attributed to using a fresher batch.

The splatter pattern seen in the left image indicates an uneven distribution of the LDS layer suggesting the layer non-uniformity. The cells on the right has a more circular pattern, indicative of a more homogeneous layer thickness distribution.

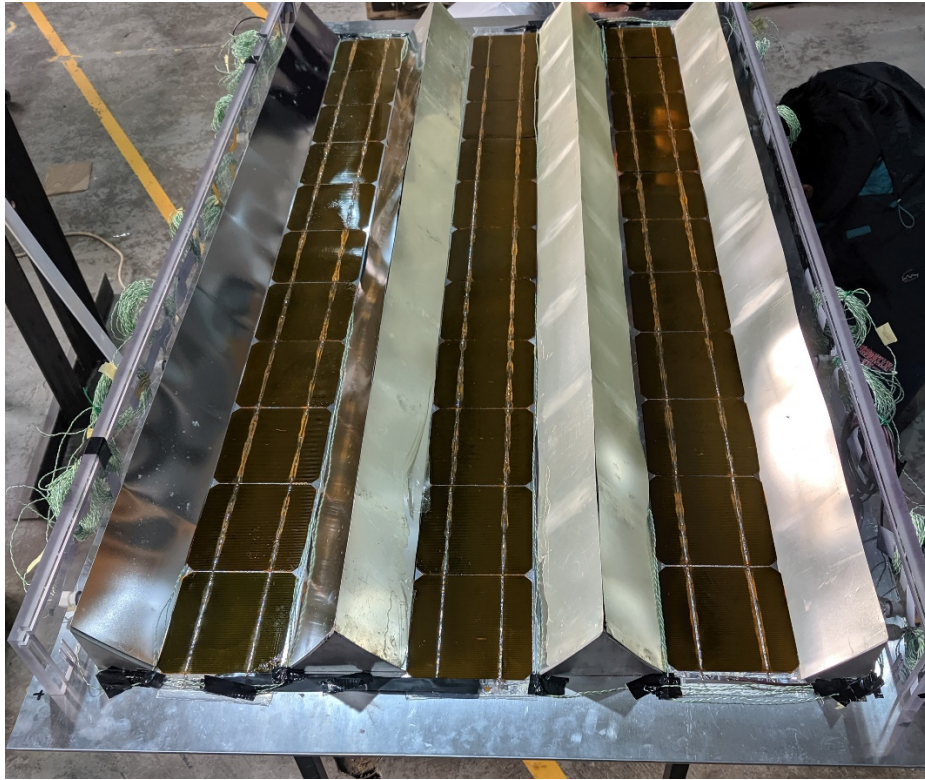


Figure 4.12 Image of CPC system with LDS layers.

The application of each LDS layer, using the spin coater at the velocities outlined in section 4.3, required a duration of 3 minutes. The complete drying process of the layers took ~ 6 hours (section 4.7). Within this 6-hour drying there was periodic visual and physical inspections of the LDS layered PV cells. In some cases, the LDS layered PV cells could be dried before the 6-hour mark. However, this was not the case for the majority of the system. This was caused by the higher room temperature variation (for the month of January) at the beginning of the fabrication process compared to the end of the fabrication process. The assembly of a string comprising 11 cells required ~ 1 hour to solder together. The entire CPC system assembly process (illustrated in Figure 4.12 and Figure 4.13) spanned from half to a whole day. This duration included additional time allocated for drying when adhesives were used to attach the LDS cells within the system.

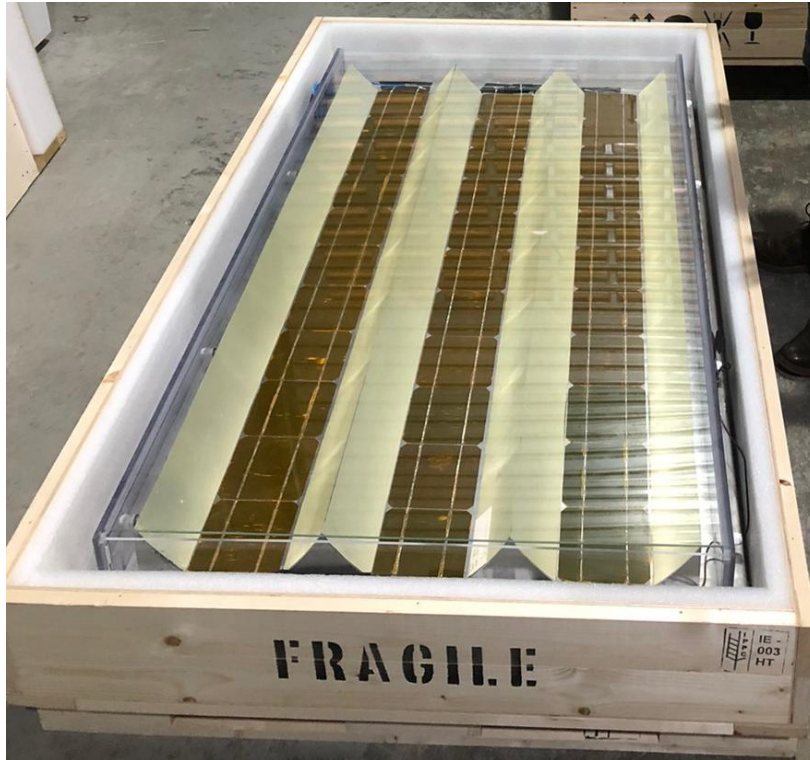


Figure 4.13 Image of Demo panel 1, LDS layered CPC system ready for shipment.

4.6 Optimisation of LDS layer

During the fabrication process, different aspects of the LDS layer required improvement. These include:

- The environment in which the LDS polymer solution being improved.
- The air supply that the mixing process takes place in.
- The long-term viability of the LDS layer after it has been applied to the PV cell.
- The application process in the spin coater where the LDS polymer solution is applied to the PV cell.
- The physical characteristics of the LDS layer that influence its enhancement capabilities.

After the original panels were completed, multiple issues were observed after the transportation to and testing of the system in Ferrara, Italy. During the CPC assembly, it was found that the layers per batch seemed uniform on initial visual inspection. However, when

integrated into the panel, the characteristics of the 33 layers varied in uniformity, as seen in Figure 4.11.

During system assembly, specific challenges arose that could have compromised the LDS layer's integrity, potentially contributing to some of the damage. For example, soldering the PV cell's busbars through the LDS layer added external thermal and physical stresses especially when soldering multiple PV cells in series.

Furthermore, an EVA sheet was laminated onto the LDS coated PV cells to enhance encapsulation between the PV cells and the CPC system. This step involved heating the EVA to adhere to the cells, imposing additional thermal stress on the LDS layers. These observations necessitated a reevaluation and enhancement of the layer fabrication process, considering the assembly techniques for effective LDS integration into the novel system.

Inert Environment: The importance of an inert environment has been described in section 3.7. It was observed that the polymer solution would begin to harden and initiate polymerisation immediately after the mixing by the magnetic stirrer had stopped. This effect resulted in only the first LDS layers of a batch retaining their optical quality, with subsequent layers suffering degradation due to premature polymerisation of the solution. Producing smaller batches proved ineffective due to time restraints; although the mixing duration decreased, the frequency increased. Implementing an inert atmosphere, specifically using a nitrogen-filled glove box, effectively mitigated premature polymerizing induced by the exposure to oxygen.

Nitrogen supply: To further refine the LDS layer fabrication process a nitrogen inert environment was used to minimise potential contamination or introduction of impurities. Nitrogen was supplied directly to the spin coater chuck chamber rather than an air supply from a vacuum pump. This was in tandem with improving the mixing of materials process within the nitrogen inert environment. Despite these modifications, LDS layers produced under these conditions resulted in thicknesses substantially below the targeted 20 μm , adversely affecting the layer's efficacy due to deviations from the optimal physical characteristics previously achieved with 20 μm layers.

Longevity: Adjusting the preparation environment improved the reliability and repeatability of the spin coating process. The transition to an inert setting contributed to a more consistent attachment of the LDS layer to the PV substrate, with reduced incidence of air entrapment and subsequent layer delamination, enhancing overall adhesion quality.

Mixing Process: Following on from section 4.4.3 regarding layer dye selection. The first batch of polymer solution produced in the inert environment used the original concentration of 3.8 g of PMMA per 10 ml of chloroform and a dye concentration of 0.001 wt%.

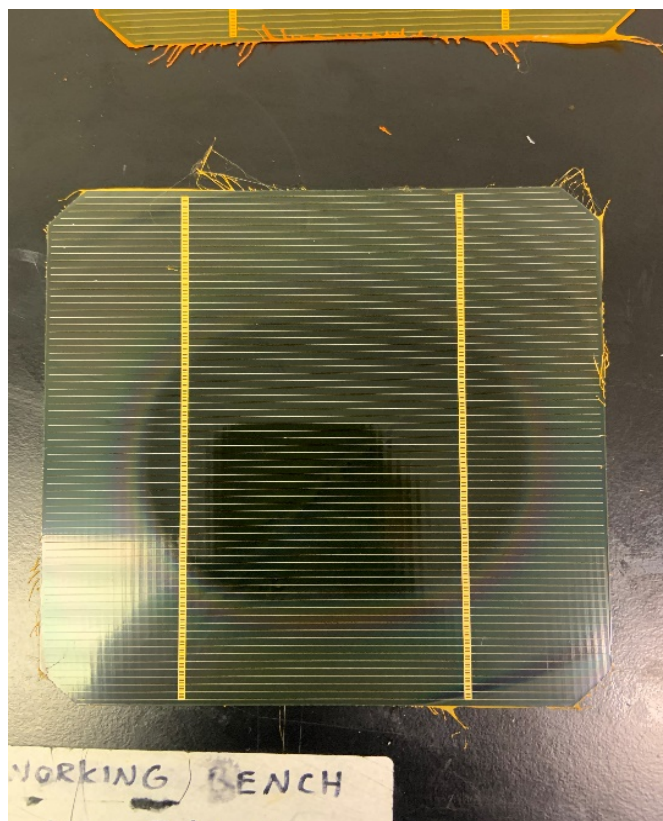


Figure 4.14 Image of LDS layer produced in nitrogen glove box.

The fabricated LDS layer exhibited a thinner profile and discolouration, as shown in Figure 4.14. The thinner the LDS layer, the reduced overall downshifting effect on the cell. The discolouring can be attributed to the proportions of PMMA, chloroform and dye. Due to the solution's reduced viscosity before application, the dye concentration was adversely affected, compromising the layer's quality upon application to the photovoltaic (PV) cell.

To counteract the reduction in layer thickness, an increased quantity of PMMA was added to the mixture to adjust the ratio to 5 g of PMMA per 10 ml of chloroform. This change successfully restored the LDS layer thickness from 5 μm to the previously optimised thickness of 20 μm . However, this higher PMMA concentration required a longer dissolution period, extending the average mixing duration from 45 minutes to 120 minutes and altering the

efficiency of batch production. Consequently, to attain the desired layer thickness, the volume of the coating solution applied per cell was increased to 20 ml.

Application Process: The resulting layers, illustrated in Figures 4.15, showed no signs of pre-polymerising, mirroring the outcomes achieved in the inert environment. The excessive solution was spilled over the sides of the cells, which formed a pendant film. In contrast to previous attempts, where such spillages proved challenging to eliminate due to its adherence to the PV cell, incorporating nitrogen in the process facilitated easier removal.

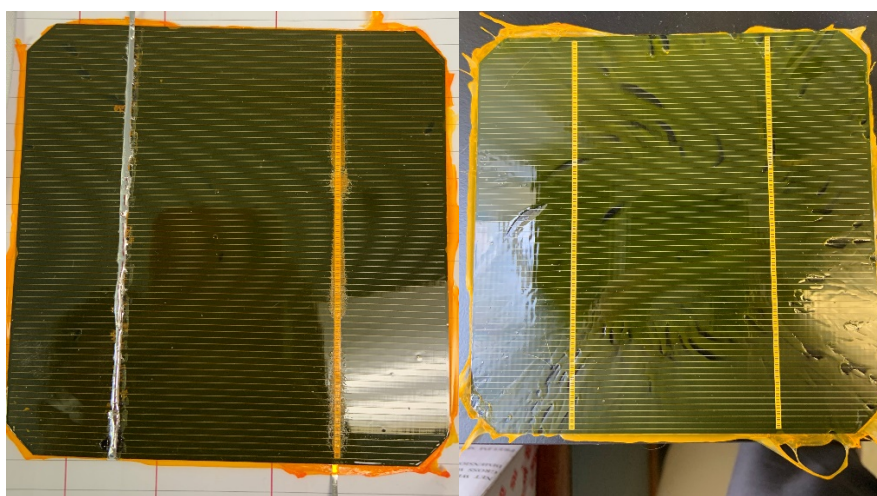


Figure 4.15 (A)

Figure 4.15 (B)

Figure 4.15. (A) Improved layers coated using 20ml solution, (B) uneven layer

The concentration of the methyl orange dye was also modified to optimise LDS layer performance. Initially, the dye concentration for layers applied on the systems for the University of Ferrara, was 0.01 %wt. However, upon measurement of absorption and emission saturation was observed, indicating a concentration which was too high and could potentially hinder the efficiency of the LDS layer. To mitigate this, the concentration of methyl orange was reduced to 0.001 %wt.

Layer Characteristics: After saturation and quenching phenomena were observed in the absorption and emission spectra, the dye concentration was decreased from 0.01%wt to 0.001%wt. This adjustment addressed the optical saturation issues and resulted in the utilization of a smaller quantity of dye per batch, thereby facilitating the production of a larger number of batches.

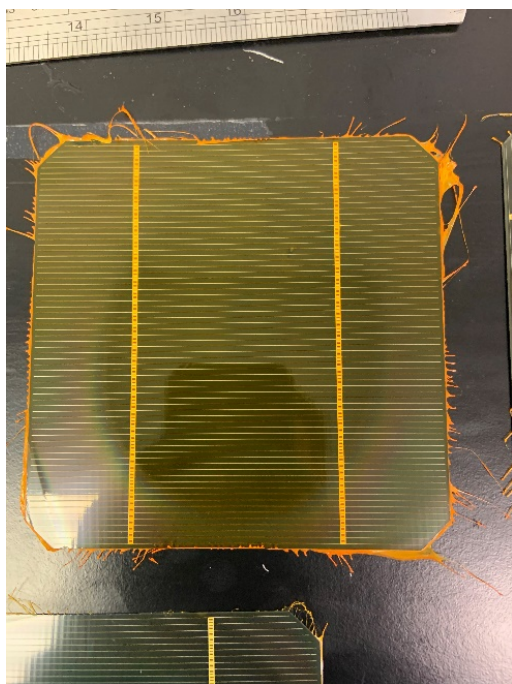


Figure 4.16 Layer coated using 20 ml spun at 1000 rpm.

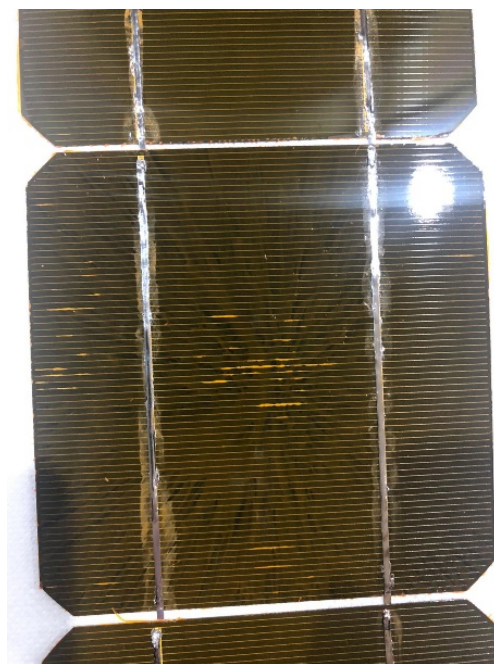


Figure 4.17 a LDS layered PV Cell from CPC system sent to Italy.

Comparing Figure 4.16 with Figure 4.17, the variations in the uniformity of the layer are noticeable. Figure 4.14 demonstrates an uneven distribution of the solution, with a distinct hew at the centre, indicating that the solution did not spread evenly. Conversely, Figure 4.10 (A) shows the most uniform layer achieved.

As previously mentioned, the thickness of the LDS layer began to vary in the inert environment. Using the older recipe for the CPC systems for the University of Ferrara, a volume of 12 ml was used, and the resulting layer thickness was measured at 5 μm . This reduction in thickness rendered the layer ineffective, offering no substantial benefits upon application to the PV cell, despite its improved stability against degradation. However, by adjusting the formulation to 5 g of PMMA per 10 ml of chloroform and employing a larger volume of 20 ml of solution, the layer thickness was successfully increased back to the desired 20 μm .

The inert environment was used to both improve and optimise the fabrication process of the LDS polymer solution. It improved the repeatability of the LDS polymer solution production

which led to similar LDS layers being applied onto PV cells. The nitrogen supply into the inert environment led to an improvement of the LDS layer as it reduced impurities contaminating the LDS polymer solution mixing process taking place in the inert environment. The longevity of the LDS layer is an aspect that was affected during this optimisation process. Ideally the LDS layer would last as long as the PV cell underneath, in this case is 20 years. However, this long-term testing is not complete at this time. The mixing process of the LDS polymer solution was optimised to consistently produce an LDS that is 20µm thick. Even though the time requirement has increased the consistent LDS layer thickness is more valuable for the research. The application process proceeded to optimise the LDS layer further as the physical inspection of a 0.01wt% followed by a spectroscopy of the layer showed there was saturation at this higher concentration. This led to a reduction in concentration to improve the enhancement capabilities. Another assessment of the layer characteristics led to another optimisation effect as when applying the LDS polymer solution using a syringe it caused an uneven distribution. Use of a larger volume for application reduced the uneven distribution and maintained the 20µm thickness.

4.7 Conclusion

In this chapter, a viable LDS layer was developed, optimised, and fabricated for a Si PV cell with both front and back busbar connection. A polymer stock solution was formulated as a base to be used with any chosen luminescent dye. This stock solution facilitated the investigation and refinement of the LDS layer application process, specifically onto a 12.5 x 12.5 cm PV cell. The polymer stock was tuned to provide the desired physical characteristics of layer uniformity and the LDS layer's thickness of 20 µm. This was achieved using a spin coater as the primary method of LDS layer application.

A downshifting viable luminescent material assessment was made using absorption, emission and EQE testing of the available dyes and their layers and how their testing was undertaken proved invaluable, as shown in Figure 4.3. (This work will be discussed in the next chapter.) The optimum dye concentration one of the more difficult processes as the possibility of over saturation, making the LDS layer ineffective, and was an important characteristic to

determine. The concentration of the dyes was determined for the methyl orange dye to be 0.02%wt.

The blending of the polymer stock solution, combined with the application technique and incorporation of a compatible luminescent dye, resulted in the production and assembly of LDS layered silicon PV cells, seamlessly integrated into a CPC system. The systems fabricated required 132 PV cells to be successfully layered with an LDS layer. This does not include the many failed LDS layers and broken PV cell during the coating process. These LDS layered PV cells that broke occurred during the application process in the spin coater. When the PV cell does not hold to the chuck at the centre of the spin coater and the spinning process begins, the PV cell will fly off and shatter, thus making it unusable. Also, during the soldering process, when an excess pressure was applied onto the edges of the LDS layered PV cells, combination of excess heat and external pressure caused the PV cells to fracture. Both instances were occurring for 1 in 5 PV cells. After the LDS layered PV cell integrated CPC systems, identifying the areas where the LDS layer was failing became prevalent. Displaying the non-uniform dispersion of the LDS polymer solution in both splatter patterns and an uneven spread. This was addressed through the revision of the LDS polymer solutions mixing process and environmental conditions (integration of inert glove box). Integrating the LDS layered cells into the CPC system also required reviewing. It was found that soldering connections between the LDS layered cells caused significant damage to the LDS layer and the PV underneath. The physical placement and encapsulation of the LDS layered PV cells required refinement to reduce extra thermal stresses, such as the addition of the EVA encapsulation sheet by thermalisation process.

Chapter 5. Modelling for LDS layer optimisation

5.1 Introduction

This chapter discusses ray-tracing modelling that was used to optimise LDS layer parameters to facilitate the fabrication process. The ray-tracing model was developed by Dr Mehran Rafiee, a previous PhD student in the same research group [Raiffee, 2019]. The model can visualize the interaction of incident solar radiation with the LDS layer and the PV cell. But more importantly, it can guide the selection of the type of luminescent materials for different PV technologies, layer thickness, optimum dye concentration, and optical efficiency of the LDS layer.

5.2 LDS layer evaluation using computer simulation

The aim of modelling LDS layers using computer simulation is to develop a more efficient LDS optimisation process. Rather than fabricating and applying multiple LDS layers with varying luminescent dyes and concentrations, a computer simulation can produce the expected optical efficiency of the layer. Thus, the experimental process can be fine-tuned, reducing the time required to optimise the LDS layer. Also, this reduces the material waste associated trial and error process to optimise production of LDS layers. Therefore, the LDS layer can be fabricated, applied, and tested to validate simulated results.

As discussed in Chapter 2 Section 2.7, modelling of LDS cannot be carried out using commercially available ray tracing-based software, firstly, as there are no such computer models that are commercially available, secondly, there is no commercial model with a function for plasmonically enhanced luminescent (pLDS/LDS) layered devices. (Glenn et al, 2019). The model developed by Rafiee (as discussed in section 2.7), which was mainly used for luminescent solar concentrator (LSC) development, has been adapted in this work. For the LSC simulation to function, the detector planes, as seen in Figure 5.1, will all be required as the LSC functions in a different set of planes to an LDS layer. For the LDS layer to be simulated, it requires just one plane of detection, 'P2'. As the LDS layer is placed on top of the PV cell,

the area for interaction that needs to be investigated is 'P2'. The dimensions used for the LDS are also different from those used for the LSC model. Both models require the length and width to correspond with the PV cell underneath. The thickness of the LDS layer is a thin film layer that, for this research, was less than 40 μm .

The data sets were produced using the Plasmon software [Raiffee, 2019]. The graphical user interface (GUI) of the Plasmon software is shown in Figure 5.1. This software can simulate and predict the parameters of LDS layers, including the thickness, dye concentration, and overall optical efficiency. The closer to 100% the better the optical efficiency. For example an LDS with 50% optical efficiency would be a poor performing LDS as it is only interacting for half of the possible interactions into the PV cell's wavelength. Experimental validation of the simulation results was still required.

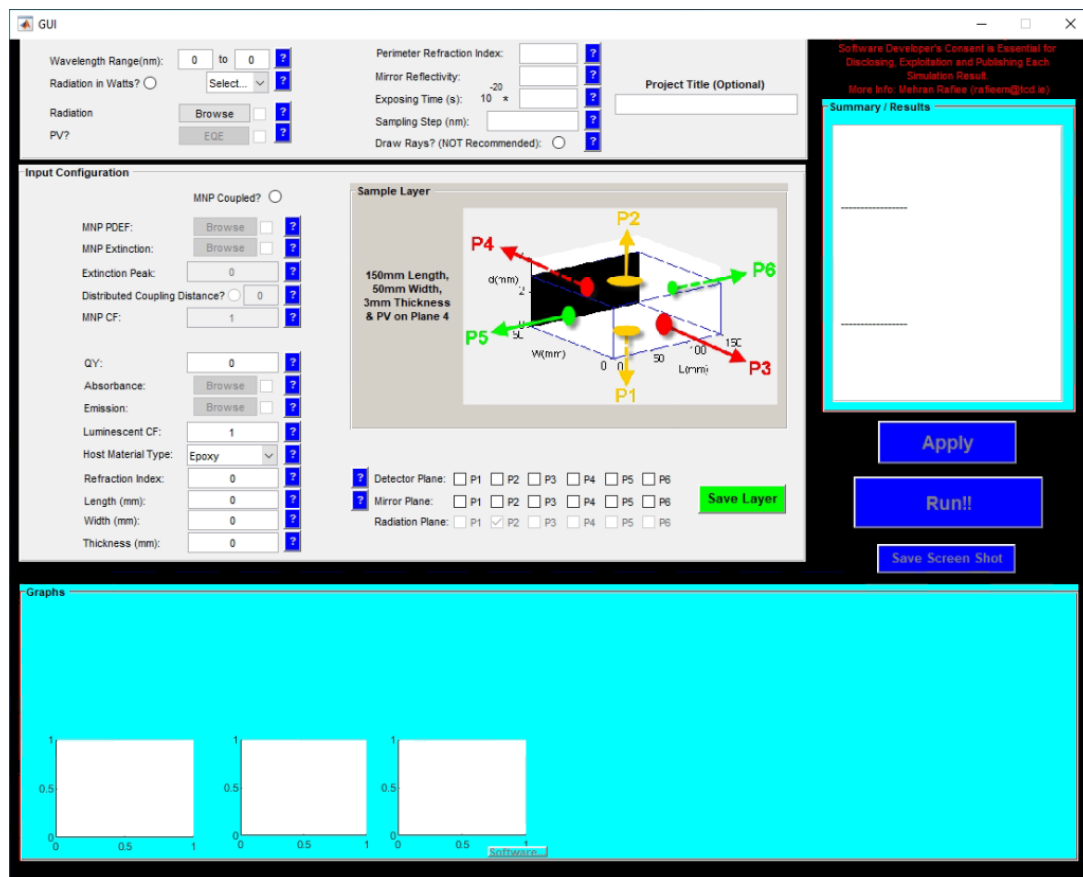


Figure 5.1 GUI of PEDAL plasmon software (Raiffee, 2019)

The input parameters used in the simulation were:

- Solar radiation spectrum (either locally or globally AM1.5).
- Number of rays
- Absorption and emission spectrum of desired dye (preferably in layer form)
- LDS layer thickness and size
- FQY of the luminescent material
- Refractive index of the host polymer
- Background absorption of the host polymer
- Exposure time; layer testing time duration.

The simulation produced the following outputs for an LDS layer :

- Optical efficiency of the layer on the various types of PV technology.
- Optical losses through various mechanisms in the LDS (%).
- Reflectance (%)
- Optimum thickness of LDS layer
- Optimum luminescent material concentration in the LDS layer

The model was used to reduce the time required to develop and test layers on Si cells. For example, for dimensions (2 cm x 2 cm x 0.02 cm) the optimal concentration can be determined for an LDS layer with a high optical efficiency (70% or higher) and low losses (under 10%). This simulation can be compared to an LDS of the same dimensions produced in the lab for validation purposes. The simulation was then used to determine how the upscaling of the LDS (12.5 cm x 12.5 cm) would be refined,

Table 5.1 Table for the lumogen red dye simulation at 0.2%wt.

Parameters	Results
Ratio of Rays Eliminated(%)	0
Ratio of Rays Reflected(%)	0
Ratio of Rays Refracted(%)	100
Ratio of Rays Enhanced(%)	0
The ratio of Rays Lost as Thermal Loss(%)	98.44472881
Ratio of Rays Exited the Device(%)	0.041834826
Ratio of Rays Arrived at PV(%)	1.513436362
Ratio of Ray LOST (Filtered)(%)	0
Geometric Gain	1
Optical Efficiency(%)	1.237321153
Solar Concentration Ratio(%)	1.513436362
Simulation Time(s)	265.5588626

Table 5.1 shows the results of a simulation assessing the impact of direct solar on a LDS layered silicon PV cell of 2 cm x 2 cm x 0.02 cm, using a 0.2 wt% lumogen red luminescent dye. The simulation indicates a low optical efficiency of 1.31% and solar concentration ratio of 1.6%. Therefore a poor performing LDS. The simulation shows the predominant mechanism of energy loss with the LDS/PV device, where thermal dissipation accounts for 98% of the total losses. This substantial thermal loss is the principal factor contributing to the observed reduction in optical efficiency.

Table 5.2 Table for Lumogen Violet 0.02%wt

Names_of_Row	Results
Ratio of Rays Eliminated(%)	0
Ratio of Rays Reflected(%)	0
Ratio of Rays Refracted(%)	100
Ratio of Rays Enhanced(%)	0
Ratio of Rays Lost as Thermal Loss(%)	7.99537356
Ratio of Rays Exited the Device(%)	2.276306723
Ratio of Rays Arrived at PV(%)	89.72831972
Ratio of Ray LOST (Filtered)(%)	0
Geometric Gain	1
Optical Efficiency(%)	88.52040165
Solar Concentration Ratio(%)	89.72831972
Simulation Time(s)	262.8926968

Figure 5.2 presents the results of a simulation using 0.02 wt% Lumogen violet luminescent dye in a LDS layer where an optical efficiency of 88.52 % and a solar concentration ratio of 89.72% was achieved. These results signify a highly effective LDS layer demonstrating substantial interaction and downshifting of solar radiation, enabling enhanced utilisation by the solar cell in contrast to the red LDS in Table 5.1. The simulation also identifies minimal losses through various mechanisms, including thermal losses at 7.96% and 2.2 % of photons escape from the top surface, indicating efficient energy conversion with minimal dissipation.

5.3 LDS Simulation Data analysis

The simulation data analysis primarily concentrates on investigating the following critical parameters of LDS layers:

- Optical efficiency (%).
- Optical losses through various mechanisms (%).
- LDS layer thickness(μm).
- Luminescent dye concentration (wt%).
- Comparative analysis of the simulation results is structured on the following: Optical efficiency of the LDS layers.
- Understanding the energy loss mechanisms in the LDS layer such as thermal or reflective losses (% in loss mechanisms).

Table 5.3 Parameters and optimal ranges for data from computer simulation

Parameters	Optimal range
Optical efficiency	70%+
Optical losses	<10%
LDS layer thickness	20 μm
Luminescent dye conc.	0.001wt%

In table 5.3, it shows the optimal ranges that are looked for from the computer simulation for producing a viable LDS layer. For this research the layer thickness was found through multiple testing using this simulation, and the dye concentration was found through the computer simulation and altered, which was stated in section 4.6

The computer simulation data that guides the effectiveness of the LDS layer is the number of photon interactions. These photon interactions indicate the number of light photons that are interacting with the LDS layer and passing through to the PV cell underneath. The tables that are produced and can be found in Appendix II, also show the percentages in which these photons are going, i.e. loss mechanisms such as reflection or heat, or reaching to the PV cell denoted by the optical efficiency.

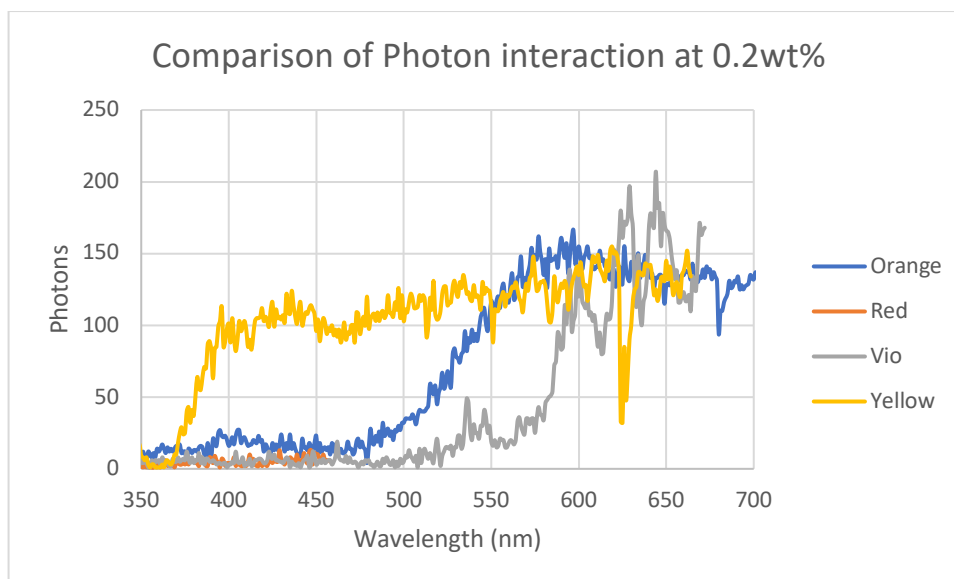


Figure 5.2 Comparison of photon interaction at 0.2 %wt

Figure 5.2 shows a comparative analysis conducted at a dye concentration of 0.2%wt, as this was the dye concentration used in the first Ferrara system (as described in section 4.5).

Concentration optimisation was determined by measuring the external quantum efficiency (EQE) of the dyes, as shown in Figure 4.3, which evaluated dye concentrations ranging from 0.1 – 0.4 %wt in 0.1 %wt increments. Lumogen yellow, violet & red dyes produced higher photon interactions, albeit with a rapid decline in effectiveness. For Methyl orange dye, suboptimal concentrations failed to significantly enhance photon interaction, yielding no beneficial effect, whereas excessively high concentrations led to parasitic absorption. Detailed discussions of these losses mechanisms are discussed in section 2.9, highlighting Methyl orange distinctive ability to increase absorption from longer wavelengths within the layer.

At elevated dye concentrations, the optical efficiency of the four dyes exhibited significant variance, as shown in Figure 5.3. Unlike at the lower dye concentration of 0.02 %wt, where each dye was effective in increasing absorption at wavelengths that the Si PV cell was less responsive, high concentrations demonstrated a substantial decrease in optical efficiency. This reduction is attributed to saturation effects prevalent at higher concentrations within LDS layers. The phenomenon of parasitic absorption, a critical mechanism, substantially influences the layer by reabsorbing photons within the layer rather than channeling them to the PV cell underneath (described in Section 2.3). This shows the importance of optimising

dye concentrations to enhance the PV cells absorption particularly in spectral ranges where they are less efficient.

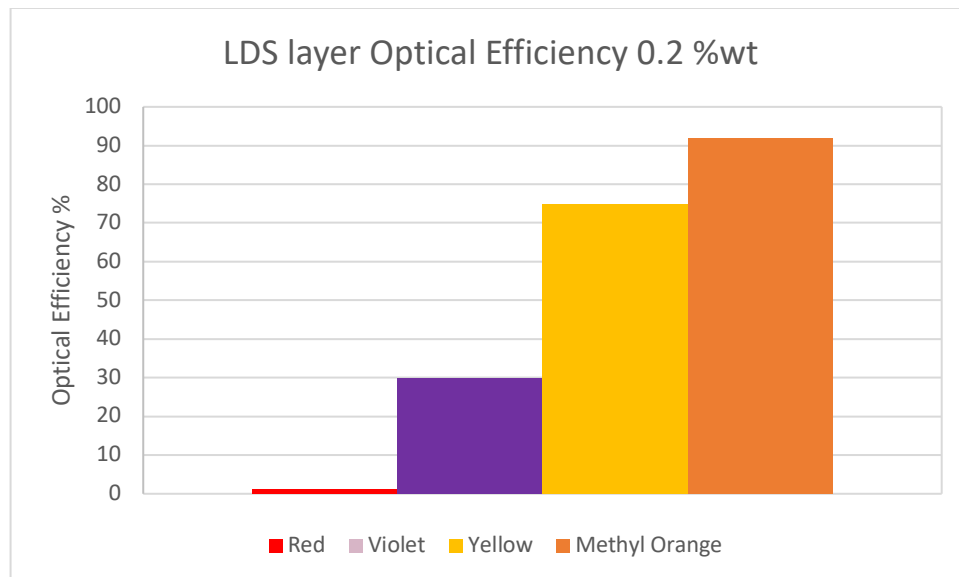


Figure 5.3 Comparison of Optical Efficiency for LDS layers at 0.2%wt

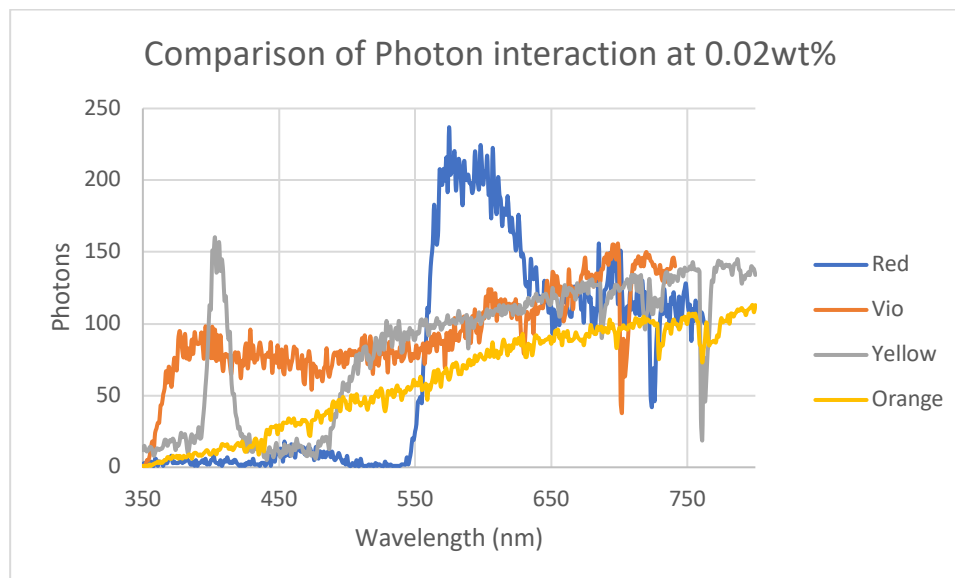


Figure 5.4 Comparison of photon interaction of dyes at 0.02%wt

The initial dataset generated was aimed at evaluating the dye concentration (0.02 %wt) corresponding to the second test system used in the IDEAS project (described in 6.3 as shown in Figure 5.4. This analysis primarily focused on lower wavelengths where Si PV cells are less effective. As illustrated in Figure 5.4, the Lumogen violet dye (BASF) demonstrates a broad

interaction range between 360 – 550 nm, with the Lumogen yellow dye producing the highest interaction peak. Methyl orange dye (Sigma Aldrich) which was applied in the actual LDS layered PV cells for the IDEAS system shows a gradual increase in interaction across the spectrum. The Lumogen red dye, in contrast, exhibits minimal photon interaction up to 550 nm which is when Si PV cells begin to operate efficiently. However, at this specific concentration, the red dye could potentially be optimised for alternative PV cell technologies that are more efficient at different wavelength ranges.

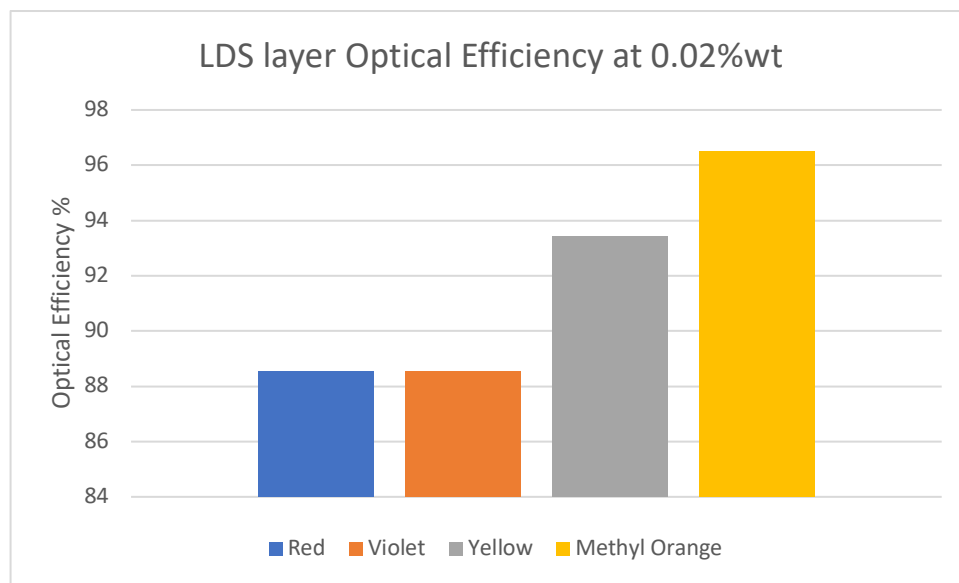


Figure 5.5 Comparison of optical efficiency for LDS layer using different dyes at 0.02 %wt concentration

Figure 5.5 illustrates LDS layers with a uniform thickness of 20 μm , where Methyl orange dye has the highest optical efficiency of 96% and Lumogen red the lowest at 67%. It is important to note that these measurements were conducted at a dye concentration of 0.02 %wt, emphasizing that varying the dye concentration directly influences both the optical efficiency and power output of the system. The losses that can occur are the ratio of rays lost due to incident photons being dissipated as thermal energy and due to photons exiting the device without contributing to energy conversion. The aggregate of these losses determines the overall optical efficiency of the LDS layers.

Additional parameters evaluated through simulation was the influence of LDS layer thickness on its efficacy. The computational model showed that a thickness of 20 μm marginally enhanced performance compared to 10 μm and 40 μm configurations where 30 μm thickness was identified as having the lowest optical efficiency for the LDS layer (as presented in Figure

5.6. This simulation thickness analysis was conducted with a dye concentration of 0.02 wt% on a 2 cm x 2 cm PV cell.

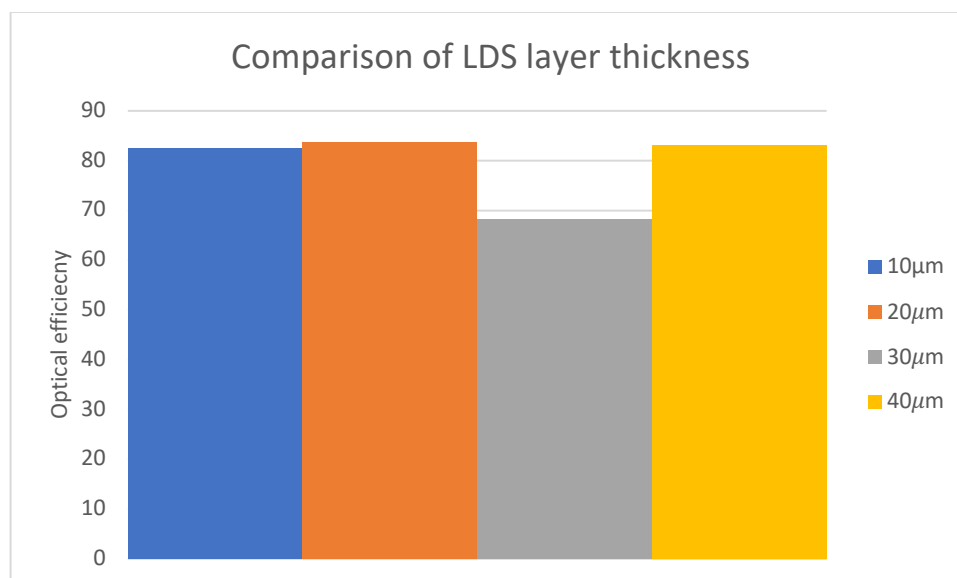


Figure 5.6 Comparison of LDS layer thickness

5.4 Conclusions

Before using this computer simulation, the validation and verification process for the LDS layer would require the LDS polymer solution for fabrication of LDS layers with multiple concentrations and various chemical recipes. All of which are long-term trial and error testing, which takes a long time commitment and waste of materials. Once that is achieved, the physical characteristic changes can be changed and tested to find the desirable contribution. This whole process has been streamlined into the computer simulation producing a testing layer at a desired LDS layer characteristic. Then a physical LDS layer fabrication can be produced to verify the matching results. This reduces time commitment, which can then be implemented in a different aspect of the research.

The deployment of ray- tracing modelling simulations has proven indispensable in the optimisation of LDS layer parameters and selection of luminescent dye, providing direction on necessary modifications to dye/layer characteristics to maximise downshifting efficiency. This approach is especially significant considering the expansion of commercially available

dyes, which could be potentially used in LDS. The computational data generated from these simulations have been pivotal in identifying dyes that enhance the performance of Si PV cells with LDS layers.

The simulation has facilitated the optimisation process using key LDS layer attributes such as dye concentration and layer thickness. This methodological approach significantly reduced the time requirement associated with the experimental process, allowing for rapid testing and modifications of layer specifications. While experimental validation remains essential, the simulations provide a starting point that enhances the efficiency of the subsequent empirical investigations.

The possibility of adapting the solar cell within the simulation from silicon to alternative PV technology has potential to broaden the applicability and efficacy of LDS technology. Aligning the appropriate dye with the specific material characteristics of the PV is paramount for achieving optimal device performance. The optical efficiencies of the four dyes were critical in illustrating the potential effectiveness of the applied LDS layers. The significance of dye concentration along with absorption, emission and EQE of the dye were invaluable to this study. These aspects which underpin the fundamental understanding of LDS layers will be further explored in the subsequent chapters.

Chapter 6. Progression of LDS within CPC LDS systems

6.1 Introduction

This chapter focuses on applying LDS on PV cells within a CPC system (as described in Section 2.8). This was partly completed in February 2020 and sent to the IDEAS partner (University of Ferrara (UNIFE)) with the aim to travel to Ferrara to complete the final system connections and installation. However, COVID-19 disrupted this plan. The quality and operational viability of the system will be discussed, highlighting necessary modifications and enhancements to optimise the performance of LDS layered PV cells.

6.2 First IDEAS Solar façade panel

The first IDEAS solar façade panel, described in Section 4.5, arrived at the IDEAS partner, the University of Ferrara (UNIFE), in February 2020. Owing to the constraints imposed by the COVID-19 pandemic, the shipment remained unopened until May 2020. Subsequent to opening, a comprehensive analysis was undertaken to assess the system's status, including the LDS layer, in terms of its structural integrity and functional performance.

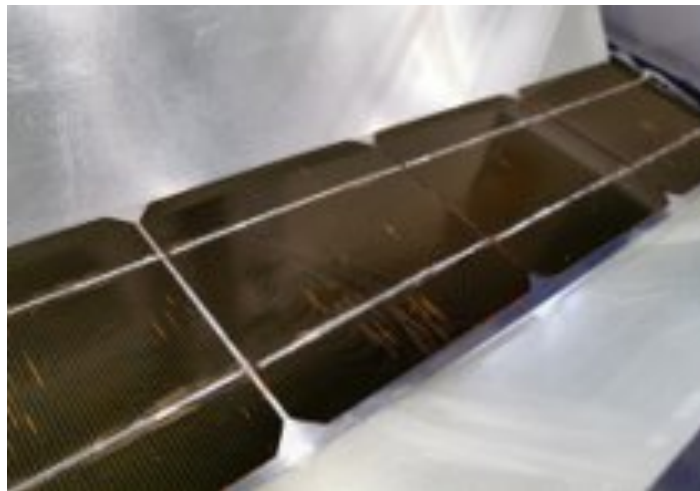


Figure 6.1 Images of LDS cells arrived in Ferrara, Italy, February 2020

As depicted in Figure 6.1, there was a noticeable delamination of the LDS from the PV cell, predominantly localised along the busbar lines.

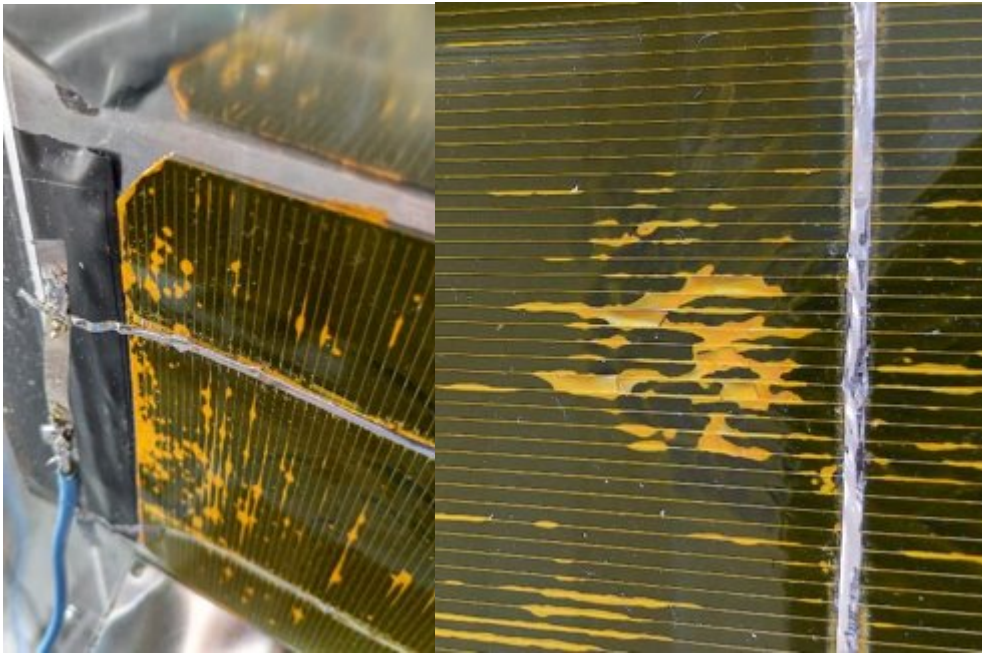


Figure 6.2 Image of LDS layer defects

Figure 6.2 illustrates the defects that have caused the LDS layer to partially detach from the PV cell. This delamination reduces the layer's capacity to enhance the cell's operational efficiency and hinders solar radiation from reaching the cell. The formation of an air gap induces total internal reflection, which diminishes photon coupling with the PV cell. As discussed in Sections 2.3 & 2.4, parasitic absorption can impede the efficiency improvement by LDS layers. This loss mechanism intrinsic to LDS layer design is modulated by the properties of the host material (PMMA) and the layer thickness.

Figure 6.3 shows additional complications observed upon the arrival at UNIFE, Ferrara. Extensive delamination was identified across numerous individual PV cells, affecting some PV cell surfaces area entirely. Several cells exhibited discolouration indicative of the degradation of luminescent dye within the LDS layer of the PV cell. The high thermal stresses experienced by these LDS layered PV cells due to the concentration effect of the CPC system could have significantly contributed to the observed material responses, including the delamination of LDS layers and the fracturing of the fragile PV cells.

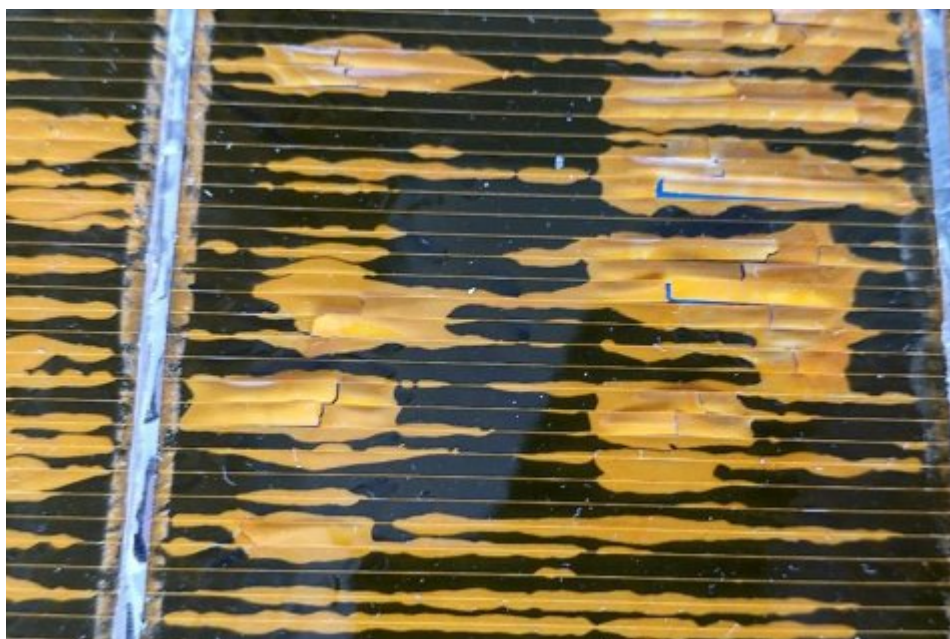


Figure 6.3 Example of delamination of LDS layer across a PV cell.

In contrast to Figure 6.4, where delamination predominantly manifested at the central region of the PV cell, Figure 6.3 suggests that inadequate adhesion may be responsible for the delamination observed around the periphery of the cell. This phenomenon could be attributed to the presence of an air gap beneath the LDS layer, potentially overlooked during inspection or formed due to contaminants such as dust present on the PV cell prior to LDS layer application. The localised delamination seen in Figure 6.4 may not result from the lack of adhesion. The cause is a result of adhesive failure. Instead, it appears to originate from the central region of the cells, likely during the application of the LDS polymer solution via spin-coating, indicating a primary adhesion issue rather than subsequent environmental contamination.

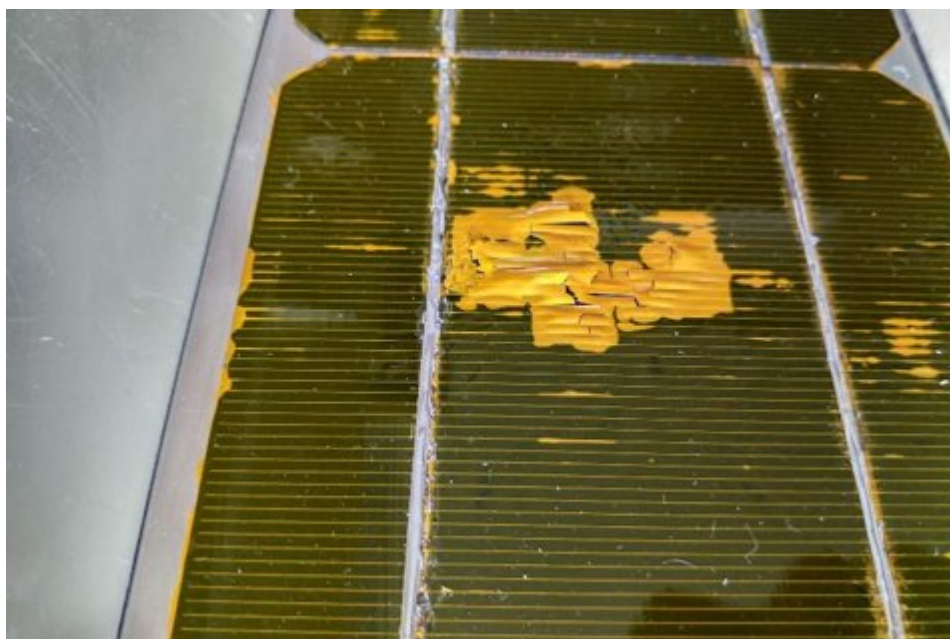


Figure 6.4 Delamination at the centre area

This indicates that multiple factors contribute to delamination, including the presence of contaminants within the LDS matrix that inhibit adhesion at localised sites, though it was presumed that these would be uniformly distributed across the cell. Additionally, layer degradation, characterised by a progressive loss of adhesive properties over time, and external factors such as environmental influences such as weather conditions (transportation in damp conditions leading to corrosion) may also play a significant role.

The delamination of the LDS layer from the PV cell could be caused during the application process when the LDS polymer solution is being applied to the PV cell to be spun in the spin coater. When the LDS polymer solution is spun too rapidly at the beginning, the LDS polymer solution would be spun out from the centre of the PV cell, which means the LDS layer does not fully adhere to the PV cell. This would not be seen after the LDS layer has dried and is only noticeable when the LDS has been exposed for an extended period. In Figure 6.4 these LDS layered PV cells had been integrated into the CPC system and have been in the system for over 2 months when they arrived in Ferrara. This was an unexpected delay due to COVID-19 during Spring 2020. Delamination can occur at the points under external heat/pressure due to soldering. This excess heat can burn away the LDS layer, causing the remainder of the LDS to peel slightly, which in turn leads to further delamination when it occurs across the soldering area of the PV cells. This is shown in Figure 6.5.



Figure 6.5 Image of soldering's effect on LDS

Figure 6.5 illustrates the complications arising in cells with front and back connections. The thermal energy discharged during the soldering process to establish electrical connections inflicted thermal damage on the LDS layer that deteriorates the LDS and undermines its efficiency.

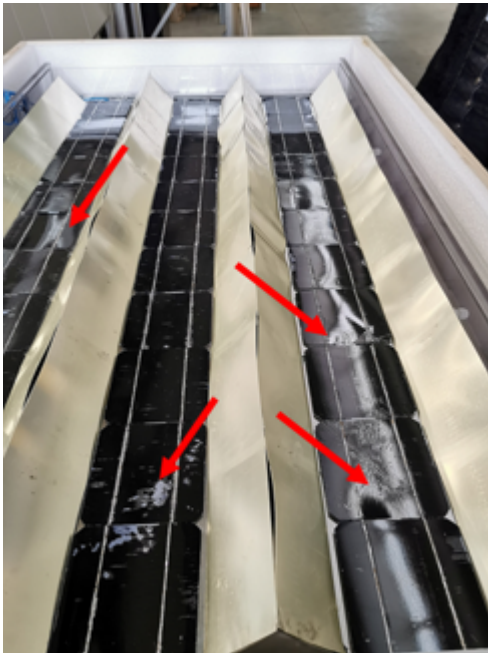


Figure 6.6 (A)

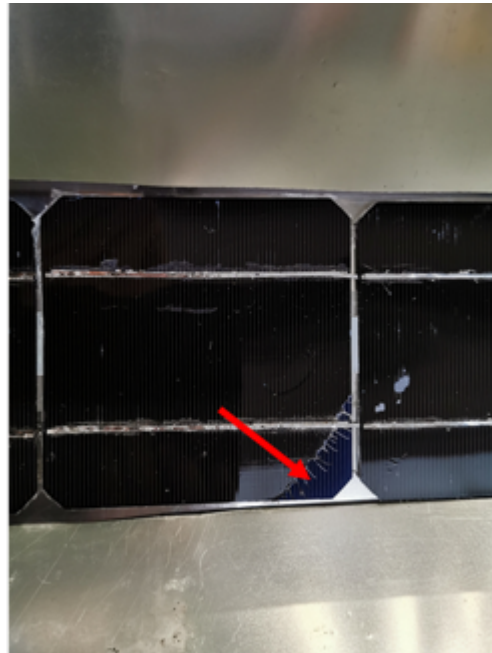


Figure 6.6 (B)

Figure 6.6 (A) and (B) Images of issues of non-LDS layered cells

In conjunction with the LDS layered system, a reference system (blank polymer layered system) was also fabricated for comparative analysis. Figure 6.6 A & B displays a clear visualisation of the diverse defects within the layers. Figure 6.6A shows regions of compromised, manifested as elevated patches within the LDS layer, whereas Figure 6.6B depicts areas where the LDS failed to completely encapsulate the PV cell surface.

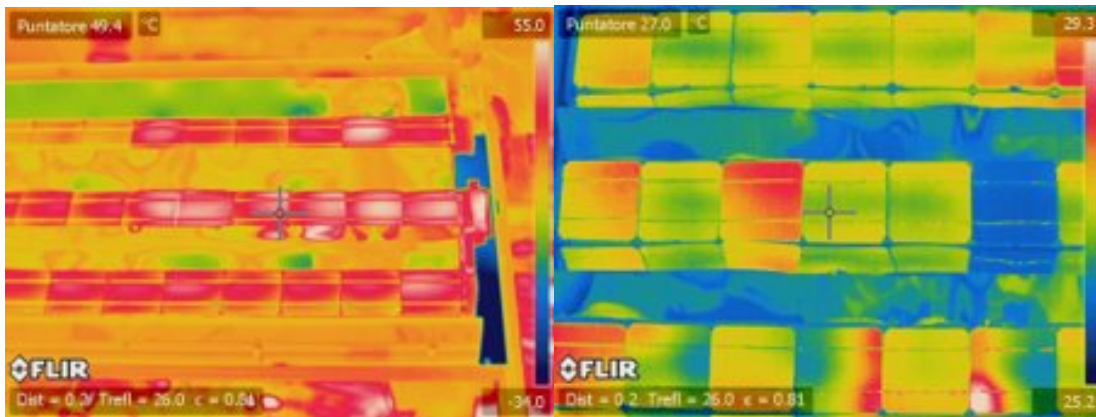


Figure 6.7 (A)

Figure 6.7(B)

Figure 6.7 Thermal imaging of LDS cells, A on the left, B on the right

The thermographic images shown in Figure 6.7 illustrate the differential distribution of thermal energy across the PV cells. It is important to note that reflective concentrators flank the cells. In Figure 6.7B a marked decrease in thermal concentration is observed with certain cells exhibiting minimal thermal activity (indicated by blue areas on PV cells).

The CPC system with the LDS installed was designed to produce 100 W per system (see Section 2.8.1); however, it was only producing 84 W, as seen in Figure 6.8. This data was taken outdoors in June 2020 in Ferrara, Italy. The average solar radiation per day for Ferrara, Italy, was 6.886kWh/m² (Italian Solar Radiation Atlas, 2022).

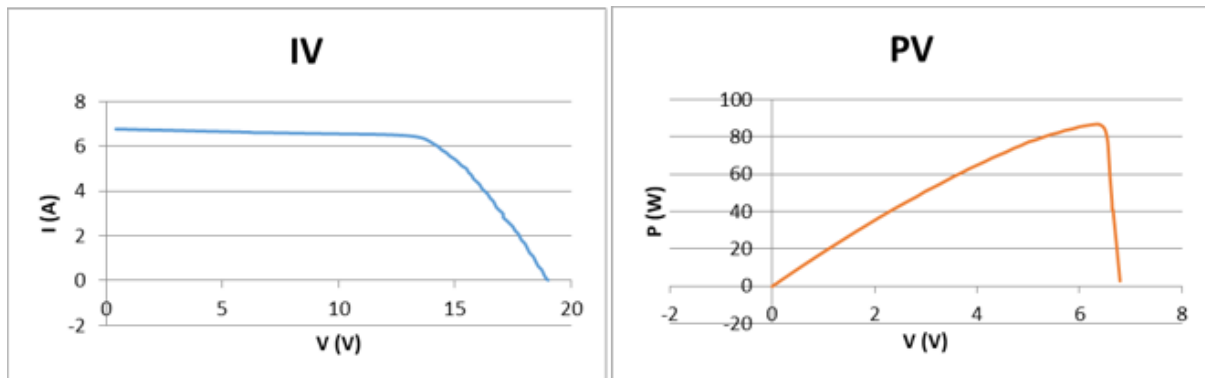


Figure 6.8 The power was 84 W, corresponding to about 8.4% efficiency.(IDEAS WP3 Collaboration workshop)

Table 6.1 Challenges to LDS

Issue with LDS	Cause	Solution
LDS layer degradation	Layer fabrication not optimal	Inert environment for layer fabrication
Busbar connection	PV cell connections in the system	rear busbar PV cells used
Delamination	Layer adhesion to PV cell	LDS application

LDS improvement: Based on the data from the first IDEAS system sent to Ferrara, LDS required redevelopment and enhancement. Critical issues identified included rapid LDS degradation post installation and delivery, as well as inconsistencies in layer application to achieve comprehensive LDS coverage on PV cells. A pivotal step in addressing these concerns entailed a thorough reassessment of the LDS solution production process, identifying and optimising specific areas for improvement. A significant variable under examination was ambient conditions prevalent during the production process, leading to the adoption of an inert environment for LDS solution synthesis.

This inert environment is described in Section 3.8.4, along with the associated modifications to the process.

With the use of the inert environment, the fabrication timing for a layer changes from 30 – 45 minutes in an open environment to allow full dissolution; now, the process requires a minimum of 60 minutes to fully dissolve into an LDS solution. This had a large impact, especially when fabricating a large quantity of layers for multiple CPC systems. The use of a nitrogen in spin coater, the use of a nitrogen inert environment in a glove box, produces a

more fluid LDS solution, resulting in a less viscous liquid compared to an oxygen rich environment (no pre-polymerisation as mentioned in section 4.2). This resulted in requiring more solution to produce the uniform and consistent LDS layers.. This allows the use of a stock solution over a longer period to fabricate LDS layers in a single batch. The batch sample sizes remained the same, with a remaining ratio of 4g (28.5 wt%) of PMMA per 10 ml (71.4 wt%) of chloroform, 1400 mg (0.001wt%) of luminescent dye. There is a slight increase of PMMA from 3.8 g to 4g to allow the less dense LDS solution to remain. To produce the desired thickness of 20 μ m. This process overcame the limitation of that batch which fabricated within 60 minutes. Led to a 90 minutes fabrication process to produce 3 LDS layered cells, compared to a previous 45 minutes requirement in the open air(inert environment). This process has been complemented with the change of PV cells.

To circumvent electrical connectivity issues encountered with the front and back contact PV cells for the first IDEAS system, due to the LDS layer obstructing the busbars and hindering the connection between the CPC and the LDS layered PV cells, back contact cells were used. This eradicated connectivity issues between each PV cell, ensuring unimpeded electrical integration within the CPC system. Figure 6.9 (A-D) illustrates the comparative structural distinctions between the two cell types. Figure 6.9A & B depict the back contact cells, and C&D show the front and back contact PV cells.

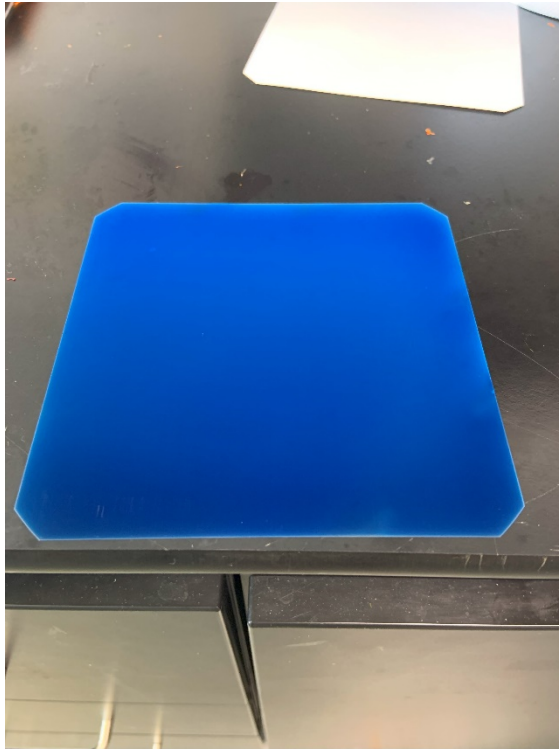


Figure 6.9 (A) Back contact cells front

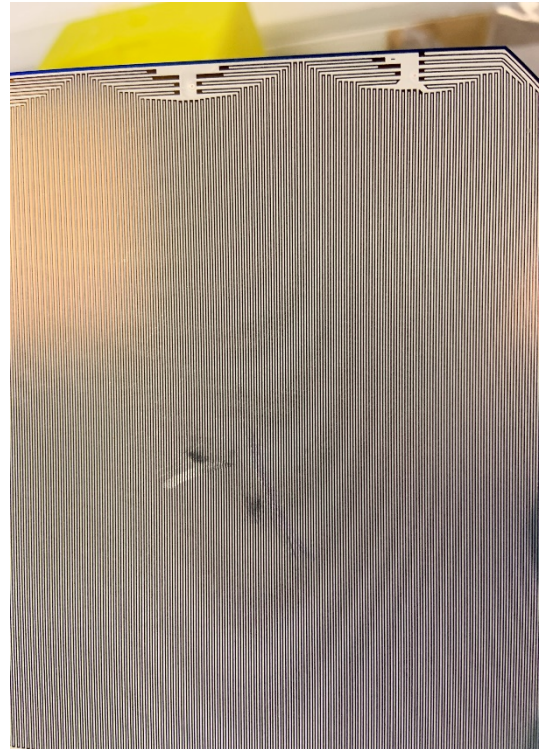


Figure 6.9(B) Back contact Back



Figure 6.9 (C) Original cells front



Figure 6.9 (D) Original back

Figure 6.9 Examples of busbar connections of PV cells

The modification of the fabrication process has extended the production time for LDS layers. Despite this increase in time requirement, this revised methodology has substantially enhanced the quality and reliability of the LDS layers, culminating in an elevated standard of production.

6.3 LDS Layer Reassessment

Issues	Alteration	Result
LDS uniformity	Reassessment in an inert environment	Uniform LDS
LDS polymer mixing	Spin speed in mixing/ inert environment	20 µm thick/clean layer
Layer application	Attachment process changed	Uniform on 12x12cm PV

Table 6.2 LDS layer reassessment challenges

After reviewing the deficiencies observed in the LDS in the first IDEAS system at UNIFE, Ferrara, a critical evaluation was imperative to enhance the LDS layer quality while rectifying the identified challenges. Pertinently, the issue of non-uniform LDS coverage across the PV solar cell necessitated a renewed focus. Consequently, the reassessment process commenced at a smaller scale of 2 cm x 2 cm on glass substrates as shown in Figure 6.10, to methodically address and improve layer consistency and coverage.

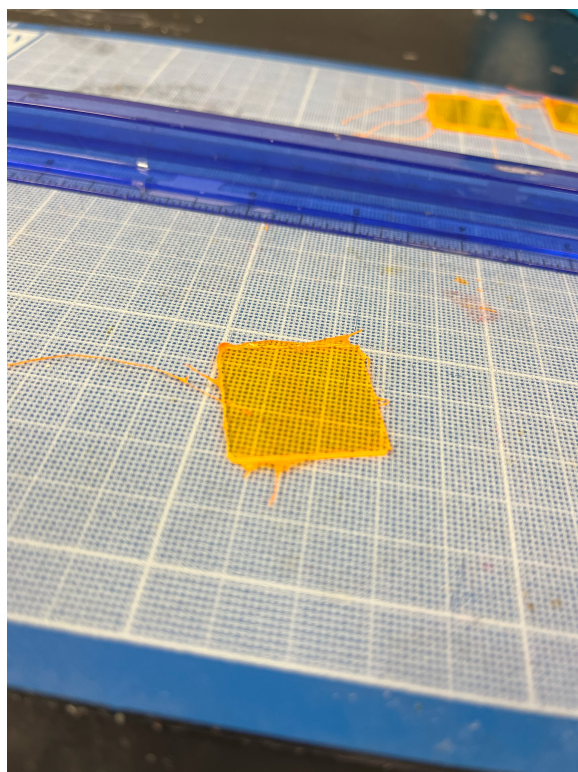


Figure 6.10 Complete covering LDS using inert environment on a 2 cm x 2 cm glass slide

As previously mentioned in Section 3.8.4, a nitrogen-filled glove box (inert environment) was used to produce the polymer solution to fabricate the LDS layer. A systematic examination to identify and rectify potential defects or inconsistencies was essential. Section 4.6 outlines these process changes for enhanced performance.

The process of polymer mixing was adapted for inside the nitrogen-filled glove box. A reevaluation of the spin coating procedure using a newly formulated polymer solution revealed that the absence of prepolymerisation resulted in a thinner LDS layer when using the original spin coater speed and recipe. To attain the requisite thickness, a modification in the spin speed protocol was introduced. Instead of instantaneously ramping to 1000 rpm, an immediate step involving 10 seconds at 500 rpm was incorporated. This modification facilitated initial polymerisation within the controlled environment, allowing the polymer to thicken on the substrate, and then the spin speed was increased to 1000 rpm, ensuring comprehensive coverage.

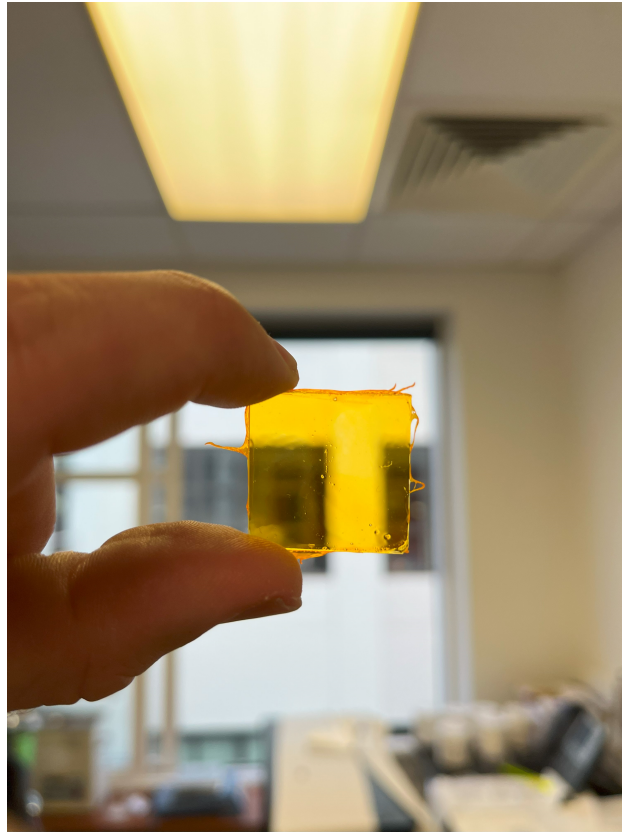


Figure 6.11 Image showing the physical quality of the LDS layer.

Figure 6.11 shows the fabricated LDS layer deposited on a glass substrate of 2 cm x 2 cm. Evaluating the layer's transparency when applied to a glass substrate was important. The presence of minor specks within the layer indicates areas of non-uniformity. However, it is critical to highlight that the layer achieves complete coverage of the substrate without delamination, effectively mitigating several of the challenges encountered in earlier experiments. The next step was upscaling to 12.5 cm x 12.5 cm PV cells.



Figure 6.12 First attempts of upscaling

In the refining the LDS layer, an alternative method for connecting PV cells via busbar soldering was implemented for the IDEAS system. This modification enables comprehensive coverage of the PV cell by the LDS layer without necessitating soldering through the LDS later, thereby mitigating potential reductions in its efficacy.

As illustrated in Figure 6.12, initial fabrication yielded a LDS layer with non-uniform characteristics not seen in the preliminary 2 cm x 2 cm scale experiments. However, in the principal areas of the cells in Figure 6.12, (indicated by lighter patches) the desired 20 μm thickness for the LDS was successfully achieved. Another challenge that became apparent when using these PV substrates was the detachment of electrical connection during the spinning process, resulting in a proportion of cells being unusable or breaking. Identifying a procedure to ensure stable cell positioning throughout spin coating is crucial for achieving consistent layer uniformity.

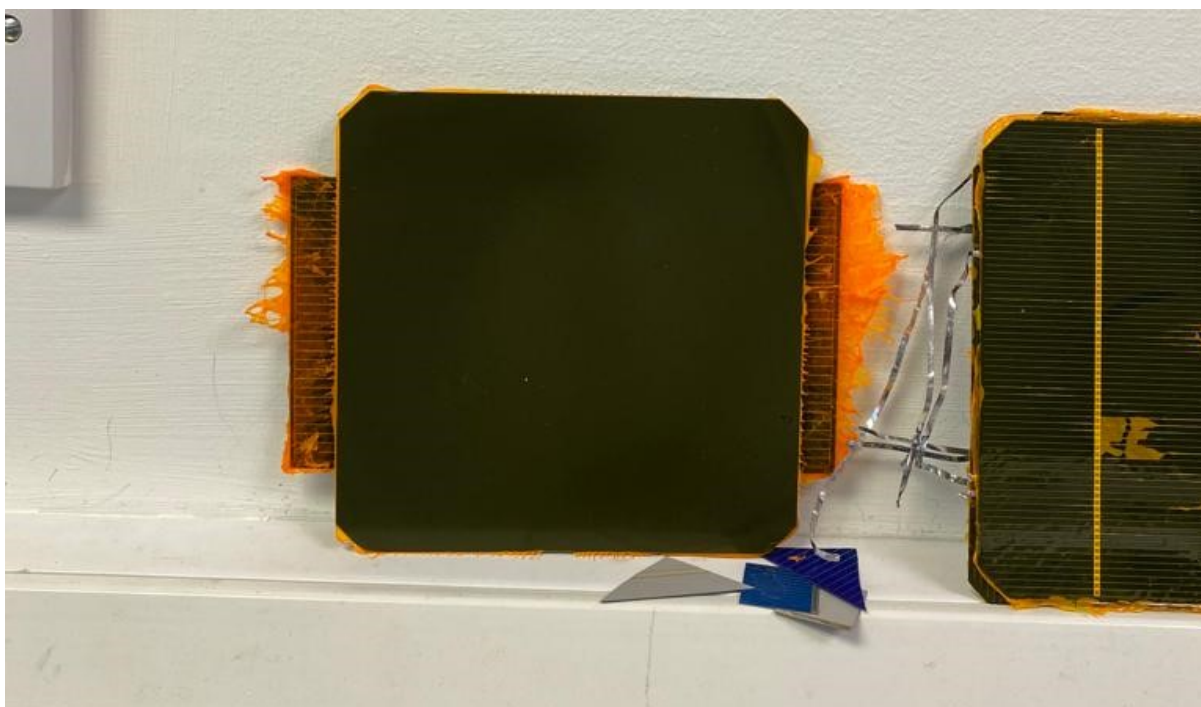


Figure 6.13 Coated LDS PV cell with back busbar connection

Back busbar connections:

To improve the cells mounting to the spincoating chuck, a smaller cell was taped to the back contact cell, as shown in Figure 6.13. This arrangement enhances the vacuum chuck's ability to exert pressure on the cell assembly, facilitating the simultaneous spinning of both cells. As described in Section 4.3, the new recipe altered the viscosity of the LDS. It enabled the polymer solution to undergo polymerisation and achieve complete coverage across the larger 12.5 cm x 12.5 cm cell. Using this methodology, the challenges of non-uniform layers were mitigated but not entirely eradicated, potentially attributable to variations in procedural repeatability. This technique diminished the risk of PV cell damage or destruction during the spin coating process, thereby enhancing the overall efficiency of the fabrication process.

The resulting LDS, shown in Figure 6.14, exhibits a homogenous and impurity-free surface upon visual inspection. This corroborates the reliability of the spin coating technique in consistently fabricating uniform LDS layers on back contact cells.

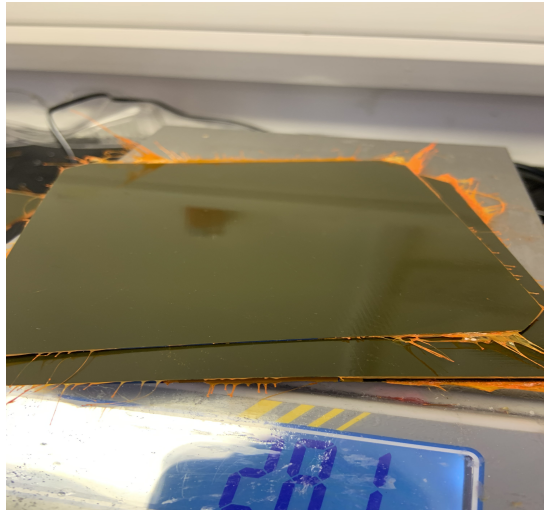


Figure 6.14 Image of improved LDS

6.4 Second IDEAS solar façade system

In October 2022, UNIFE, Ferrara, received a site visit. During this visit, two panels with LDS were inspected.



Figure 6.15 LDS layer PV integrated CPC systems at Site 1 in Ferrara, Italy.

These systems used LDS coated PV cells with back contacts. The first site is a research building part of the University of Ferrara (UNIFE). As the systems were accessible on the ground, detailed inspections were carried out. Figure 6.15 shows the site where they were installed.



Figure 6.16 (A) & (B) Examples of layer decay and non-uniformity occurring

The initial phenomena observed encompass both the degradation of the polymer matrix and the discolouration of the layer. The LDS layered cells maintained their polymer coating, however, the luminescent dye exhibited signs of volatilisation. Notably, the presence of lighter-coloured patches on the layers, as shown in Figure 6.16, indicated that this degradation process may have facilitated the dye evaporation. Despite this LDS layered cells retained a slight tint of luminescent dye, which distinguishing them from the blank PMMA layer.

While the layer application process was improved using the inert environment for production and modifications to spin coating, there were still circumstances in which inconsistencies existed. Such variability can be attributed to disparities in the quality of PV cell surfaces or the inadvertent adherence of particulate matter to the cell surface prior to LDS application, as shown clearly in Figure 6.16 (B). Conversely, in Figure 6.16 (A), there were specks seen adjacent to soldered connections, albeit with the remainder of the layer remaining intact. On

examining the PV cell's surface, minor damage was detected at junction points, particularly at the end of cell rows, where increased damage was noted compared to other cells within the same row. Cells situated at row ends, necessitating direct connections to the CPC system, underwent more extensive soldering, potentially contributing to cell damage.

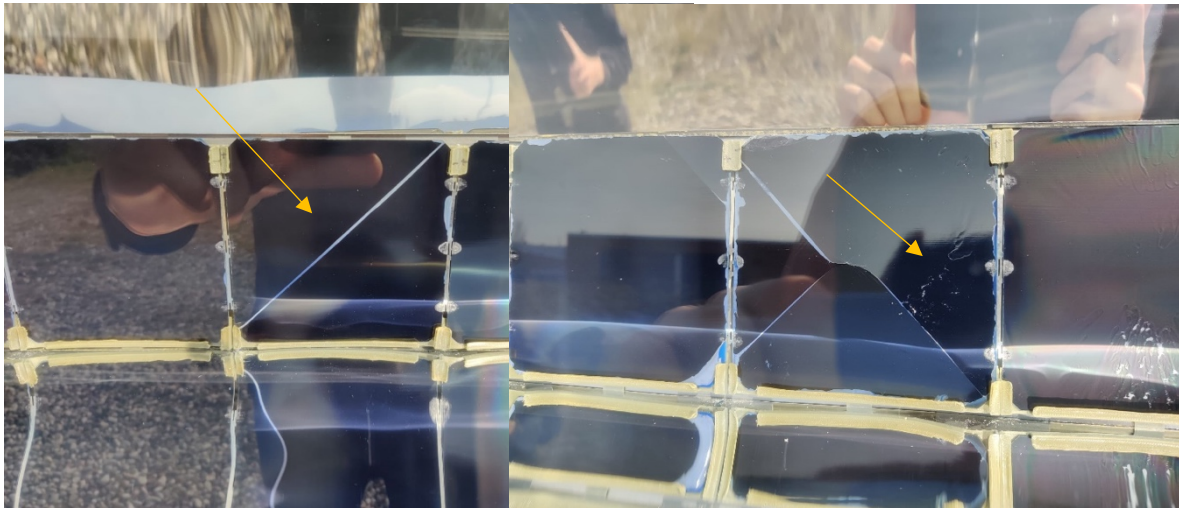


Figure 6.17(A)

Figure 6.17(B)

Figure 6.17 Images of cell fractures and breaks in the CPC system.

Similarly to the initial systems sent to Ferrara, occurrences of PV cell breakage were observed subsequent to their installation within the IDEAS system. Figures 6.17 (A) & (B) show the fractures identified in PV cells coated with LDS layers. As discussed in Section 3.7, a byproduct of applying an LDS to a PV cell is the potential increase in the cells' fragility, which can manifest during the spin coating procedure. Consequently, this increased fragility renders the cells vulnerable to cracking under conditions of pressure applied either at the periphery or unevenly across the cells' surface. Instances such as those depicted in (B), where multiple fractures were observed on the LDS-layered PV cells, highlight this susceptibility.

Due to the series connection, if a single cell malfunctions, that will compromise the operability and output of the string of cells. Even though spare LDS layered cells had been prepared in case of breakages during the assembly process, once the cells and rows were attached to the IDEAS solar façade system, they could not be replaced.



Figure 6.18(A)



Figure 6.18(B)

Figure 6.18 (A) & (B) Examples of defects & discolouring of LDS layer in CPC systems

The final challenge encountered with the LDS layered cells is the discolouration and degradation of the layer. Throughout both indoor and outdoor experimental characterisation conducted on campus at Trinity College, Dublin, there was no observable fading of the LDS layer. However, the majority of the cells at the Ferrara site exhibited notable dye discolouration, with some cells also demonstrating extensive detachment, which was not replicated in laboratory assessments.

During the onsite inspection, condensation was detected within the sealed system enclosures, the pigment of which corresponded to the dye used in the LDS polymer solution. This observation indicates that the LDS layer underwent both physical and chemical degradation, as evidenced in Figure 6.18. The luminescent dye appeared to have partially evaporated from the LDS layer at an indeterminate juncture during transit from Trinity College Dublin to the UNIFE site in Italy.

6.5 Testing of CPC with LDS at site 2.

Figure 6.19A shows the solar resource measured at UNIFE, and Figure 6.19B shows the output power for the IDEAS system and the reference system. The reference system has no LDS layered cells, similar to a commercially available PV system.

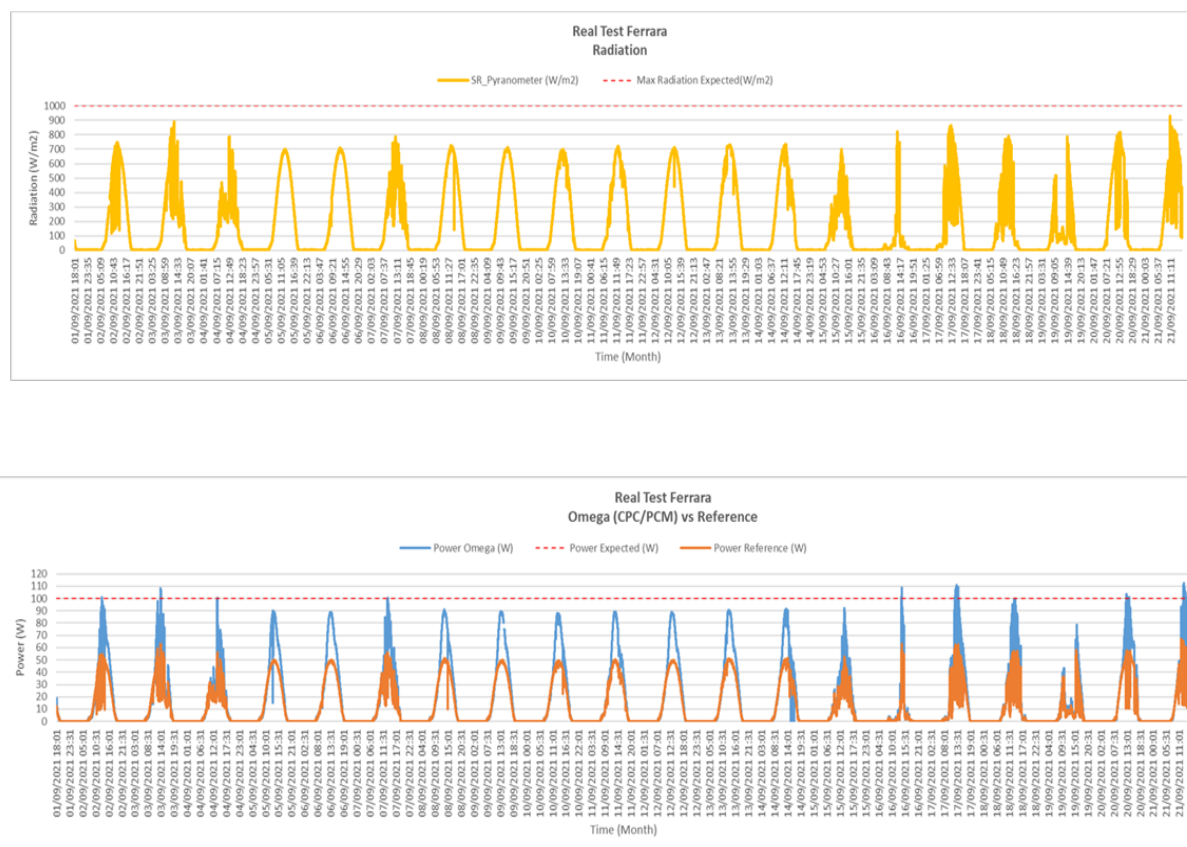


Figure 6.19 Reference system compared to CPC with 24 LDS PV cells at Ferrara, Italy, on 22/11/2021

Figure 6.19 B compares the IDEAS system (blue) with a reference system (orange) over a 20-day period during Winter 2021. The graphs' analysis reveals a noticeable enhancement in the power output of LDS layered cells compared to the bare PV cell CPC system.

Figure 6.20 presents a simulated analysis of the LDS layered cells, focusing on their wavelength-specific interaction profiles, to demonstrate the advantages of LDS technology on PV cells. This simulation indicates heightened absorption below 400 nm (a region where silicon cells exhibit suboptimal performance) with an anticipated increase in emission occurring above the 500 nm wavelength range.

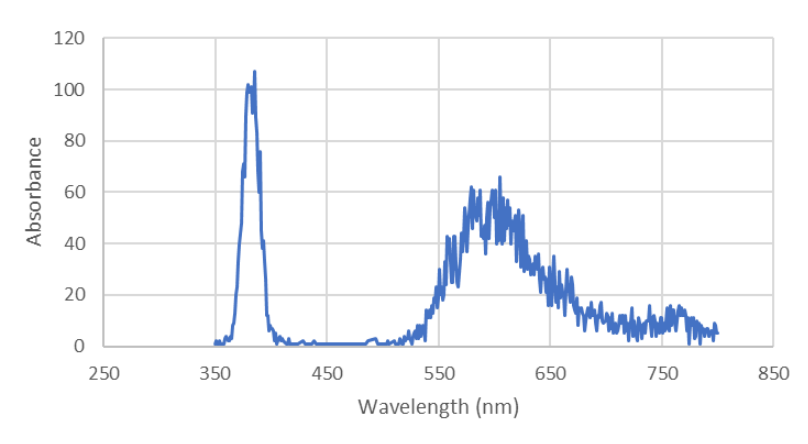


Figure 6.20 Simulation of LDS absorbance expected with 10K rays excitation spectra.



Figure 6.21 2nd set of LDS coated CPC systems used at test site on UNIFE campus in Ferrara.

The 2nd set was installed onto the façade of the building, as shown in Figure 6.21 . Attached to a student union café, which is integrated with a heat pump system, commercial solar panels and an AI system to automate the entire system.

6.6 Conclusion

This chapter focused on the large-scale LDS layer integrated into the IDEAS systems for UNIFE, Ferrara. Following the installation, initial challenges emerged and this chapter focused on how these issues were addressed. A critical focus was the potential contamination of the LDS polymer solution by environmental particulates, necessitating the adoption of an inert environment (detailed in Section 3.7). Consequently the LDS layer fabrication process underwent meticulous reassessment to enhance adhesion between the LDS layer and the PV cell.

A particular emphasis was placed on the soldering regions along the busbars, which experienced damage from the heat necessary to establish electrical connections. The transition to using back-contact solar cells resolved this issue. However, it required a modification to the spin coating process by attaching a supportive substrate under the PV cell, facilitating successful LDS application. Furthermore, strategies were refined to ensure the uniform application of the LDS layer, including carefully distributing the LDS stock solution.

Despite these advancements, the cause of discolouration observed in the LDS layered cells remains elusive and difficult, warranting further investigation. As discussed in Section 6.4, the evaporation of luminescent dye may have transpired during transport or post-installation in the IDEAS system. This issue may have been exacerbated by moisture entrapment within the systems, accelerating LDS degradation. This requires further scrutiny under both enclosed and ambient testing conditions. These improvements were implemented before the assembly of the second IDEAS system.

Analytical comparisons depicted in the graphs from Section 6.5 illustrate the correlation between solar radiation levels over the testing period. This facilitated a relative evaluation of performance under direct solar radiation. The projected output for an optimised LDS integrated IDEAS system was established at 100 W, achievable under peak irradiance conditions. Comparative analysis with reference systems, comprising only Si PV cells, demonstrated an increase of approximately 40 W or a 67% enhancement over the 60 W output observed from the reference configurations.

Chapter 7. LDS development for various PV technology & pLDS integration

7.1 Introduction

In this chapter, LDS layers were applied to various types of PV cells, such as silicon, a-Si, and CdTe PV cells, are discussed. The variation in the PV cells, along with the challenges associated with each, are detailed. Comparative characterisations of CdTe cells in both pre- and post-LDS application were conducted; evaluations were carried out at Trinity College Dublin (TCD) and LEITAT Technological Centre (Spain), an EU IDEAS project partners. TCD fabricated and applied LDS layers onto the various PV cells and conducted preliminary EQE testing of the LDS layered PV cells. LEITAT researched and procured the specific PV cells used and carried out verification EQE testing of the LDS layered PV cells. This was to validate the measurements taken in TCD and their experimental setup.

Section 2.7 outlined the integration of pLDS and the differences between LDS and pLDS. This chapter presented layer production, fabrication, and application. The incorporation of metal nanoparticles (MNPs) into the polymer layers introduced a series of compatibility challenges. A full solar panel of 64 pLDS-layered PV cells were assembled and characterised plus a comparative analysis was undertaken.

7.2 LDS applications to various PV technology

The LDS technology devices in this research was precisely engineered to increase the operational efficiency of silicon-based PV cells. For more comprehensive LDS application, LDS layers were applied to various PV technologies such as cadmium telluride (CdTe) and amorphous silicon (a-Si); these PV cells are shown in Figure 7.1 and 7.2, respectively. The a-Si cells were encapsulated with a glass substrate on top of the PV cells, with fixed positive and negative electrical connections soldered to the cells' busbars. These PV cells were connected in series and then sealed. The CdTe PV cells were connected similarly to the a-Si PV cells in a mini-module. The CdTe were encapsulated between 2 glass substrates with soldered

electrical connections used without interacting with the cells directly, thereby preventing direct LDS application onto the PV cell surface. Encapsulation introduced an additional layer, therefore increased the probability of absorption of incident photons, and reduced the effectiveness of the LDS layer. These samples were procured through collaboration with LEITAT (an IDEAS project partner) from Antec Solar.

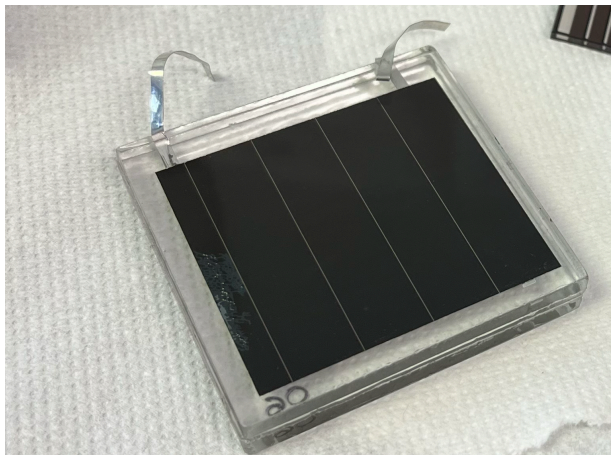


Figure 7.1 (A) Cadmium Telluride PV cell

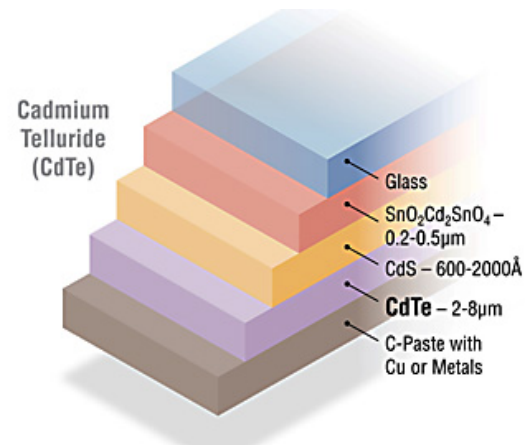


Figure 7.1 (B) Cadmium Telluride structure (NREL, 2019)

Figure 7.1 CdTe PV cells used

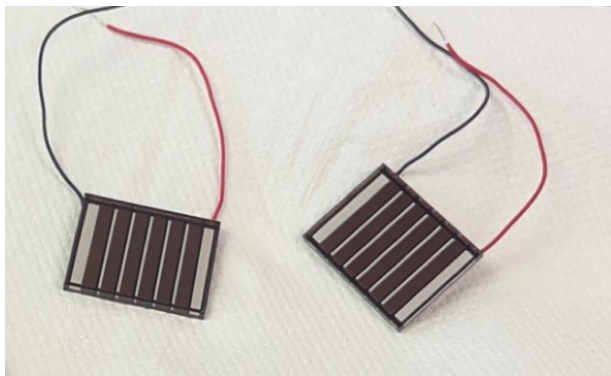


Figure 7.2 (A) Amorphous silicon PV cell

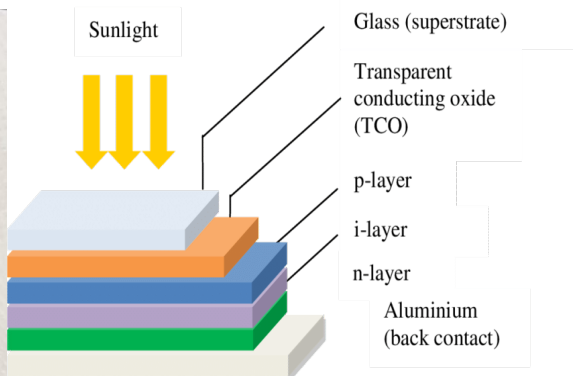


Figure 7.2 (B) A-si structure (Karzazi & Arbouch, 2014)

Figure 7.2 A-si PV cell used

7.3 Types of PV Cells

External Quantum Efficiency (EQE), defined in section 2.6, was the benchmark for comparative analysis, used to assess the performance of the two types cells with and without LDS layer application. EQE measurements were also conducted at LEITAT to provide comparative data. The methodology used to apply the LDS to these PV cells necessitated a critical evaluation to ensure robust adhesion.

The initial layering procedure followed the application process for Si cells (defined in Section 3.6). Similarly to the back contact cells, CdTe cells presented difficulties to achieve rotation due to the interaction interface between the PV cell and the chuck of the spin coater. This challenge was due to the surface of the CdTe cell being a glass encapsulant, which does not facilitate a vacuum seal as efficiently as the surface of an a-Si PV cell. To circumvent this, a larger chuck was used, as the hole of the vacuum pump connection was slightly larger, which allowed the glass base to sit flush with it. The application of the LDS layer on these cells is shown in Figure 7.3.



Figure 7.3 (A) LDS applied to all CdTe



Figure 7.3 (B) close up of LDS on CdTe

Figure 7.3 (A) & (B) LDS applied to CdTe.

Following the successful application of the LDS layers on these two types of solar cell., Challenges similar to those encountered with the Si applications emerged, particularly in terms of uniformity and layer adhesion. CdTe PV cells, which were encapsulated by glass on top and beneath the PV cell (see schematic in Figure 7.1), presented substantial difficulties in coating application, culminating in the complete detachment of the LDS layer from the upper glass surface. Figure 7.4 showed the extent of layer peeling from the glass substrate. Despite having achieved complete surface coverage, some instances occurred where the lack of adhesion led to the entirety of the LDS layer peeling off without fragmentation.

A contributory factor to this issue was the weight of the sample, which, at 50 g, was a significant increase in weight compared to other solar cell samples used in this research. This required a stronger vacuum mounting , which was achieved through repositioning and adjusting the busbar connections. As the weight of the sample caused the sample to detach from the chuck when the speed increased, this required a gradual increase of spin speed to ensure consistent LDS layer formation.



Figure 7.4 Image of LDS layer peeling from CdTe cell surface.

To address the challenges associated with the application process, four interventions were undertaken:

Vacuum holding of encapsulation: By positioning the cell centrally on the chuck of the spin coater, vacuum pressure was uniformly exerted across the glass surface securing the sample. Despite the apparent simplicity of this measure, accurate positioning was challenging due to

the CdTe PV cells wiring which protruded from the glass encapsulant. Achieving balance required prioritising the PV cell's mass distribution over mere geometric centrality, as the protruding connection wires causes imbalances.

Clean contact surface: To improve the LDS application to a glass encapsulation, the surface was chemically cleaned with acetone to remove dirt or dust particles and any organic impurities, ensuring a pristine substrate for the LDS application.

Wire-wrapped: As the connection wiring protruded between the top and bottom glass substrate it posed a risk of destabilising the cell during the spin coating process. These wires were carefully wrapped around the glass edges to prevent dislodgement or damage to the cell and to mitigate the risk of glass fracture.

Coating solution volume: Only 3 ml of polymer solution was used for a cell of this size. However, to fully apply the layer, 5 ml was used, ensuring the polymer solution covered the whole substrate and not just the center of the PV cell. It was important not to apply excessive LDS polymer solution as the polymer can polymerize rapidly upon exposure to atmospheric oxygen.

Employing these four methodologies facilitated the successful application of the LDS layer as can be seen in Figure 7.5.

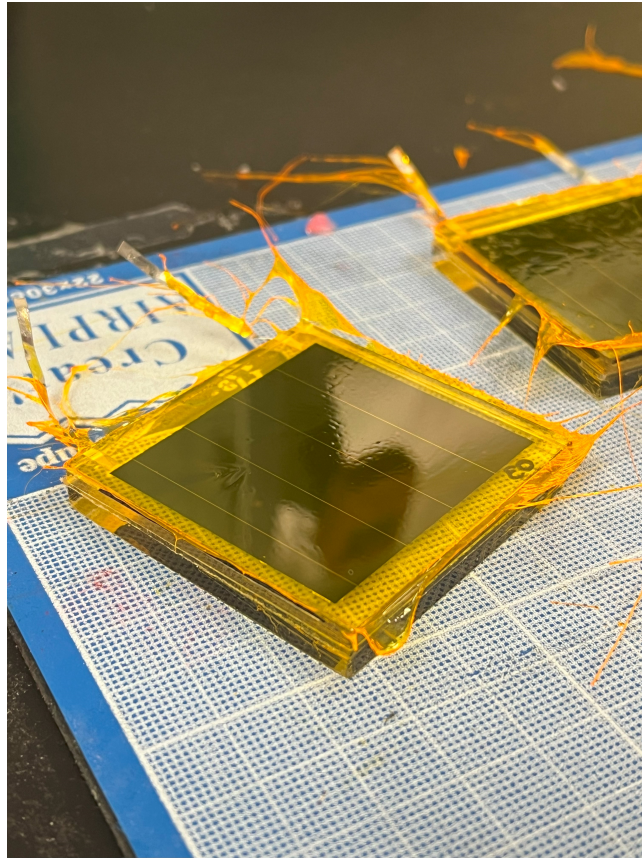


Figure 7.5 LDS layer coated onto CdTe cell

The next step was to apply the LDS to the a-Si cell. This process paralleled the method used for the Si cell, with modifications to accommodate the glass substrate. Given the presence of the thin glass layer on top of the a-Si cell, an increased volume of LDS polymer solution was deployed to ensure comprehensive coverage. Additionally, the pre-fabricated connection wires were shortened and secured to prevent dislodgement of the cell from the vacuum chuck during the spin coating process. The successful application of the LDS is shown in Figure 7.6, which demonstrated the adaptability of the LDS application procedure to suit the specific requirements of different cell substrates.

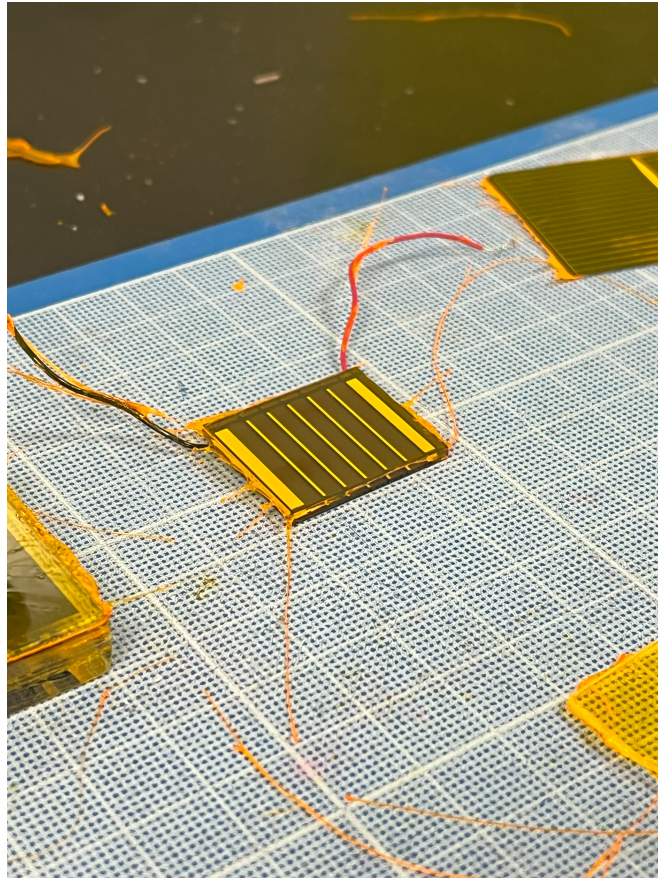


Figure 7.6 LDS applied on a-si cell.

When measuring the EQE, there was a difference noted when testing Si PV cell compared to an a-Si PV module or CdTe PV module. For Si PV cells, the incident light beam was placed anywhere on the cell surface as it was a single PV cell. However, for a-Si or CdTe PV modules, the incident light beam must be placed on a singular strip as the PV cells are connected in series within the module (shown in Figure 7.1). It was imperative that the width of the cell did not exceed the beam spot diameter, which was 4 mm.

A further complexity arose when assessing modules composed of cells arranged in series or parallel configurations, necessitating the application of bias light or voltage to ensure that the generated current and voltage traversed each junction and are collected by the terminals. These requirements complicated the attainment of precise measurements, with potential inaccuracies arising if the light beam inadvertently hits the edge or at a split between the connecting PV cells, thus skewing the EQE value.

This methodology also produced results with lower spectral responses, as shown in Figure 7.7, which represented data from a single PV cell strip connected in series within the glass encapsulation. These results were obtained when the incident light beam was placed on the leftmost cell strip, which was closest to the terminal electrical connection.

While six CdTe PV cells were coated with LDS layers only four cells were successful. These were denoted as ID 1, ID 2, ID 3 & ID 4. The samples recorded in LEITAT had similar labels with CdTe before each ID to make the comparison clearer. The reference was denoted as bare CdTe and was one of the cells evaluated before LDS application. ID 1 & ID 3, demonstrated an improvement compared to the CdTe PV cell without an LDS. While ID 2 & ID 4, showed a decrease in performance. Figure 7.7, illustrated two CdTe PV cells with LDS applied, ID 1 & ID 3 (CdTe 1 & CdTe3) which had an improved spectral response with the LDS applied. While ID 2 & ID 4 (CdTe 2 & CdTe 4) showed a reduction in response compared to the reference CdTe PV cell.

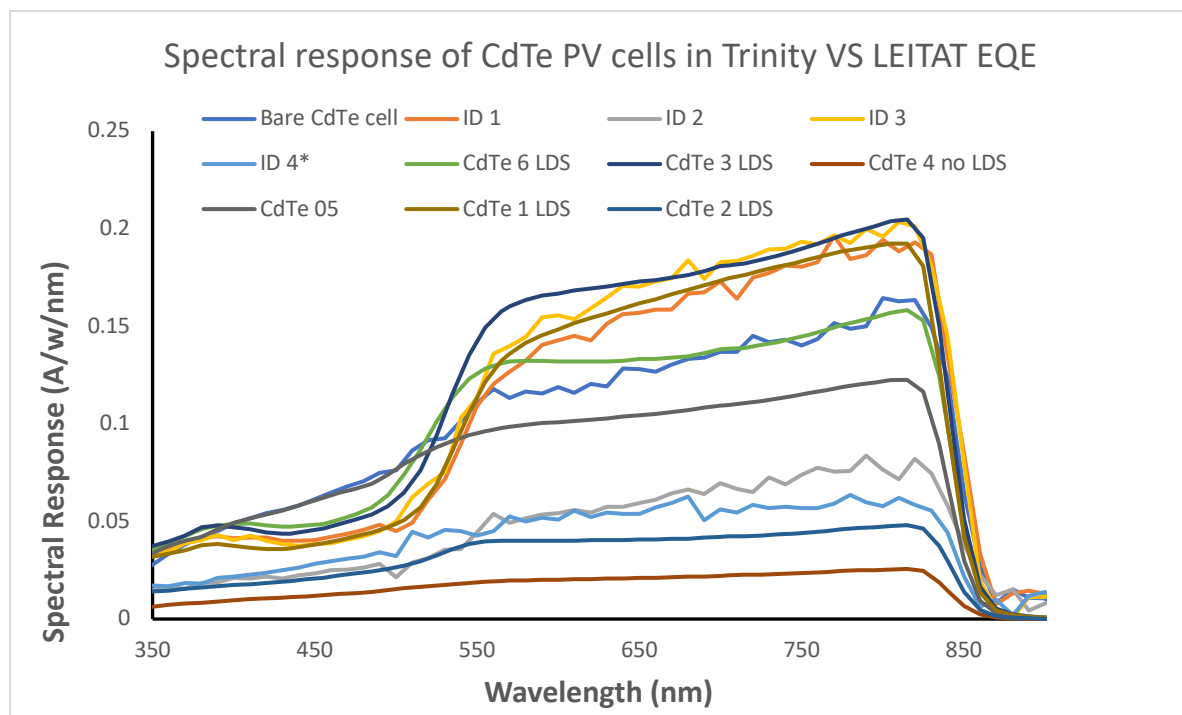


Figure 7.7 Comparison of spectral responses of LDS coated CdTe samples

Despite originating from the same batch of LDS stock solution, the efficacy of LDS application on CdTe PV cells exhibited variability. This inconsistency in the uniformity of the LDS layer when compared to previous LDS application on Si PV cells (described in Section 6.3),

potentially resulted in regions of larger LDS thickness. Such disparities may attenuate the interaction between the incident light and the LDS layer, therefore reducing the light photon interaction with the PV cell encapsulated in glass with LDS on top.

Following the application of the LDS layer, another innovative developmental step was made with the integration of metal nanoparticles (MNPs), aiming to enhance the LDS layer's capacity for photon interaction while preserving a light funneling effect into the PV device underneath, (as outlined in Section 2.7). This addition was introduced due to the prospects discussed in section 2.7 that showed MNPs as a viable addition to a polymer solution; this complemented the initial development of the LDS layer.

The plasmonic LDS (pLDS) was based on the same LDS polymer stock solution previously developed during this research (described in Section 3.2). Incorporating MNPs required careful consideration of their compatibility, stability within the PMMA and chloroform matrix without the luminescent dye, and stability of the resultant pLDS layer upon application to the PV cell.

7.4 Plasmonic enhancement with the addition of metal nano particles

To further optimise the LDS layer optical efficiency and increased photon interaction [Wen Jeng et al, 2018], MNPs were added to induce plasmonic interactions within the LDS layer (described in Section 2.7). Prior to incorporating MNPs into the LDS process, their compatibility with PMMA and chloroform, along with their stability in the presence of luminescent dye, required a thorough evaluation. Table 7.1 illustrated that silver nanorods exhibited a better match for the current LDS layer, primarily because their absorption range aligned with the wavelength range at which Si PV cells began to operate effectively.

Table 7.1 Parameters of MNP to be considered (Xie et al, 2013, Paramelle *et al.* ,2014)

Type	Shape	Compatibility	Absorption nm
Silver Ag	Nanorod	Organic Solvent Chloroform	428 – 575
Gold Au	Nanosphere	Organic Solvent Chloroform	610 – 1310

Silver metal nanoparticles (Ag MNPs) were synthesized in LEITAT and supplied in powder form for this research. Three samples were provided and were designated as MNP1, MNP2, and MNP3, respectively. To achieve uniform dispersion, MNP were suspended in 5 ml of dichloromethane (DCM) and subjected to ultrasonication for 7 minutes. In parallel, a stock solution was prepared with 4 g (28.5 wt%) of PMMA per 10 ml (71.4 wt%) of chloroform. This preparation took place under a nitrogen atmosphere to prevent premature polymerisation and oxidation. The MNP solution was gradually added to the PMMA solution, ensuring gentle stirring using a stirring rod to achieve a uniform solution without the formation of bubbles. The MNP solution was then carefully drop cast into a petri dish, to achieve even dispersion and minimise bubble formation, as shown in Figure 7.8. Subsequently, the solution was left to polymerize at room temperature, leading to the formation of a solid composite material.

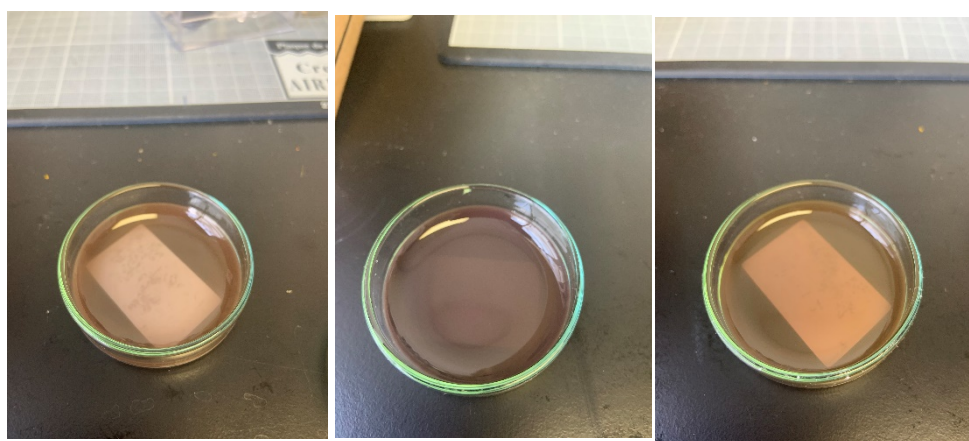


Figure 7.8 From left to right, images of MNP1, MNP2, MNP3

By leaving the samples in the open air enabled the evaporation of any excessive chloroform and DCM in the samples. Once the sample was left to dry (ideally for 24 hours), the sample was removed from the petri dish and cut to size to match the sample holder, 10 x 5 x 2cm, (Figure 7.9) in the optical set up.



Figure 7.9 Sample cut to the size of sample holder; 2 cm wide and 5 cm long.

Challenges were encountered in achieving homogeneous MNPs dispersion in the PMMA polymer matrix, relating to the uniformity of MNP dispersion, entrapment of air bubbles and the formation of thin layers. DCM solvent was used for the dispersion of powdered MNPs and was partially or completely evaporated during the dispersion of MNPs/solvent in PMMA polymer solution, by stirring for a longer duration of 3 minutes. This led to an increase in solution viscosity, which subsequently hindered the uniform dispersion of MNPs, facilitated the entrapment of air bubbles and precluded the feasible fabrication of the film.

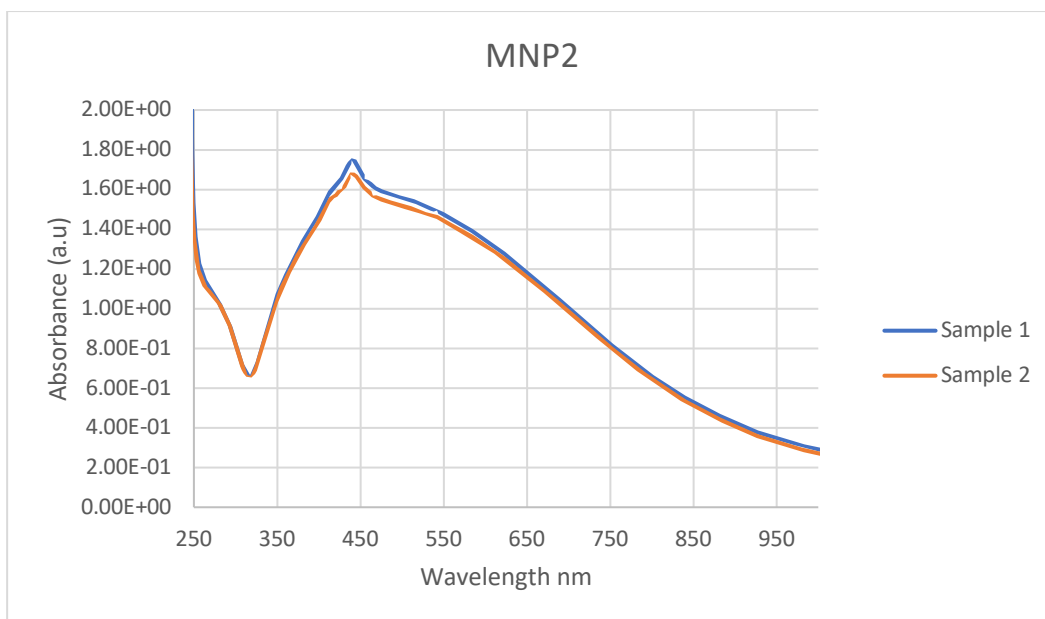


Figure 7.10 Sample MNP2's absorption

Figure 7.10 shows the absorbance of two samples of MNP2. Three samples of 10 cm x 5 cm x 2 cm were cut and characterised. The objective was to ascertain the uniformity of MNP dispersion within the layer. The absorption was monitored over 2 weeks. Initial testing, (as shown in Figure 7.11) revealed that ID 052 aligned with the characteristics in the current LDS layer being developed. Post-drying, these MNP samples were characterised and separated into sample sizes of 5 cm for analytical purposes.

The MNP data was first recorded when the layer was fully dried, with subsequent measurements every two weeks. This sequential characterisation aimed to assess the temporal stability of the MNP-enhanced LDS layer. The results of this analysis indicated a negligible degradation of the MNPs within the time period. Such stability enhanced the potential integration of these MNPs into an LDS layer, contributing to the longevity of the layers over time.

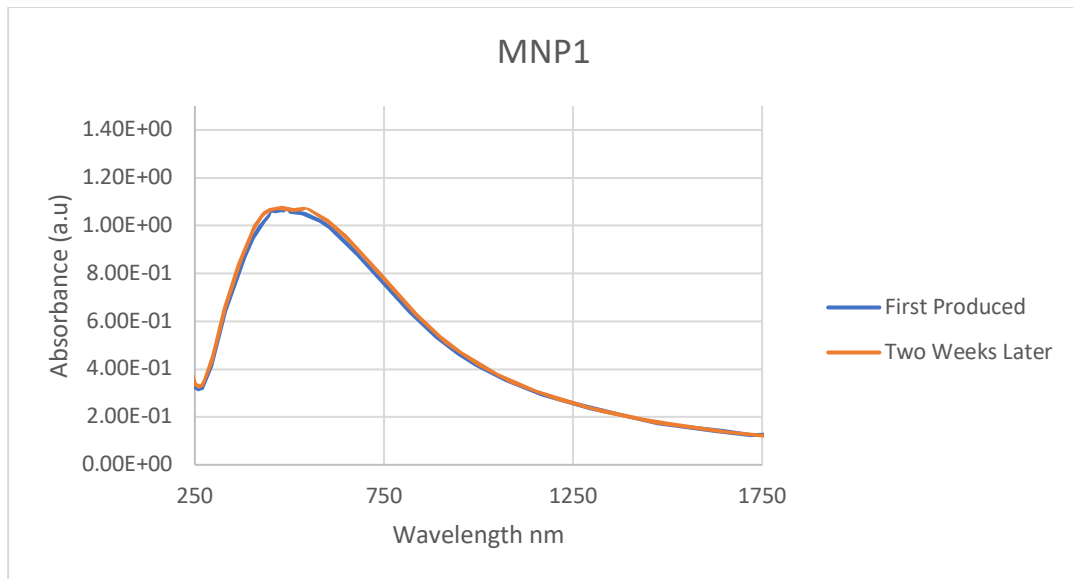


Figure 7.11 MNP 1 absorption

7.5 pLDS Fabrication & Testing:

The characterisation of these MNPs were conducted using the same polymer matrix as the one used for the LDS layer, in order to verify the MNPs optical properties, stability, efficacy and compatibility with an LDS. The MNPs extinction spectra overlapped with the absorption peaks of the LDS layer intended for use on a silicon PV cell. This benefited the LDS layer by increasing the potential for further photon interaction. The peaks shown in Figures 7.10 & 7.11, could represent a valuable enhancement when integrated with the current LDS layer. This demonstration illustrated the potential for incorporating MNPs into an LDS to enhance its future performance.

Given the requirement for a large number of samples for pLDS fabrication, additional silver MNPs were acquired from Sigma Aldrich. Silver MNPs can and improve the light-matter interaction through the plasmonic properties; as a result, the improved optical properties of the pLDS layer. This was because they conducted electrons on the metal surface, which undergo collective oscillations when excited by light at specific wavelengths, leading to their strong interaction with light known as surface plasmon resonance, which maximises the local electric field for interaction (Paramelle et al., 2014). These particular MNPs were chosen due to their compatibility with the chemical solution (Chloroform) and their commercial availability. The silver MNPs provided in a water solution created a challenge, necessitating

the evaporation of water before integrating the MNPs into the PMMA polymer solution for the pLDS layer. This process was undertaken in a nitrogen-filled glove box before adding the polymer solution and luminescent dye. Two processes were used for evaporation; the first involved stirring the MNPs solution in a fume hood without a lid and using a magnetic stirrer, varying the stirring time duration based on the solution volume, (e.g. for a 10 ml batch size, the stirring time was 90 minutes); the second method involved mixing the water solution directly into the polymer or LDS, as water and chloroform are immiscible; the water would evaporate when left open. The water containing MNP solution was added to the 30 ml chloroform solution with PMMA, similar to the LDS stock solution while being stirred at 700 rpm with a magnetic stirrer. This initiated the mixing process, with the water evaporating while the MNPs dispersed into the chloroform and PMMA. This was conducted in an inert environment to adhere to the best practice of LDS fabrication (as outlined in Section 3.7).

Ultimately, the second method was used due to the efficiency in producing the pLDS polymer solution, considering the time required to produce the pLDS polymer solution, and the LDS stock solution (discussed in Section 3.2). By combining the evaporation of water to obtain the MNPs with coating of layers, the time required to fabricate a pLDS was estimated at 100 to 120 minutes per batch of three layers (excluding spin coating).

The pLDS layered cells were assembled into a 48-cell panel comprising 6 strings of 8 PV cells. Each string of 8 PV cells was connected in series by soldering connections onto the back contacts. PV cells with an LDS were used as a reference to evaluate the pLDS, along with a string of bare cells without an LDS (reference). All systems were configured to monitor the power outputs, with a solar module analyser used to record the I-V curve and a pyranometer to measure the solar radiation at 15-minute intervals. A schematic of the outdoor solar set-up is shown in Figure 7.12

This real-world testing setup provided a better comparison between commercially available PV panel systems and the LDS layered PV-CPC systems demonstrated throughout this research. This setup enabled the daily variations in diffuse radiation to more accurately indicate the specific times of day when the PV and LDS-layered PV performed better, and the pLDS layered PV systems produced a greater power output. This was a comparison that can

apply directly to a commercial application as there were not always perfect conditions for PV systems in daily usage.

Another experimental setup that provided valuable comparisons for a PV, LDS layered, and pLDS layered system that could be set up in a similar venue in Italy. As mentioned previously in Chapter 2, Italy is a good comparison to Irish renewable energy generation and usage of the sources associated with it.

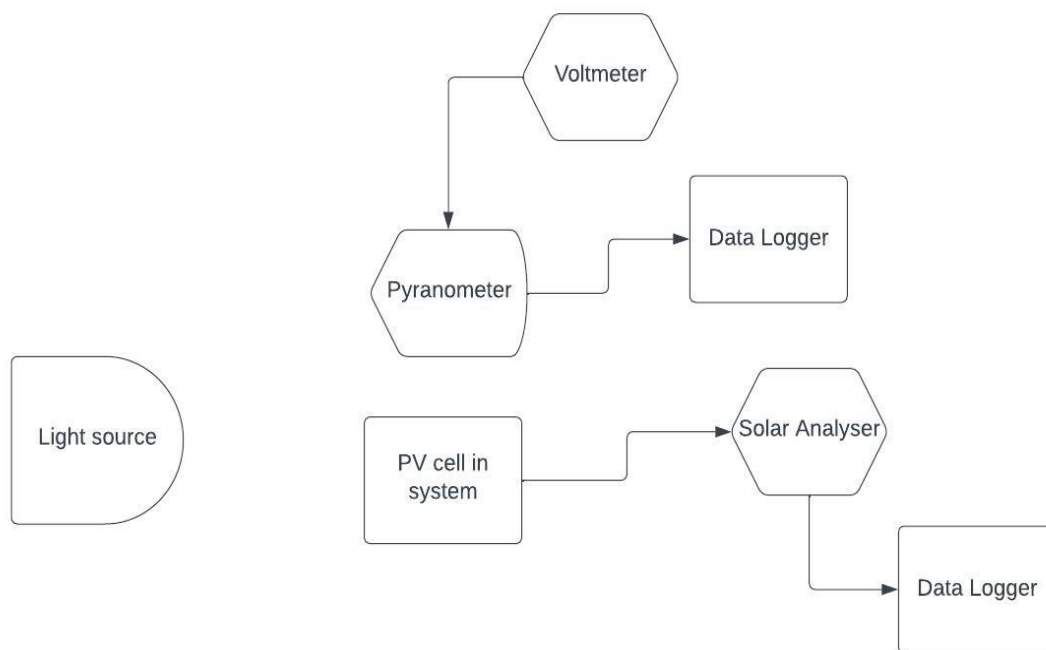


Figure 7.12 Schematic for outdoor testing of PV panels.

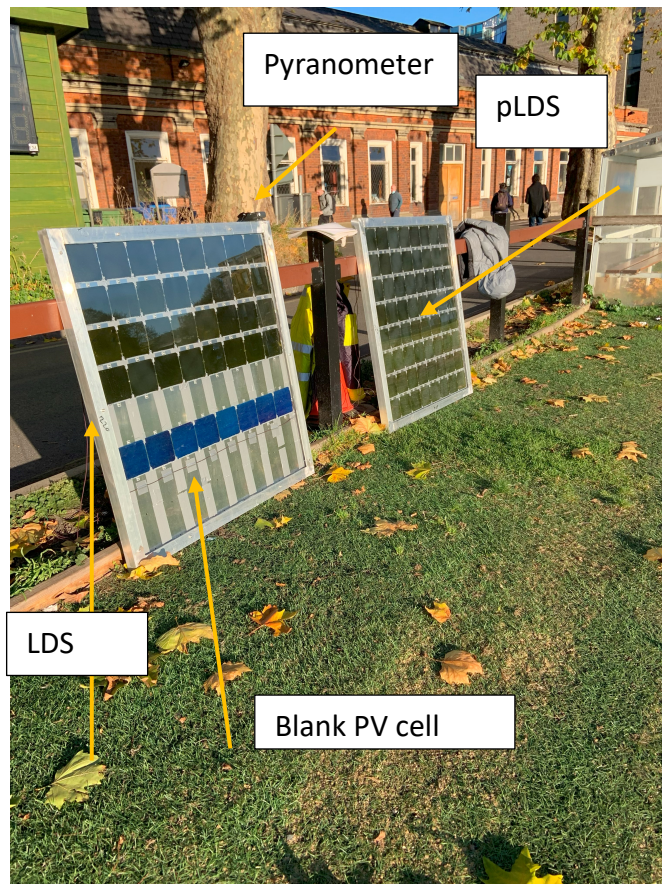


Figure 7.13 pLDS & LDS outdoor testing

The schematic of Figure 7.12 was installed behind both panels in Figure 7.13.

The first pLDS system was measured for the whole system with 8 strings of 8 pLDS PV cells, while the second system had 2 separate measurements; one was of LDS layered cells, and the other bare PV cells with no pLDS. The data was averaged to allow for comparison.

Figures 7.14 to 7.21 showed the performance data from the outdoor characterisation of the LDS & pLDS systems with the reference system of bare PV cells. Solar radiation for the days of testing is presented in Figures 7.14 & 7.15. Power output of both days are displayed in Figures 7.16 & 7.17, giving insight into how each system performed under the same conditions. The efficiency of the three types of solar cells was compared in Figures 7.18 & 7.19, showing how the LDS and pLDS modifications affected the solar cell performance. Figures 7.20 & 7.21 focused on the improvements observed in the modified systems compared to the bare PV cells, quantifying the benefits of the LDS and pLDS enhancements.

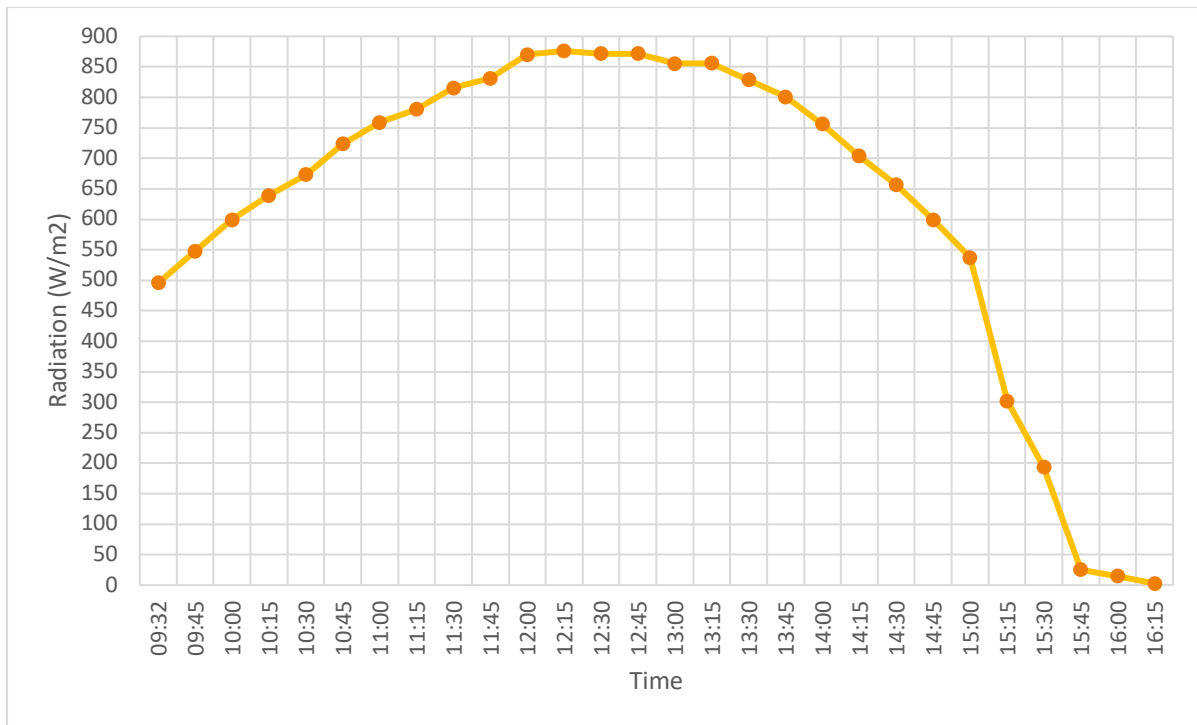


Figure 7.14 Solar irradiation for the 22/11/2021.

In Figure 7.14, the solar radiation measurements (as obtained from the pyranometer(detailed in Section 7.5) are presented.

Data was recorded every 15 minutes between 09:00 and 16:15. This timeframe corresponded with daylight hours with sunset approximately 16:15 as it was late November. It was important to note the pyranometer position was consistently checked in direct sunlight and aligned parallel to the plane of the PV panel, corresponding to the set up as seen in Figure 7.13.

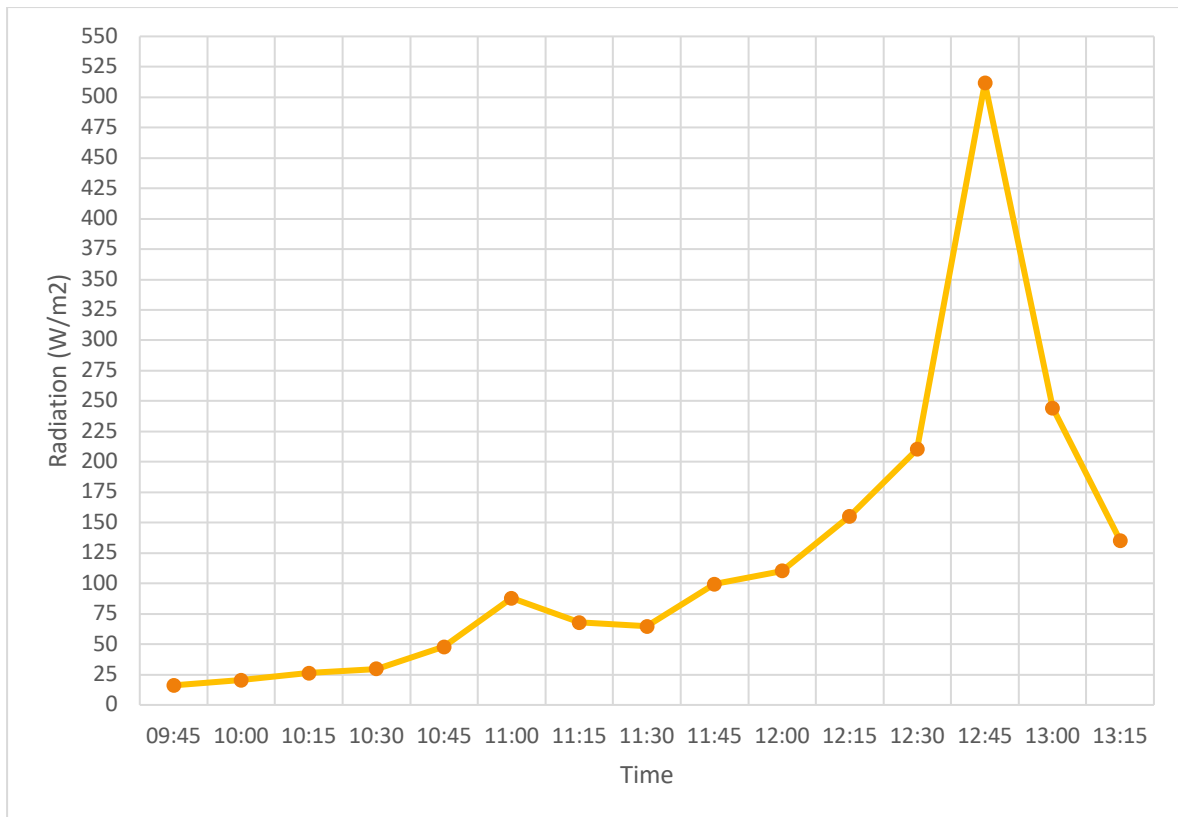


Figure 7.15 Solar irradiation on 28/11/2021.

A subsequent characterisation was conducted using the same three systems, the only variable change was the location and orientation of the systems. During the initial assessment phase, Intermittent obstructions to the sensors were encountered, resulting from passersby walking past the panels impeding the solar radiation. As shown in Figure 7.18, the duration for this testing period was much shorter (from 09:45 – 13:15). This reduction in testing timeframe was due to adverse environmental conditions, which were beyond experimental control. Notably, there was significant cloud cover, followed by rain, which adversely affected the outdoor characterisation.

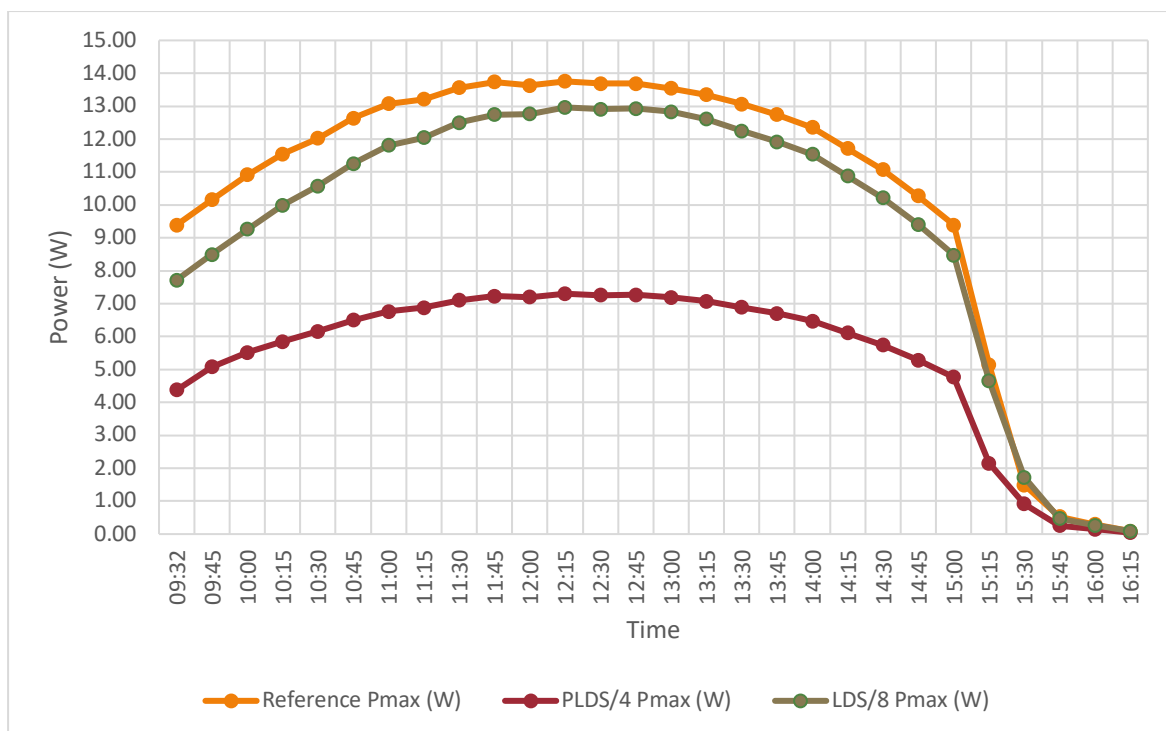


Figure 7.16 The power of PV reference, LDS & pLDS systems on 22/11/2021.

The power output of each system on the testing day of 22/11/2021 is shown in Figure 7.16. It was observed that the reference system (consisting of bare PV cells) produced the highest power generation in comparison to both the LDS & pLDS configurations. Although the LDS system demonstrated, produced a power output comparable to the reference, the pLDS reduced in power output. This trend in power output was consistent with the solar radiation data from Figure 7.14, indicating a direct correlation.

The power output was lower for the LDS and pLDS systems as both of these systems have additional layers and interactions compared to the reference system. These additional components may impede the interaction of photons with the PV cell (these losses are discussed in Section 2.4). These losses are increased further within the pLDS layer as the MNPs added an additional layer that can further increase associated losses.

As Section 6.5 outlined there were instances where LDS enhanced cells surpassed the power output of the bare PV cell systems. However the LDS and pLDS cells utilised in this study were derived from a new batch of LDS polymer stock solution, produced after the first IDEAS system was fabricated and evaluated.

As discussed in Chapter 5, the process in which LDS layers are produced is very thorough and was susceptible to variations in factors such as the duration for mixing or LDS application. These variables can significantly affect the efficiency of the resulting LDS or pLDS layers. Furthermore, the incorporation of MNPs into the LDS layers introduced complexity, particularly the challenge of dissolving water-based MNPs in chloroform. Residual water content in the pLDS solution can further compromise the efficiency of the resultant layer, illustrating the multifaceted nature of optimising these layer enhancements.

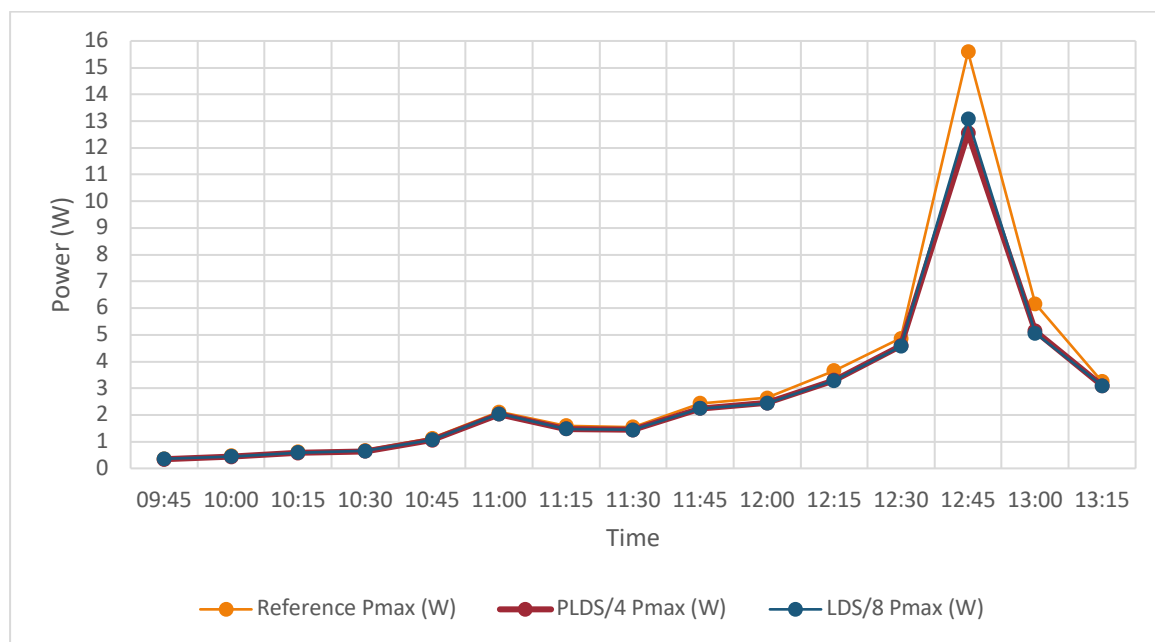


Figure 7.17 The power output of PV reference, LDS & pLDS systems on the 28/11/2021.

In Figure 7.16, the power production from the reference PV system was consistently higher than the pLDS & LDS systems. It followed a similar pattern to the prior days characterisation where the electrical output correlated with the incident solar irradiation as shown in Figure 7.17.

A variable in the experimental environmental conditions – specifically the presence of more diffuse solar radiation resulted from increased cloud cover – may have differentially impacted the performance of the LDS and pLDS systems.

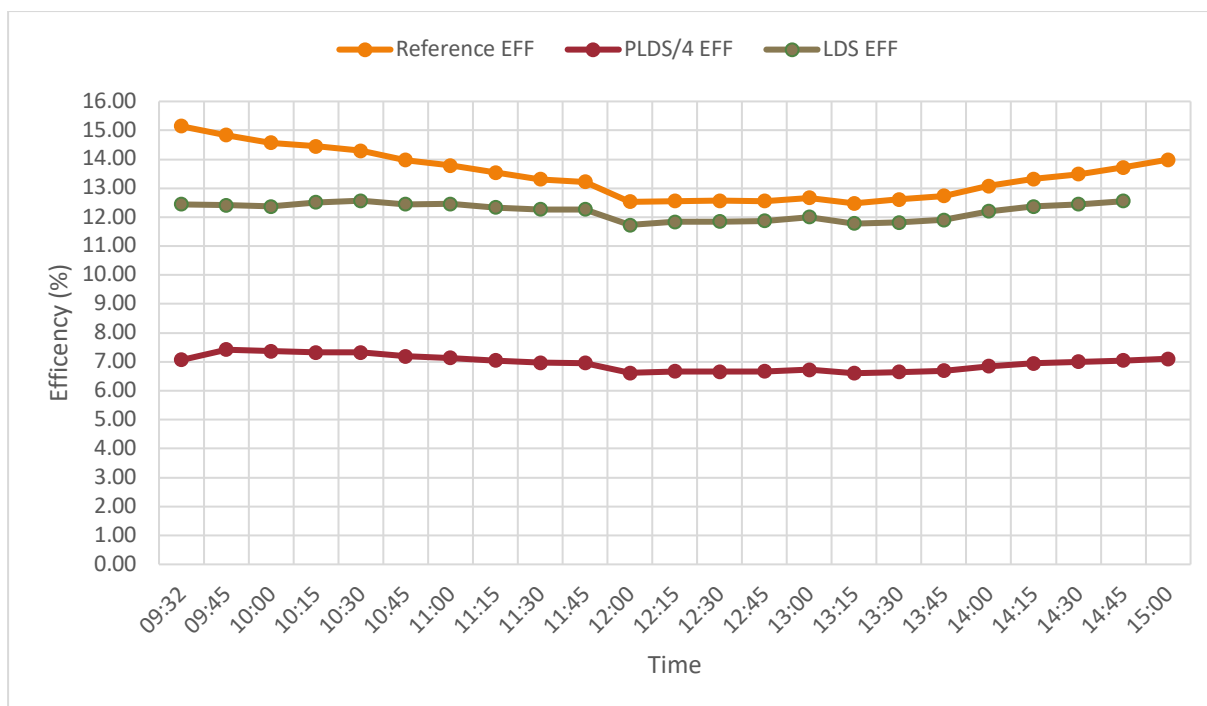


Figure 7.18 PV reference, LDS and pLDS systems efficiency on 22/11/2021.

Figure 7.18 presented the comparative efficiency of the PV systems where the reference system has the best performance, closely followed by the LDS system within 1% of efficiency for a 3 hour period. While the pLDS vastly underperforms. The reasons for the underperformance will be discussed on the following pages in detail.

As previously shown in Figure 7.16 and discussed in Section 7.5; the MNPs were in a water solution and had to be integrated into a chloroform based LDS stock solution which could have caused a lack of full dissolution residual water traces remaining. The MNPs may not have fully mixed causing large aggregation of MNPs, which acted as impurities in the layer reducing the effectiveness of the pLDS layer. Also, the water traces adversely interacted with the PMMA polymer that lead to decrease in optical transparency.

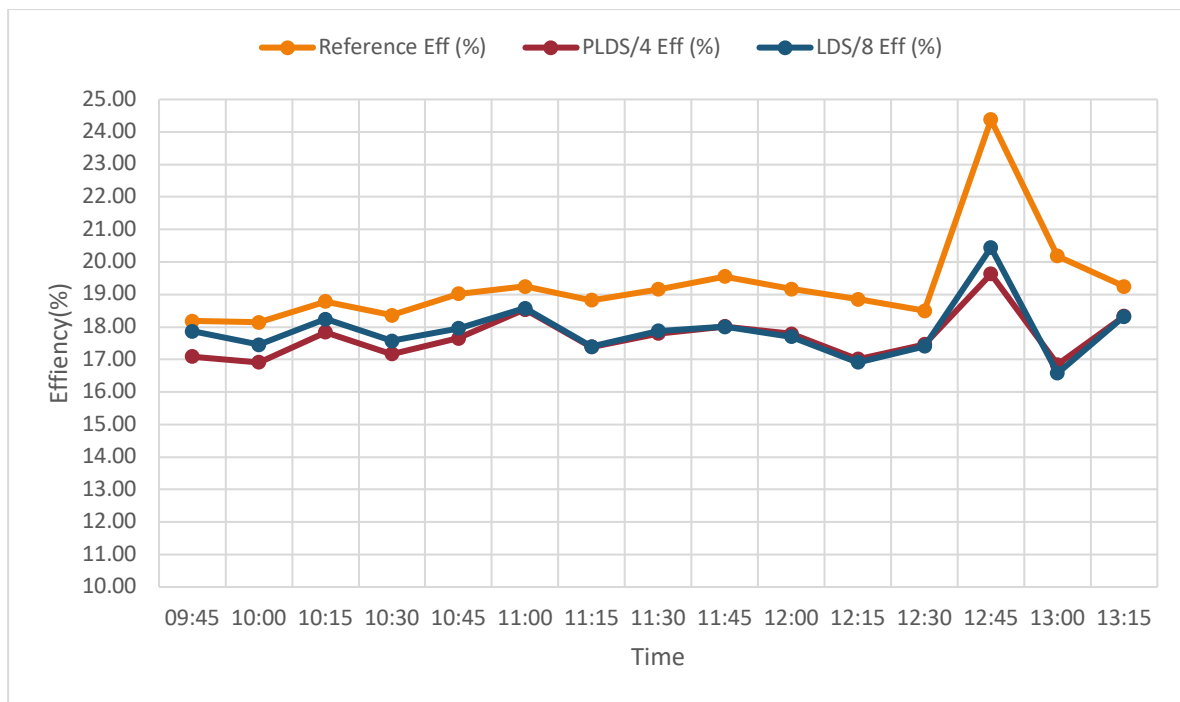


Figure 7.19 PV reference, LDS and pLDS systems efficiency on 28/11/2021.

As mentioned with the power output, the same pattern applied on both the 22/11/2021 & 28/11/2021, although all three systems efficiency have a higher %, with the highest peak at 24.5% with a baseline of 17% shown in Figure 7.19. With the highest peak of 15% and baseline of 7% shown in Figure 7.18. The reference system still out performed the other two systems. The variation seen in the solar irradiation recorded between the 22/11/2021 and the 28/11/2021 showed a large disparity. The fact that there was a larger average incident solar irradiation on 22/11/2021 only dropping under 500 W/m^2 after 15:00, and on 28/11/2021 only reaching above 250 W/m^2 for a 45 minute period. The power output and efficiency of the respective systems showed larger disparity when compared. It was associated with the large difference of interaction and exposure to solar irradiance time. This was due to the very different environmental conditions that the two different tests were undertaken in.

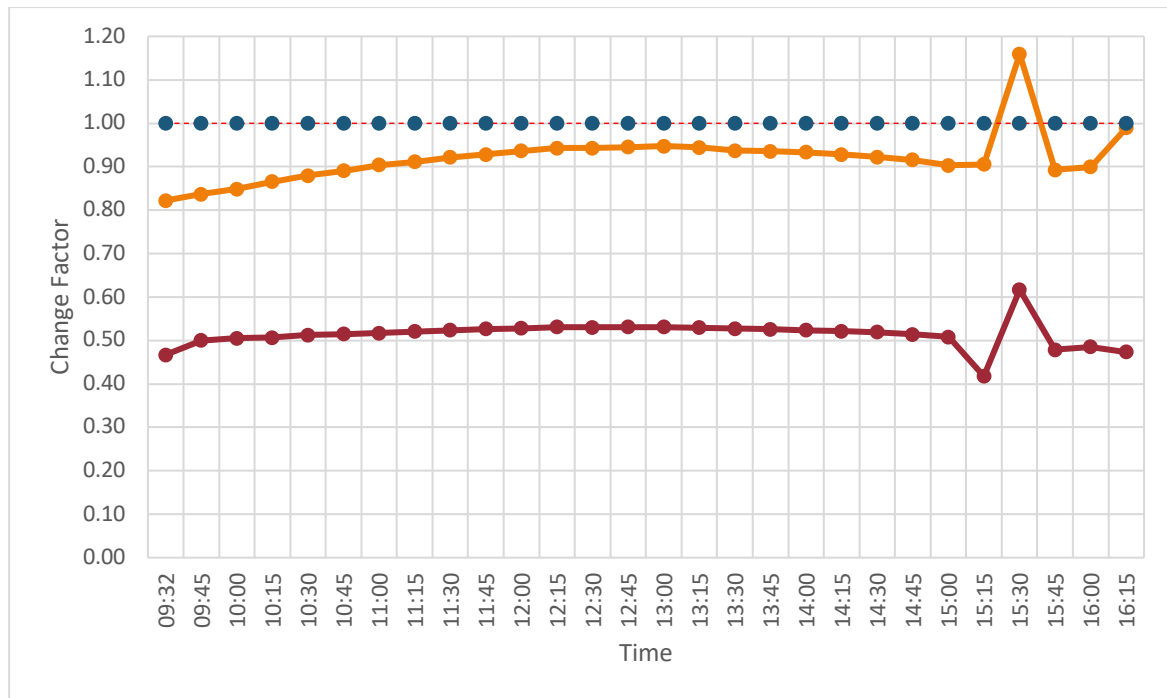


Figure 7.20 Change Factor for testing on 22/11/2021.

Figure 7.20 presents the relative improvement factor compared to the reference system. It quantitatively demonstrated that LDS system experienced a maximal as its lowest reduction in performance efficacy, quantified as a factor of 0.80. This value indicated a 20% decrease in performance relative to the reference system. At one point at 15:30 there was an improvement factor of 1.10, meaning there was a 10% increase in performance compared to the reference. This was accepted as an experimental error.

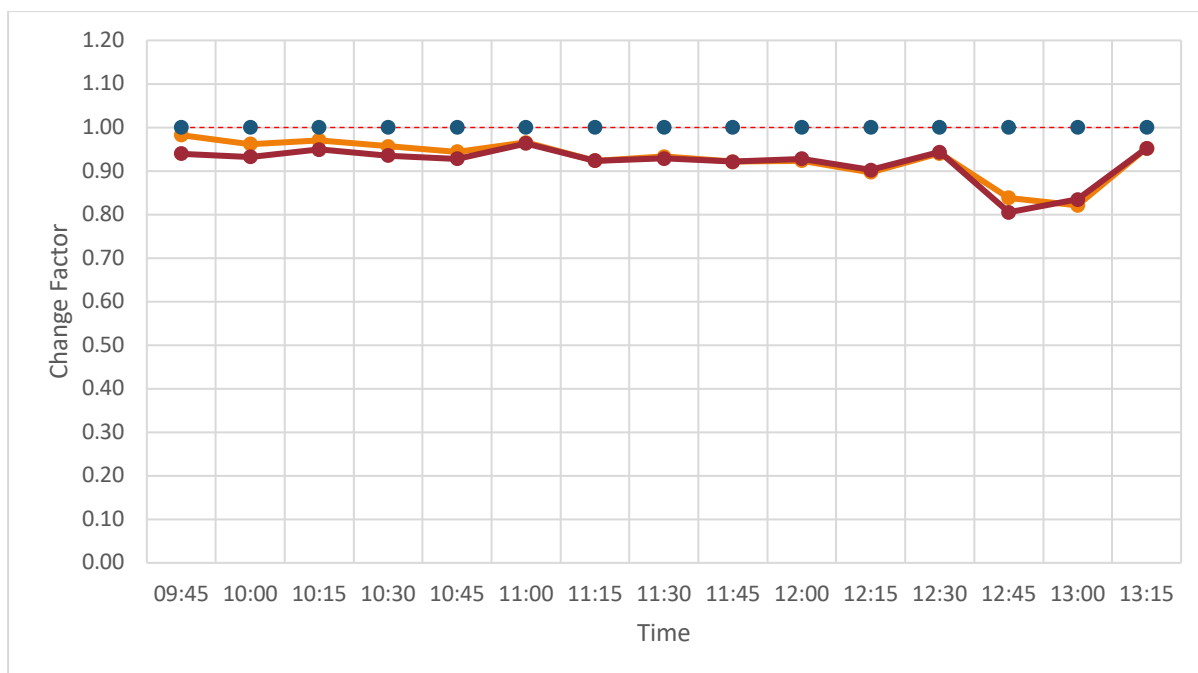


Figure 7.21 Change factor for the 28/11/2021.

On 28/11/2021, the comparative analyses presented in Figure 7.21 demonstrated that both the LDS and the pLDS exhibited lower performance in comparison to the reference bare Si PV cell system. However it was imperative to note that the pLDS system performed close to the LDS system with respect to the improvement factor of system output.

This diverged from previous tests where the LDS outperformed the bare cells (Figure 5.19). Such discrepancies suggested potential issues such as experimental errors associated with scaling the technology from a small scale system of 3 – 5 layered cells at a maximum up to a system of 64 (LDS) and 48 (pLDS), respectfully.

Identified challenges during the fabrication and assembly processes that may have contributed include:

- Inconsistent layer production: The application of the pLDS was not as refined and of high quality compared to the LDS. This was due to commercially sourced Ag MNPs and was not compatible with PMMA polymer solution
- Electrical connectivity: The series connection of the LDS & pLDS systems through soldering may have induced resistive losses, adversely affecting overall system efficiency.
- Comparative analysis: The averaging of experimental data to allow comparison, as the bare PV cell has only one string of cells, totaling 8 bare PV cells. While the LDS has 4 strings

of PV cells, totaling 32 LDS PV cells, and the pLDS has 8 strings of PV cells, totaling 64 pLDS PV cells.

- Material integration challenges: The pLDS polymer batches used were the first attempt at integrating MNP into an LDS layer, that process is not optimised and has left much room for improvement in future work on pLDS development.
- The change in location and environmental conditions influenced the system results

Post – characterisation visual inspection showed impurities such as specks or particles on the surface of the LDS layers and incomplete dissolution of MNPs in the pLDS layers even after an extended dissolution period (over 3 hours). These observations suggest that such imperfections could further reduce the effectiveness of the pLDS layers. These imperfections included not fully dissolved silver MNPs from the mixing process. Again since the MNPs were in a water based solution the mixing process in the beginning was skewed time wise and the inspection of the pLDS layers has proved to be different to the LDS layer inspection. There could also be residual water in the polymer solution and this could cause induce haziness in the LDS. Again due to the way in which the MNPs were integrated into the LDS polymer solution proved to be the main change to the pLDS fabrication process.

7.6 Conclusion

The optimisation of the LDS layer application, as detailed in Chapter 4, focused on resolving issues that arose during the initial installation of the IDEAS system. These challenges necessitated adjustments for different types of silicon PV cells,, such as the front and back contact busbar silicon PV cell or the no back contact silicon PV cell. Yet, the reduction in damage to the PV cell's busbar and LDS layer are a result of these changes it was deemed both reasonable and justifiable.

Applying the LDS layer to various PV cell types, such as a-Si and CdTe, presented additional difficulties. The glass substrate encapsulating the PV cells complicated both the application of the LDS layer and the subsequent EQE spectral response measurements.

The four methods outlined in Section 7.3 were identified as the most viable approaches for applying LDS layers to different PV technologies using the spin coating method. Notably, the improvement showed by two different LDS-layered CdTe PV cells in Figure 7.7 demonstrated potential, warranting further development and refinement for use with CdTe PV cells.

While MNPs were successfully incorporated into the pLDS layers, further development and optimization are necessary. As initially demonstrated in Section 7.4, the MNPs provided by LEITAT successfully produced an MNP polymer layer, and Figure 7.8 highlighted complementary characteristics with the developed LDS. These MNPs proved viable, though production was limited by the small quantity available.

Commercially available MNPs posed integration challenges due to their water-soluble nature, and their incorporation into the pLDS did not yield any discernible improvement over a bare PV cell system or an LDS-layered PV cell system. Theoretically, adding MNPs to the LDS should enhance efficiency, but in this case, the LDS underperformed. However, in Section 6.4, the LDS demonstrated improvement over the reference system. The suboptimal performance could be attributed to the poor quality of the LDS layer, which was hastily applied before optimization to meet the needs of the IDEAS CPC systems. Additionally, testing during the short daylight hours and poor weather conditions of a Dublin November was not ideal.

This chapter concludes objective number 3 set out in Chapter 1, focusing on the integration of MNPs into the LDS as a critical step for further development of LDS layer applications. It marked the initial phase of integrating MNPs into the LDS polymer solution, fabricating an MNP polymer layer, and incorporating MNPs into the pLDS layer.

Chapter 8. Discussion & Conclusion

8.1 Introduction

In this chapter, the culmination of the research undertaken throughout this project is discussed. From the initial conceptualization and development of the LDS layer tailored for Si PV cells, through to the advanced integration into the IDEAS CPC systems. The optimisation of the LDS for Si, a-Si and CdTe PV cells and progressing towards the innovative incorporation of MNPs for pLDS layers to enhance PV cell efficiencies.

The refinement of LDS and pLDS characteristics will be discussed, including adjustments in physical properties and the examination of environmental factors affecting system efficiency. Through this analytical lens, the chapter aims to offer insights into the broader implications of the research findings and highlight the pathway for future developments in PV system enhancement technologies.

8.1.1 LDS Layer Fabrication

The first key milestone achieved was the fabrication of the LDS layer. In that process first stock polymer solution was prepared in chloroform and optimisations for consistency and repeatability. The tuning of the polymer solution to produce a thin film polymer layer of 20 μ m using a spin coater was adjusted slightly when a nitrogen inert environment was introduced where the ratio was 5g of PMMA per 10ml of chloroform, 1:2.

The polymer stock solution was adjusted from the original recipe of 2.3 g (15.4wt%) of PMMA to 10 ml (85.4wt%) of chloroform into the ratio of 3.8g (21.2 wt%) of PMMA to 10ml (78.6 wt%) of chloroform, 3.8:10, (when being produced in open air/ under a fume hood).

The inert glove box improved the quality of the LDS polymer stock solution through its clean and oxygen free environment. The nitrogen-based environment provided a consistent LDS polymer stock solution compared to open-air production, where pre-polymerisation and oxygen trapping would occur, reducing the quality of the LDS layer being applied and making the batch unusable over an extended period.

The application process (spin coater) variables remain the same, when changing the environment. The max spin speed is 1000 rpm, which is achieved by ramping up the speed from 0 – 500 – 1000 rpm, with a total dwell time of 3 minutes for the layer to be applied. Note that the main difference between oxygen vs nitrogen-based environment spin coating, shows in the quality of the layer. More impurities can be found on the LDS layer when applied in an oxygen environment.

The layers did not degrade in the same time span compared to the CPC systems sent to Ferrara. There were also fewer air gaps between the LDS layer and PV substrate seen in the batches made using the inert environment. This work is part of objective one. This achieved the successful application of the LDS layer from an initial small scale at 2x2cm PV cells, onto the larger scale of 12.5x12.5cm PV cells that can be used for a PV system that can be integrated into a domestic or commercial building. The initial aims 1 and 2 are also developed during the LDS layer development process. As it has focused on the LDS layers application onto PV cells.

8.1.2 LDS layered CPC System for Ferrara

After the original CPC system was delivered to Italy, multiple issues arose during its construction and after it arrived in Ferrara. During the CPC assembly, it was found on first inspection, the layers per batch appeared to be uniform, however, grouped into strings of 11 and full systems of 33, the layer characteristics varied in uniformity.

The LDS layers also degraded over the two weeks of transportation before arriving at our partners in Italy. This led to the rethinking of the polymer mixing process and the layer application method. This resulted in a more fine-tuned process in terms of the making the solution and its LDS application on solar cells.

This has resulted in trying to eliminate different effects that can occur during the synthesis process, such as the purity of the solution, uniformity and spreading process of the layer, and repeatability.

After being transported to Ferrara, the LDS layers some cases peeled, almost completely off. Air bubbles had formed and removed the layer from the cells. Short circuits occurred in some of the CPC systems.

As part of objective 1, the LDS layered CPC systems were initially deployed to the first demo site in Ferrara, Italy. It addressed the first aim of developing the LDS to enhance the PV cells efficiency they were applied to; this was first tested at this site. However, the LDS CPC systems first attempted showed that the LDS layers were not durable enough at this point to last longer with the PV cells they were applied to. This was seen through the layer degrading, leading to the redevelopment of the LDS layer application process to focus again on the enhancement of the LDS layered systems.

8.1.3 LDS layer optimisation process

The most challenging part of the LDS layer production has been optimising the whole methodology. While there is still a margin of error in the production of the LDS layer, trying to both improve quality and produce a layer simultaneously has hindered the overall process. This is due to a deadline within the IDEAS project and in making five systems for testing in Ferrara. This can be observed in the change of concentration of the methyl orange dye post-Ferrara.

While the LDS layer was effective on the solar cell, it could have been improved if more steps and /or precautions had been taken when producing and testing the dye's characterisation instead of basing solely on the EQE data. In hindsight, this would have streamlined the further development of the LDS layer. However, since the layers deteriorated on their way to Ferrara, a new area to focus on also emerged.

As part of objective one, this optimisation of the LDS layer fabrication and application process improved the LDS layer characteristics that affected the enhancement capabilities of the LDS

on the PV cell. This included the improvement of the reliability and durability of the LDS layers when applied to the PV cells through the use of the inert environment.

8.1.4 Optimisation of LDS layer for integration into CPC

For the IDEAS Project, two systems were meant to be implemented: one for a test site in Ferrara, Italy, and one in Mayo, Ireland. However, when the first set of systems was delivered and received in Ferrara, the issues previously mentioned caused a reassessment of the whole work undertaken at the time. This was the first nine months of this Ph.D. research.

The timing of the arrival of the system and COVID reducing the ability to work on site delayed any hands-on change for a period of 1-2 months. Still, at this time, further research into the areas that could lead to the improvements that were needed was carried out. Even with the issues that occurred, there was a huge learning process during the application and fabrication processes.

The layers' decay refocused the mixing process of polymer solution for the LDS layers. The addition of the inert environment proved invaluable in the further development of the LDS, even after the polymer production, as it was continually used for any LDS and with the introduction of MNPs (which will be discussed further below).

The reassessment of the spin coating application required a broader understanding of the machine used. The use of speed ramps and steps proved very useful when applying to other substrates and varying the thickness/uniformity. This was especially useful with uneven LDS-layered PV cells, i.e., PV cells with wiring built in, as seen with CdTe or a-si cells.

This PhD research project was aligned with the IDEAS project, so it was required to meet the timeline of deliverables and milestones. As a result, the first LDS-layered PV cells integrated with a CPC system was also the first instance where partners outside my institution would assess the work. This provided additional pressure to produce and reaffirmed the knowledge of the processes involved and any shortcomings.

With the delivery of the second system, along with the changes that occurred within the entire CPC system, such as the change in PV cell used and adhesion used for the cells in the system, the LDS had been altered to perform better and created a larger capacity.

The inspection of the system at the demo site, the layer had decayed again, but this time, it differed from the first systems. The LDS was still present but without colour. Droplets of condensation could be observed. Compared to the first systems sent to Ferrara, there were also fewer layers with non-uniformity or cells not fully covered with LDS. The LDS CPC systems were able to produce 100W per system for their contribution for the demo sites in Ferrara, Italy. Compared to the commercial PV panels that produced 60W per system. This has demonstrated the LDS enhancement of the PV cells

However, this time, there was more justification in the fabrication process and examples of LDS in outdoor and laboratory settings that maintained LDS intact (The thought process for development will be discussed in the Future works section). The developed work was reassessed for a second time with a larger colleague base from IDEAS project. Establishing the process and methodology was an important milestone during this PhD as it gave a chance for onsite review and discuss what could/did happen to the cells and how to advance the technology further.

Also, the difference in time between the first CPC system, which was prepared nine months after the start of my PhD, and the second system, which was produced after 37 months, indicates a significant development in knowledge in the area, as well as a development of a research process and ability to justify the work.

As the final part of objective one, the optimised LDS layer was shown to enhance the CPC systems' power output to 100W by improving the application process of the LDS layers onto the PV cells in the inert environment.

8.1.5 LDS on different PV technologies

Once a reliable LDS layer was being produced repeatedly, it was important to determine its effectiveness with different PV technologies. As stated in previous sections, the only cells that could be successfully measured beside the Si cells were the CdTe cells supplied by IDEAS project partners in LETAIT, Spain.

It was also stated how useful it was to use EQE as a comparison method of the LDS's effectiveness on the PV module. Unfortunately, the resulting data showed that the LDS was hindering the CdTe cell's performance. Two factors greatly affected this performance.

The first is an added 'hindrance' of an LDS layer. Since the added LDS is on a glass substrate, as mentioned previously, there is now another obstacle for photons to pass through and interact with the cell. This could have led to parasitic absorption within the LDS and between the LDS and the glass substrate beneath it. As well as increased reflection out of the PV cells. The second possible hindrance due to the addition of the LDS layer that was tailored for Si cell, not as a general LDS layer. Since the development and testing of LDS for both small and large scales had been completed using si cells.

Colleagues in LETAIT compared the a-si cells to the LDS-layered a-si cells through EQE measurements. They corroborated and validated the results produced at Trinity College. It was observed that the a-si had a similar underperformance with the added LDS, by EQE data. The application of the LDS layer onto a-si and CdTe cells achieved aim three and objective two of applying the LDS onto various PV technology in order to enhance the power output. However, it was shown in Chapter 6 that the LDS layer developed for the silicon PV cells was able to be applied successfully but was not as effective on the other two devices. This has not discouraged any development as the LDS layers used throughout this thesis was initially developed for the silicon PV cells.

8.1.6 LDS with MNP integration into PLDS

The addition and implementation of MNPs in a polymer should have been relatively straightforward for the fabrication of pLDS. Disperse the MNP in powdered form into the LDS polymer solution and then spin coating or drop casting a pLDS layer. the

This was the for the MNP supplied by partner LNEG, this was the case with some slight adjustments in the fabrcaition process (to avoid any air bubbles in the drying process as it was drop cast). However, to produce multiple and repeatable pLDS, a commercial MNPs supplier was required.

The commercially supplied MNPs arriving in a water solution added difficulty in consistently mixing this to the Polymer solution for the pLDS. While there had been multiple chemical interactions and reactions due to the chemical incompatibility between water and chloroform proved the most difficult to overcome in mixing process.

Two methods were tested: evaporating the water before mixing and then mixing just the remaining MNP and mixing the water-soluble MNP directly in the LDS solution. The issue with the water evaporation step is that the MNP degrades rapidly when not in a parent liquid solution; the timing of this method is very difficult and unreliable when repeated for a system fabrication using pLDS. The second method was used and is a repeatable but lengthy process, while still maintaining the MNPs as usable. This method had issues of repeatability and consistency. .

This process of developing and reviewing the pLDS layer, although similar to the original LDS process, was a much complex process during the research as the LDS mixing process was more streamlined, the almost continuous issues appearing with the MNP were very difficult to overcome. The performance of the pLDS is so low compared to both the regular PV cell and LDS layered cells.. The most important that the issues were diagnosed, but it required a change in the solvent, which is beyond the work of this research. However, is room for

improvement and possible development, which will be discussed further in the future works section. The integration of MNPs into a polymer layer and then into a pLDS achieved objective 3 of this research.

8.1.7 LDS layer simulation

Using a computer simulation to optimise the LDS layer and its parameters is invaluable. once It requires a set of input data, such as, absorption and emission data of a luminescent dye and obtaining these data was challenging. The simulation requires specific steps, as the wavelength of the spectrum that is entered must be in steps of 1nm and be a whole number. (i.e. 367.5nm would not work)That required meant absorption and emission data formatting before input for the simulation. .

Once the dataset was formatted and usable, the datasets could be varied to different concentrations using simple division or multiplication. Thus, multiple concentrations could be tested from a single dataset.

Another aspect that influenced the accuracy of simulation was determining the number of rays for interacting with the simulating LDS layer. The number of rays represents the solar irradiation photon count at each wavelength. The smaller the number of rays, the fewer interactions. Since the model is based on probability statistics, therefore, it requires an optimum number of rays for the accuracy of simulation results.

However, the higher the number of rays, the longer the simulation takes, with some simulations crashing when there are over 200,000 rays. 400,000 rays were used for simulations with very clear output to validate spectral responses.

The simulation predicted the optical interaction parameters in terms of the percentage of the incoming photon interaction outcome such as reflection, refraction, thermal loss . moreover, it optimises the overall optical efficiency of the LDS layer. The usage of the computer simulation to optimised the LDS layer parameters for different types of solar cell completed the fourth and final objective of the research tasks set out at the beginning of this thesis.

8.1.8 Viability for domestic usage

One of the main focuses of this research is improving the efficiency and integration of existing PV technology for deployment. Therefore, some considerations must be given to the commercial and industrial usage of this research through the alignment with the IDEAS project.

The LDS layers that were produced throughout this research project were subjected to an integration process and viability test to be usable with a CPC system. This required the LDS layers produced to be durable in this process as the LDS layers would not be valuable if they had deteriorated before the full system assembly being completed. Once installed into the CPC systems, the LDS layers were tested to real conditions and practical application as they were fixed onto external façades of buildings or at installation setups in demo sites. The LDS layers endured these tests, and any associated issues have been discussed and assessed within this thesis. The LDS layers show potential commercialised application potential.

For example, a commercial system may be 8 cells x 8 cells, using 64 cells in total. Throughout this research, well over 300 layers have been fabricated and applied to 12.5 x 12.5 cm si cells alone (not including 2 x 2 cm si cells, a-si, CdTe, or glass). That demonstrates the consistency and reliability of the fabrication of the large-scale LDS layer, which is essential for commercialisation

Determining the commercial viability of this work is a difficult matter. The most obvious solution and question is, can this process be automated? This is possible; the polymer making can be made in batches of much larger sizes if time requirements are not limited (initially). The stock polymer solution for spin coating can also be achieved,. This, too, can be automated for repeated use.

The area that may cause difficulty could be the ability to spin coat multiple layers at any time. However, once this is completed, the drying process does not require excess heat or conduction, as air drying has been used throughout this research. As for moving to commercial-grade production, an industrial automated facility will minimise the errors associated with the handmade fabrication process and consistently produce the same desired result.

The resulting data sets show an improvement in the system's power production through the Ferrara demo site and its 2 separate system productions. At certain time of the day, the power production exceed 100 Watts per demonstrates that there is more than 33% increase in the power production compared to reference system.

This increase is appealing for implementing an LDS for commercial or industrial use It is very important to note that the cells and layers used in the systems were the best ones produced at the time, with many PV cells being discarded due to damage, non-uniformity, or impurities in the layer. The degrading layers can also impact the viability of commercial usage at the time of this research. So, further development would be required in both the overall repeatability of uniformity and the application process, which will be discussed in future works.

Also, stepping away from the technology's ability to improve power output and energy usage, the use of luminescent dyes allows for changes to building design while integrating energy improvements.

The contribution to the IDEAS project using LDS was for a façade mounted system, and the use of different dyes could be appealing to those who wish to use different coloured dyes available.

8.2 Future Work

- **PLDS:** Currently, the LDS layer fabrication has been completed but for the pLDS layer metal nanoparticles must be added to the layer. Currently being tested and applied is the addition of silver nanoparticles (AgNP) to the mixture of PMMA and chloroform. AgNP is dispersed in the solution and mixed to test its stability with the current mixture. AgNP were made in dichloromethane, while the recipe used for the LDS was based on chloroform.

Since AgNP have a short shelf life, once they can be introduced into the mixture and remain stable, the NP can be added into a stock solution of the LDS to make a pLDS solution to be applied to solar cells. This addition of commercial MNPs to the LDS stock solution showed the issue of incomplete dissolution in the organic solvent (chloroform used in this research) due to the MNPs synthesis commonly found in water. This contradiction of solvents being solved would increase the speed of pLDS production and improve the assimilation time required in the preparation phase.

- **Different Types of Cells & Dyes:** Silicon based cells were the only PV cells used for large scale of the LDS layers. For future characterizations, different types of solar cells, such as DSSC, Organic, Multi-junction, and Perovskite solar will be characterised and used as a comparison. Dyes created by IDEAS partners can be used for comparison if they cannot be produced on a larger scale. These dyes can also lead to a more effective and broader use of an LDS layer.
- **Development of LDS for transportation:** future work could be invested of travel and longevity viability for an LDS layer based on a blank substrate like glass or on various PV cells of different make-up, like si or CdTe. This area of development would also be a very large improvement and incentives for further usage in the commercial viability of LDS.
- **Development of LDS for longevity:** It is important to mention that some PV systems guarantee 20 years of degrading efficiency, which is less than 10% a year. The LDS layer should have a similar lifetime. The LDS layers produced during this research have had varying success. With controlled environments and short intervals of site exposure, it still maintains a good

layer quality with little deterioration, while the systems delivered to Ferrara showed rapid of layer degradation.. This area would also be a great and focus and would require a lot of sole commitment to this issue with a long-time requirement. It Also required various situations being tested, including travel in different situations.

- **Further development of LDS on different PV technologies:** The testing that was done on the CdTe was a good indicator of LDS layers impact on different types of PV cell.. As the layer was developed for si initially, so to apply this layer requires to tailor it for different PV technology. While there is already a glass substrate on CdTe, the added LDS reduced its spectral response further. So, to further develop this area, the criteria of:
 - LDS being applied directly onto the cells without a moderator in between.
 - both positive and negative connections are reachable and unhindered for testing for specific responses and, therefore, EQE.
 - Sizing and shapes manageable to be spin coated, as this was the method used for the research to reach the desired characteristics.
- **EQE measurement technique for PV module:** When assessing the EQE of a single PV cell or a single PV module the EQE testing was manageable and useful when guiding the direction of which thickness or concentration of LDS layer to use. This process, however, is very limited due to the physical limitations of PV cell connections in series or for a larger PV cell module.
- **Stable supply of different PV devices:** one of the aims of this research is the application of the LDS onto other PV cells, not just Si PV cells. The procurement of different PV cells, such as Perovskite, Organic PV cells and Dye-sensitized solar cells

Publications & Contributions:

- Cass, B., Chandra, S., Sethi A., & McCormack, S. J. Characterisation of Luminescent Downshifting Layer effects on Silicon Solar Cells, World Renewable Energy Congress 2021

- Cass, B., Chandra, S., Ortega, A.& McCormack, S. J. Development from a small to large scale luminescent downshift layer fabrication on silicon solar cells, World Conference on Photovoltaic Energy Conversion, 2022
- Cass, B., Chandra, S. & McCormack, S. J. Understanding the impact of environmental conditions on the Development & Application of LDS on Photovoltaics , World Renewable Energy Congress, 2022
- Y. Jestin, S. Chandra, B. Cass, H. Ahmed, SJ McCormack, 1.26 - Down-Shifting of the Incident Light for Photovoltaic Applications, 2021
- Deliverables of IDEAS Project :
 - D1.2- LDS and plasmonic-LDS developed model and validation -
<https://ec.europa.eu/research/participants/documents/downloadPublic?documentIds=080166e5d1f65e17&appId=PPGMS>
 - D1.3- Fabrication and Characterisation of optimised LDS/Plasmonic-LDS layers and optimised LDS/PV and Plasmonic-LDS/PV prototypes -
<https://ec.europa.eu/research/participants/documents/downloadPublic?documentIds=080166e5d555d864&appId=PPGMS>
 - D1.4 & D1.5 - Paper Publication -
<https://ec.europa.eu/research/participants/documents/downloadPublic?documentIds=080166e5d76c7ce9&appId=PPGMS>
 - D1.7 - Fabricated LDS layer on top of the asymmetric CPC designs systems - both direct and diffuse system and paper on characterisation and optimisation of integrated systems and validation of the model developed -
<https://ec.europa.eu/research/participants/documents/downloadPublic?documentIds=080166e5fd5d9173&appId=PPGMS>
- Technical Reports for Work package 1 in IDEAS project -
<https://cordis.europa.eu/project/id/815271/reporting>

Modules completed:

- RESEARCH INTEGRITY AND IMPACT IN AN OPEN SCHOLARSHIP ERA (5 ECTS)
- TEACHING AND SUPPORTING LEARNING FOR GRADUATE TEACHING ASSISTANTS (5 ECTS)

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Appendix

Appendix I

Comptuer model simulation data

Lumogen Red

Table appendix 1, lumogen red at 0.02 %wt

Ratio of Rays Eliminated(%)	0
Ratio of Rays Reflected(%)	0
Ratio of Rays Refracted(%)	100
Ratio of Rays Enhanced(%)	0
Ratio of Rays Lost as Thermal Loss(%)	24.24451226
Ratio of Rays Exited the Device(%)	1.990845556
Ratio of Rays Arrived at PV(%)	73.76464219
Ratio of Ray LOST (Filtered)(%)	0
Geometric Gain	1
Optical Efficiency(%)	66.7882816
Solar Concentration Ratio(%)	73.76464219

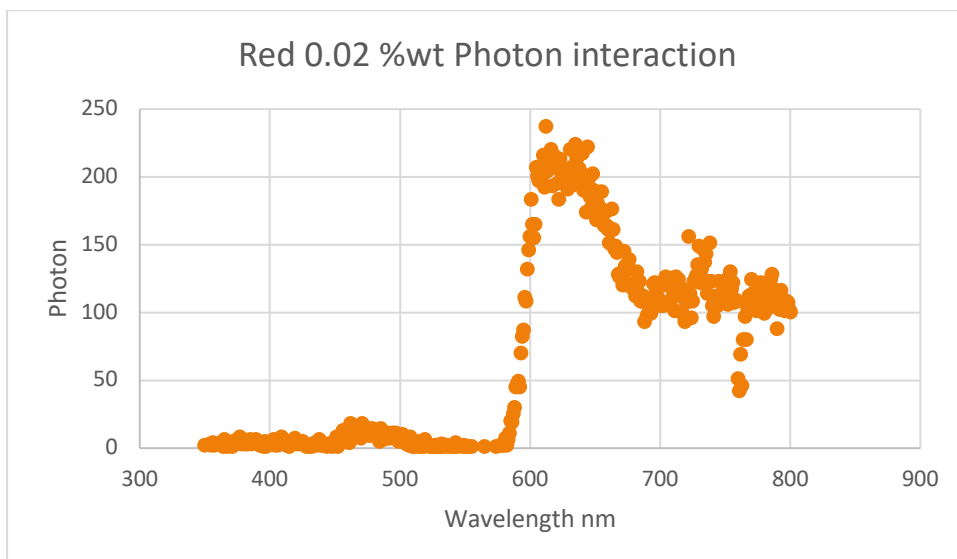


Figure Appendix 1, Photon interaction for lumogen red at 0.02%

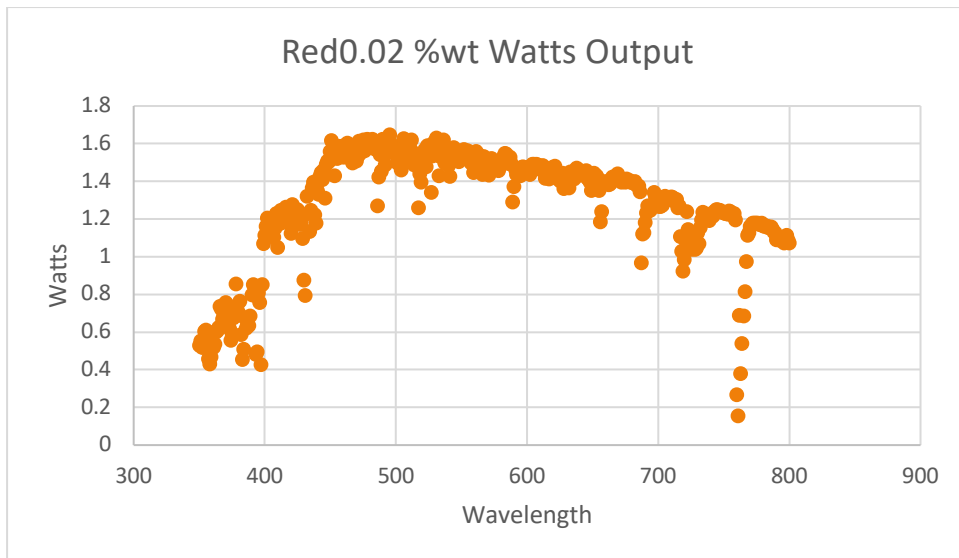


Figure Appendix 2, Watts output for lumogen red at 0.02%

Table appendix 2, lumogen red at 0.2%wt

Ratio of Rays Eliminated(%)	0
Ratio of Rays Reflected(%)	0
Ratio of Rays Refracted(%)	100
Ratio of Rays Enhanced(%)	0
Ratio of Rays Lost as Thermal Loss(%)	98.44472881
Ratio of Rays Exited the Device(%)	0.041834826
Ratio of Rays Arrived at PV(%)	1.513436362
Ratio of Ray LOST (Filtered)(%)	0
Geometric Gain	1
Optical Efficiency(%)	1.237321153
Solar Concentration Ratio(%)	1.513436362

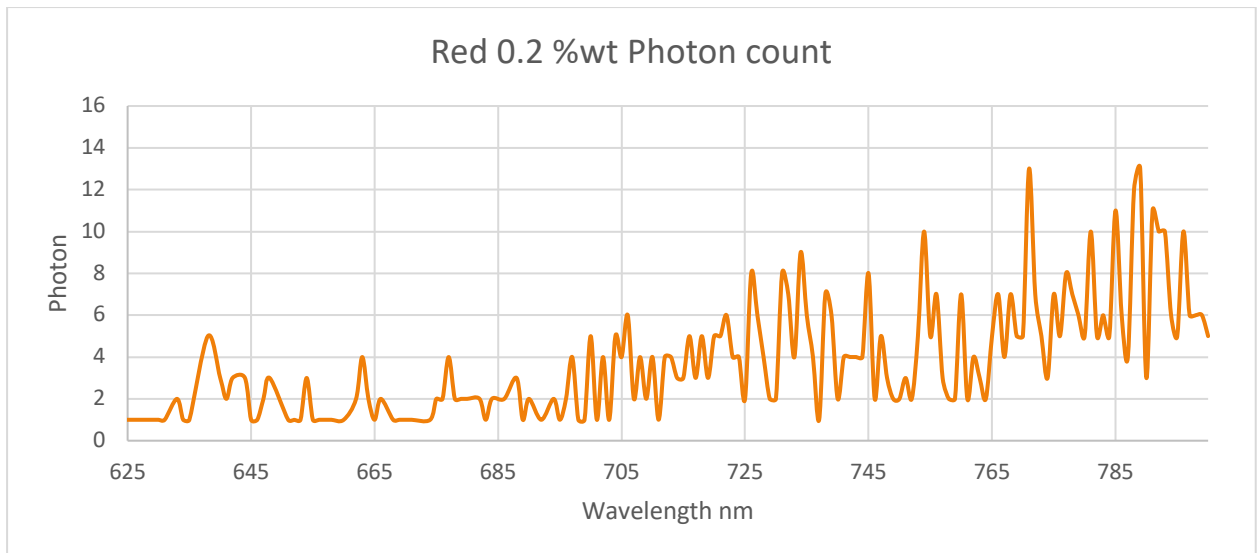


Figure Appendix 3, Photon interaction for lumogen red at 0.02%

Efficiency % is very low at 1% High saturation meaning nothing its escaping so no reading. i.e 100% parasitic absorption.

Lumogen Violet

Table appendix 2, lumogen violet 0.02%wt

Ratio of Rays Eliminated(%)	0
Ratio of Rays Reflected(%)	0
Ratio of Rays Refracted(%)	100
Ratio of Rays Enhanced(%)	0
Ratio of Rays Lost as Thermal Loss(%)	7.99537356
Ratio of Rays Exited the Device(%)	2.276306723
Ratio of Rays Arrived at PV(%)	89.72831972
Ratio of Ray LOST (Filtered)(%)	0
Geometric Gain	1
Optical Efficiency(%)	88.52040165
Solar Concentration Ratio(%)	89.72831972

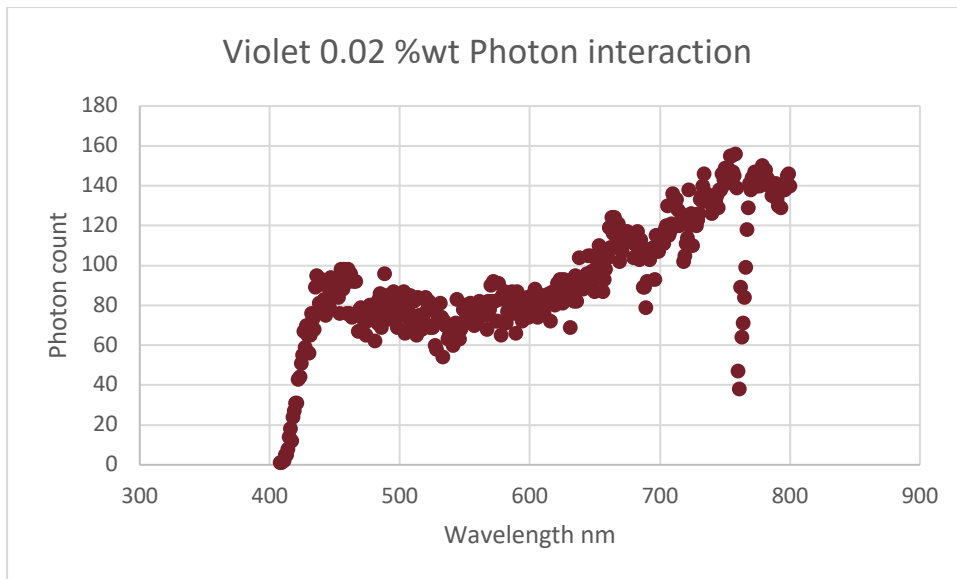


Figure Appendix 4, Photon interaction for lumogen violet at 0.02%

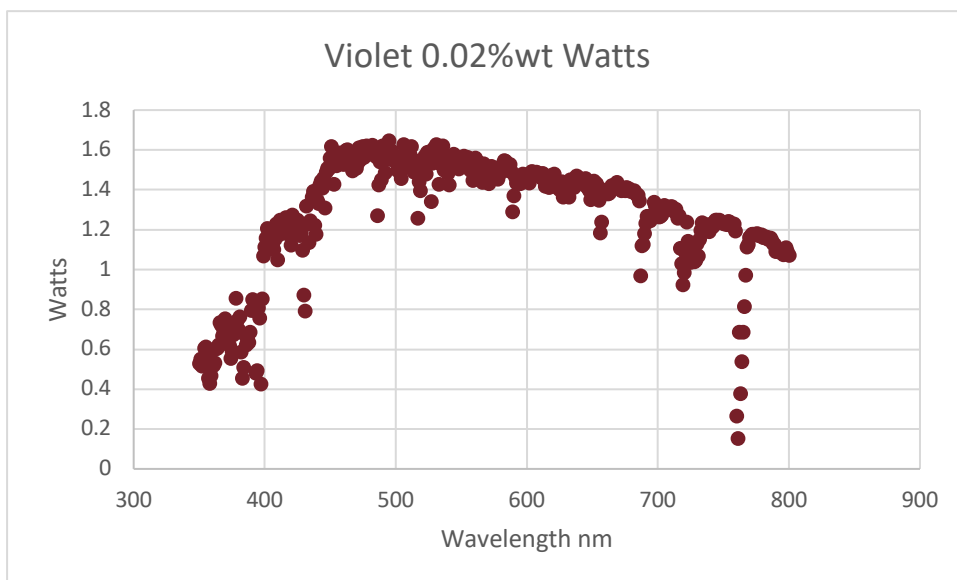


Figure Appendix 5, Watts output for lumogen violet at 0.02%

Table appendix 2, lumogen violet 0.2%wt

Ratio of Rays Eliminated(%)	0
Ratio of Rays Reflected(%)	0
Ratio of Rays Refracted(%)	100
Ratio of Rays Enhanced(%)	0
Ratio of Rays Lost as Thermal Loss(%)	63.31085737
Ratio of Rays Exited the Device(%)	0.952357516
Ratio of Rays Arrived at PV(%)	35.73678512
Ratio of Ray LOST (Filtered)(%)	0

Geometric Gain	1
Optical Efficiency(%)	29.97438323
Solar Concentration Ratio(%)	35.73678512

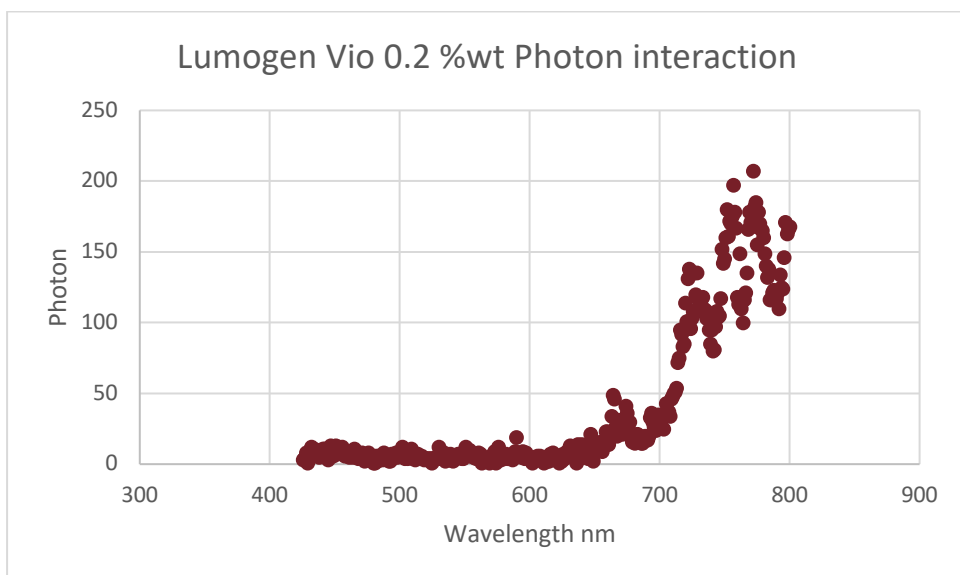


Figure Appendix 6, Photon interaction for lumogen violet at 0.2%

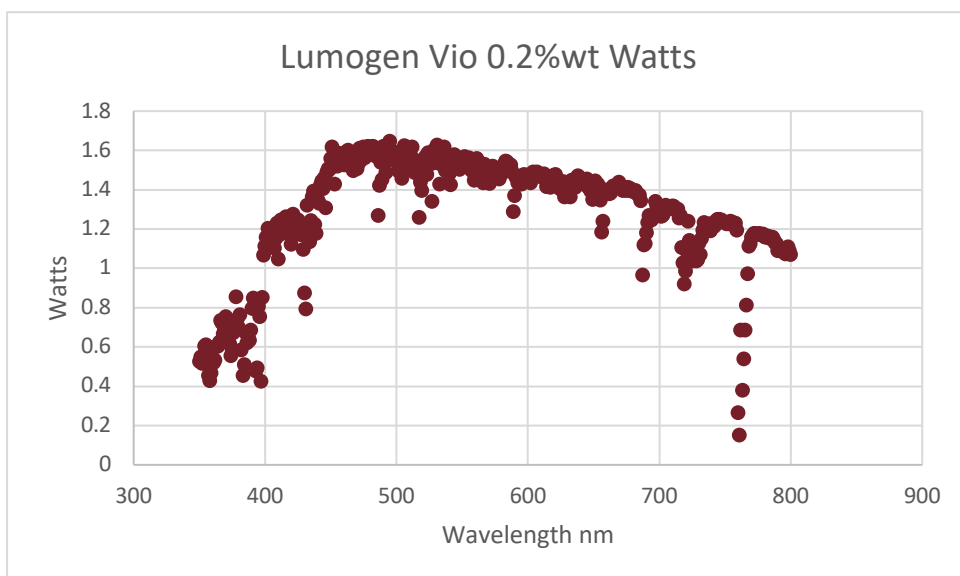


Figure Appendix 7, Watts output for lumogen violet at 0.2%

Lumogen Yellow

Table appendix 3, lumogen yellow 0.02%wt

Ratio of Rays Eliminated(%)	0
Ratio of Rays Reflected(%)	0
Ratio of Rays Refracted(%)	100
Ratio of Rays Enhanced(%)	0
Ratio of Rays Lost as Thermal Loss(%)	3.312333891
Ratio of Rays Exited the Device(%)	2.613446205
Ratio of Rays Arrived at PV(%)	94.0742199
Ratio of Ray LOST (Filtered)(%)	0
Geometric Gain	1
Optical Efficiency(%)	93.42401514
Solar Concentration Ratio(%)	94.0742199

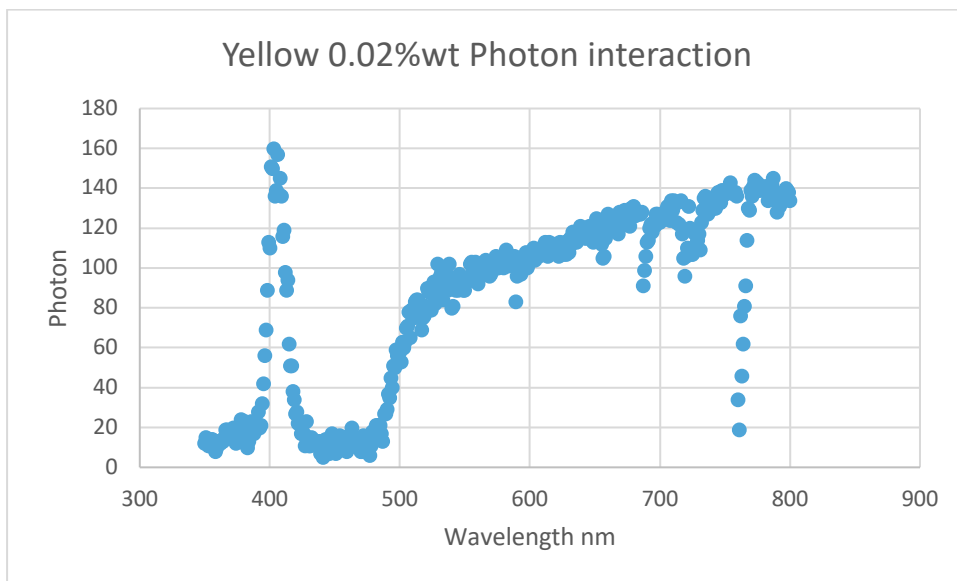


Figure Appendix 8, Photon interaction for lumogen yellow at 0.2%

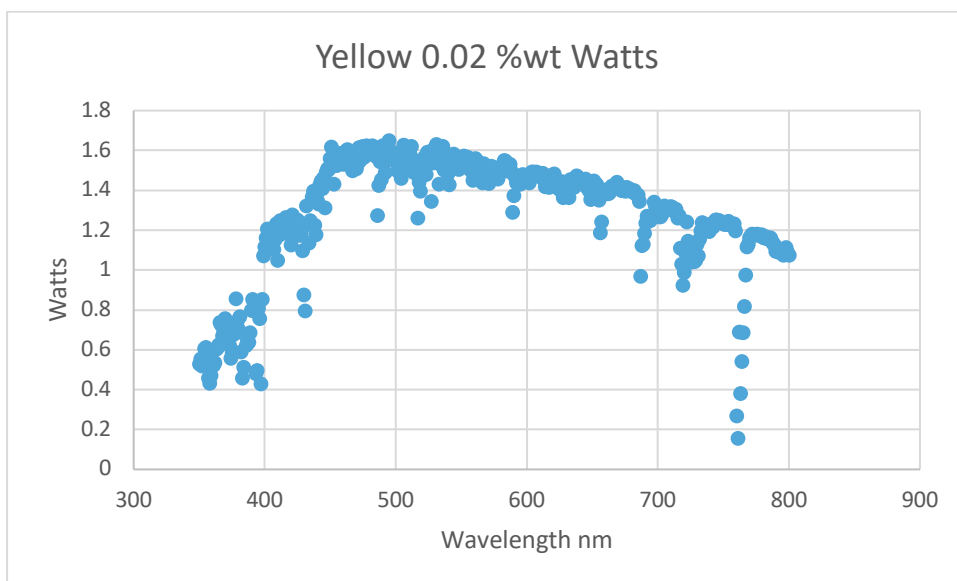


Figure Appendix 9, Watts output for lumogen yellow at 0.02%

Table appendix 4, lumogen yellow 0.2%wt

Ratio of Rays Eliminated(%)	0
Ratio of Rays Reflected(%)	0
Ratio of Rays Refracted(%)	100
Ratio of Rays Enhanced(%)	0
Ratio of Rays Lost as Thermal Loss(%)	16.94310464
Ratio of Rays Exited the Device(%)	2.239393641
Ratio of Rays Arrived at PV(%)	80.81750172
Ratio of Ray LOST (Filtered)(%)	0
Geometric Gain	1
Optical Efficiency(%)	74.91090509
Solar Concentration Ratio(%)	80.81750172

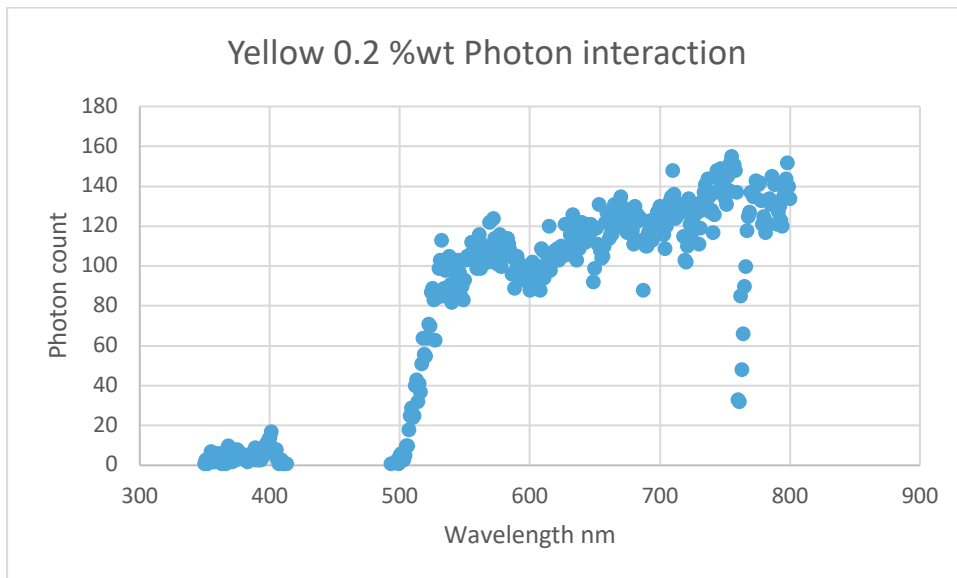


Figure Appendix 10, Photon interaction for lumogen yellow at 0.2%

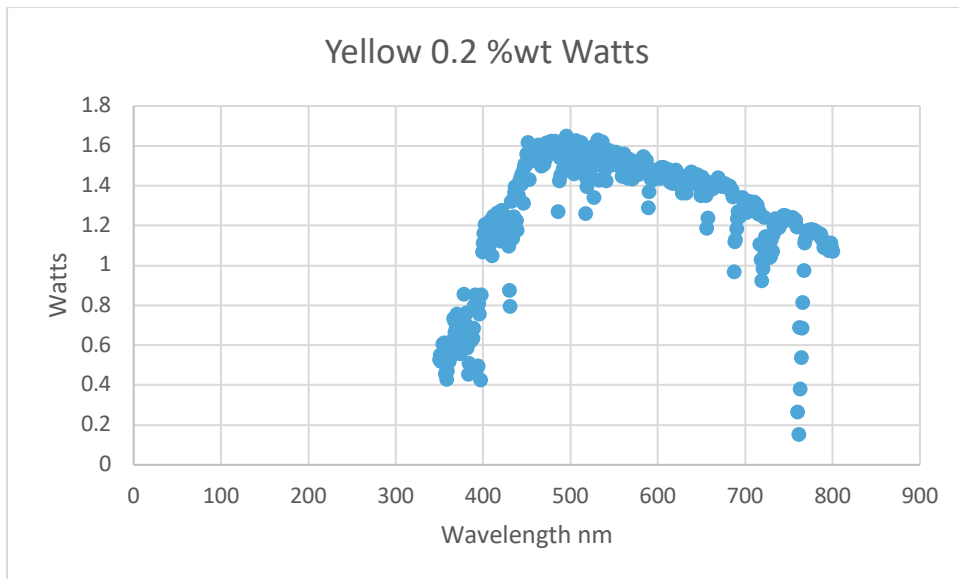


Figure Appendix 11, Watts output for lumogen violet at 0.2%

Methyl Orange

Table appendix 5, methyl orange 0.02 %wt

Ratio of Rays Eliminated(%)	0
Ratio of Rays Reflected(%)	0
Ratio of Rays Refracted(%)	100
Ratio of Rays Enhanced(%)	0
Ratio of Rays Lost as Thermal Loss(%)	0.302266033
Ratio of Rays Exited the Device(%)	2.664561714
Ratio of Rays Arrived at PV(%)	97.03317225
Ratio of Ray LOST (Filtered)(%)	0
Geometric Gain	1
Optical Efficiency(%)	96.4859786
Solar Concentration Ratio(%)	97.03317225

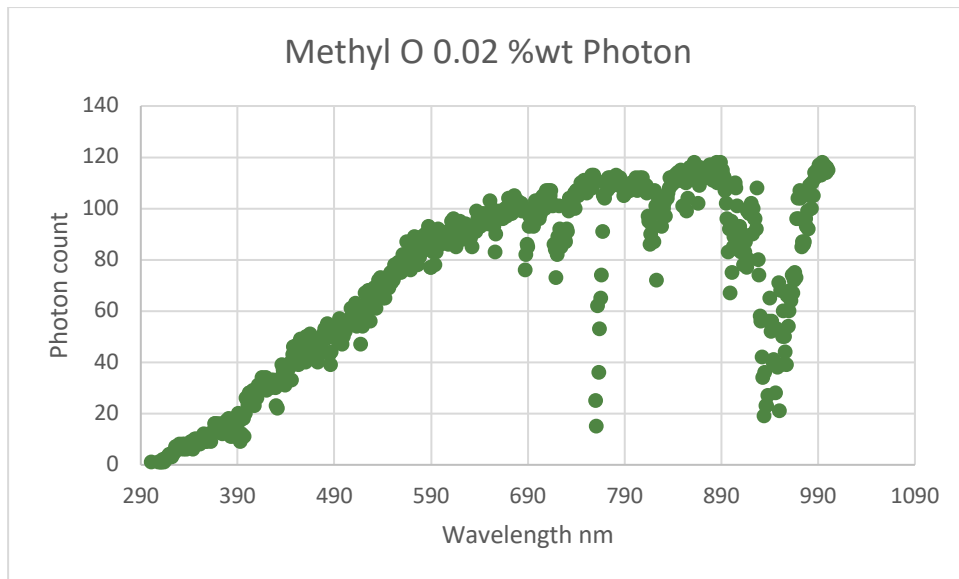


Figure Appendix 12, Photon interaction for methyl orange at 0.02%

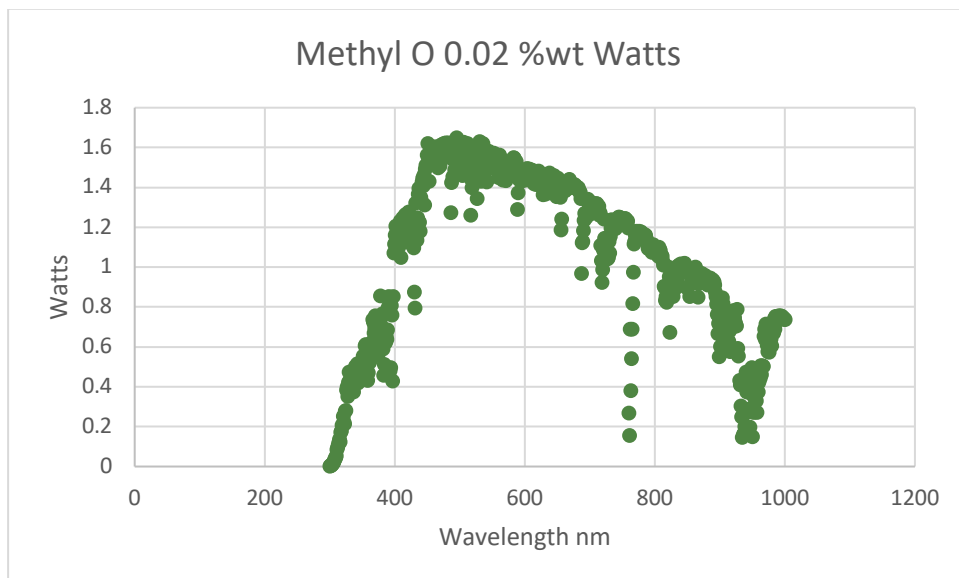


Figure Appendix 13, Watts output for methyl orange at 0.02%

Table appendix 6, methyl orange 0.2 %wt

Ratio of Rays Eliminated(%)	0
Ratio of Rays Reflected(%)	0
Ratio of Rays Refracted(%)	100
Ratio of Rays Enhanced(%)	0
Ratio of Rays Lost as Thermal Loss(%)	2.1006268
Ratio of Rays Exited the Device(%)	2.538000708

Ratio of Rays Arrived at PV(%)	95.36137249
Ratio of Ray LOST (Filtered)(%)	0
Geometric Gain	1
Optical Efficiency(%)	91.9262352
Solar Concentration Ratio(%)	95.36137249

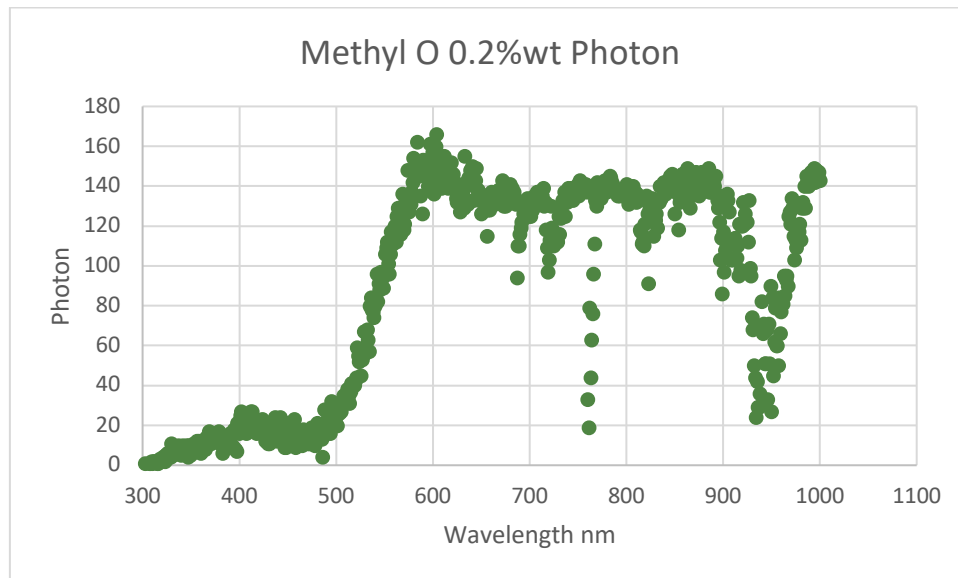


Figure Appendix 14, Photon interaction for methyl orange at 0.2%

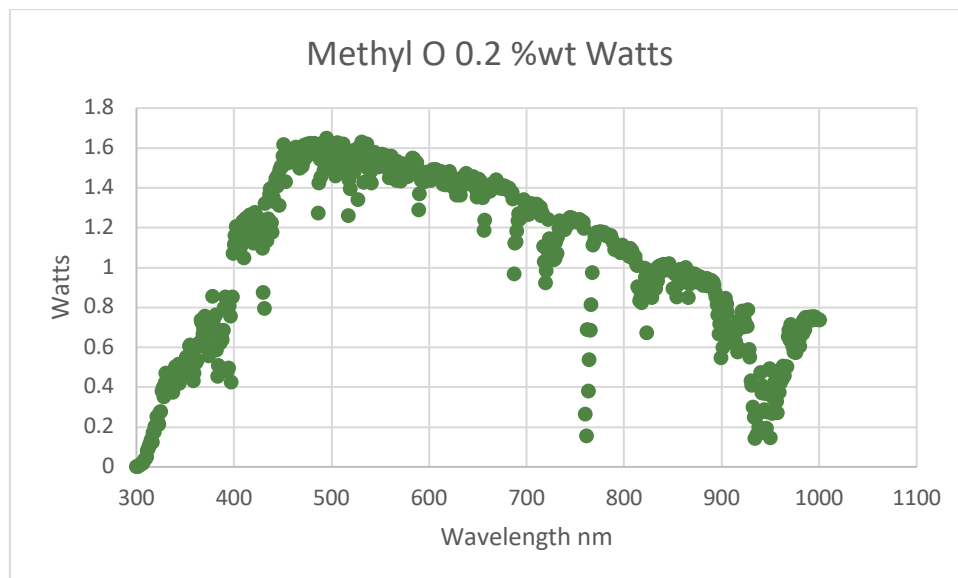


Figure Appendix 15, Watts output for methyl orange at 0.2%

Thickness testing

Table appendix 7, methyl orange at 0.02%wt with 10 μ m

Ratio of Rays Eliminated(%)	0
Ratio of Rays Reflected(%)	16.30200308
Ratio of Rays Refracted(%)	83.69799692
Ratio of Rays Enhanced(%)	0
Ratio of Rays Lost as Thermal Loss(%)	0.416024653
Ratio of Rays Exited the Device(%)	0
Ratio of Rays Arrived at PV(%)	83.28197227
Ratio of Ray LOST (Filtered)(%)	0
Geometric Gain	1
Optical Efficiency(%)	82.51926941
Solar Concentration Ratio(%)	83.28197227
Simulation Time(s)	12.4024875

Table appendix 8, methyl orange at 0.02%wt with 20 μ m

Ratio of Rays Eliminated(%)	0
Ratio of Rays Reflected(%)	15.60862866
Ratio of Rays Refracted(%)	84.39137134
Ratio of Rays Enhanced(%)	0
Ratio of Rays Lost as Thermal Loss(%)	0.30816641
Ratio of Rays Exited the Device(%)	0
Ratio of Rays Arrived at PV(%)	84.08320493
Ratio of Ray LOST (Filtered)(%)	0
Geometric Gain	1
Optical Efficiency(%)	83.53579273
Solar Concentration Ratio(%)	84.08320493
Simulation Time(s)	12.4239617

Table appendix 9, methyl orange at 0.02%wt with 30 μ m

Ratio of Rays Eliminated(%)	0
Ratio of Rays Reflected(%)	15.65485362
Ratio of Rays Refracted(%)	84.34514638
Ratio of Rays Enhanced(%)	0
Ratio of Rays Lost as Thermal Loss(%)	0.369799692
Ratio of Rays Exited the Device(%)	15.14637904
Ratio of Rays Arrived at PV(%)	68.82896764
Ratio of Ray LOST (Filtered)(%)	0
Geometric Gain	1
Optical Efficiency(%)	68.30494366
Solar Concentration Ratio(%)	68.82896764
Simulation Time(s)	12.2576966

Table appendix 10, methyl orange at 0.02%wt with 40 μ m

Ratio of Rays Eliminated(%)	0
Ratio of Rays Reflected(%)	15.60862866
Ratio of Rays Refracted(%)	84.39137134
Ratio of Rays Enhanced(%)	0
Ratio of Rays Lost as Thermal Loss(%)	0.477657935
Ratio of Rays Exited the Device(%)	0.030816641
Ratio of Rays Arrived at PV(%)	83.88289676
Ratio of Ray LOST (Filtered)(%)	0
Geometric Gain	1
Optical Efficiency(%)	83.07842215
Solar Concentration Ratio(%)	83.88289676
Simulation Time(s)	12.2206596

Appendix II

MNP ABSORPTION GRAPHS

Absorption graphs of samples

NOTE: with graphs taken after first testing, the scaling may be different due to equipment reading at the time. E.g below 300 nm there may be peaks of noise but not of sample. So graphs may see different but the results are similar in magnitudes.

MNP1

Sample1

Thickness (mm) 0.55

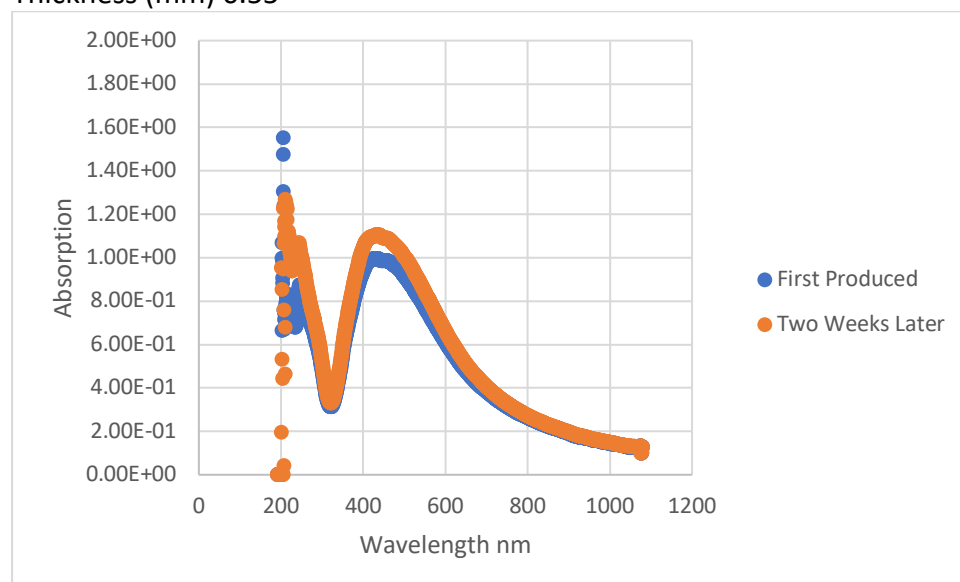


Figure Appendices II 1, Absorption of MNP 1 sample 1

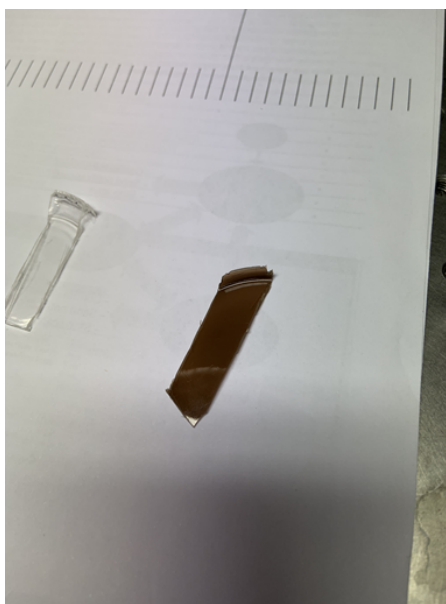


Figure Appendices II 2, MNP 1 sample 1

Sample 2

Thickness (mm) 0.576

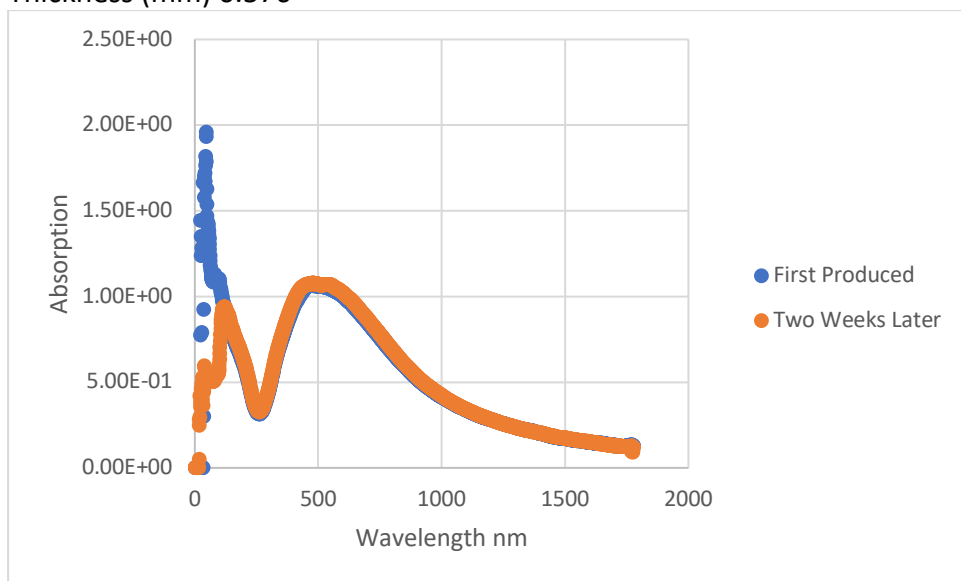


Figure Appendices II 3, Absorption of MNP 1 sample 2



Figure Appendices II 4, MNP 1 sample 2

Sample 3
Thickness (mm) 0.598

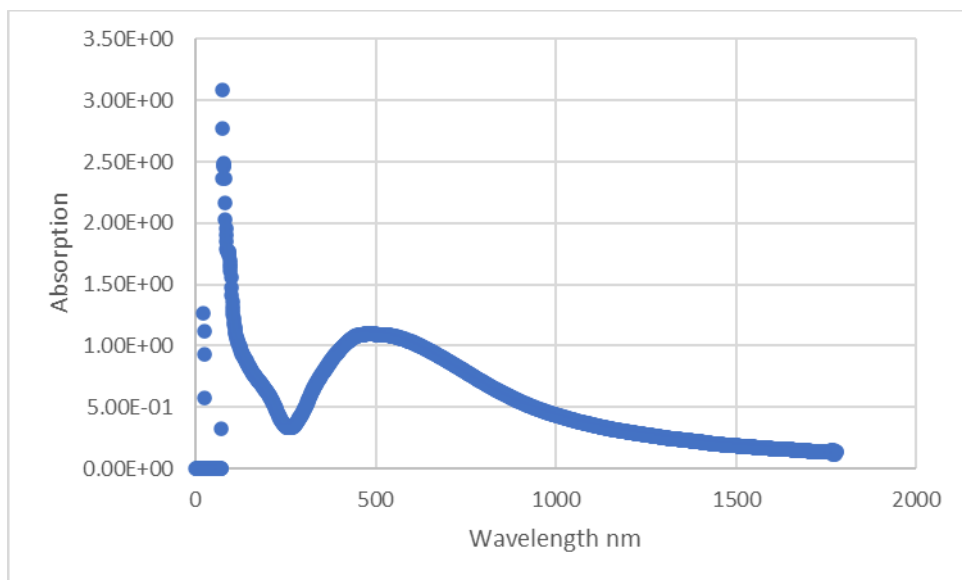


Figure Appendices II 5 Absorption of MNP 1 sample 3



Figure Appendices II 6, MNP 1 sample 3

MNP 2
Sample 1
Thickness (mm) 0.562

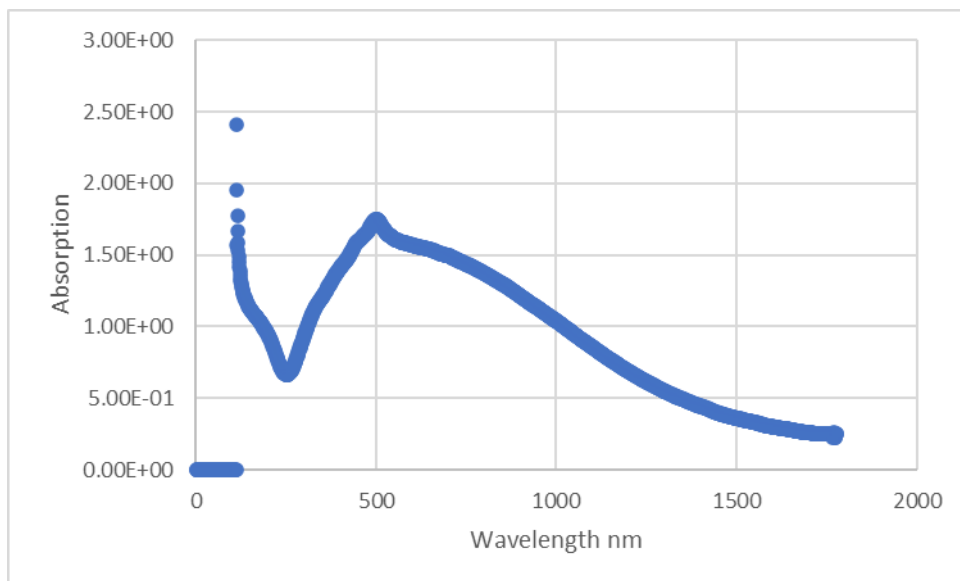


Figure Appendices II 7 Absorption of MNP 2 sample 1



Figure Appendices II 8, MNP 2 sample 1

Sample 2
Thickness (mm) 0.533

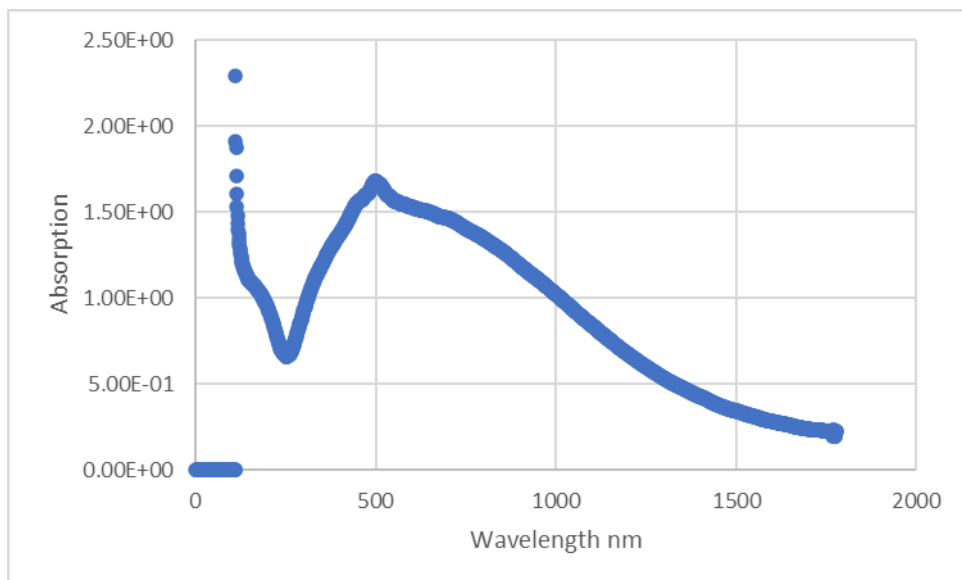


Figure Appendices II 9 Absorption of MNP 2 sample 2



Figure Appendices II 10, MNP 2 sample 2

MNP 3

Sample 1

Thickness (mm) 0.472

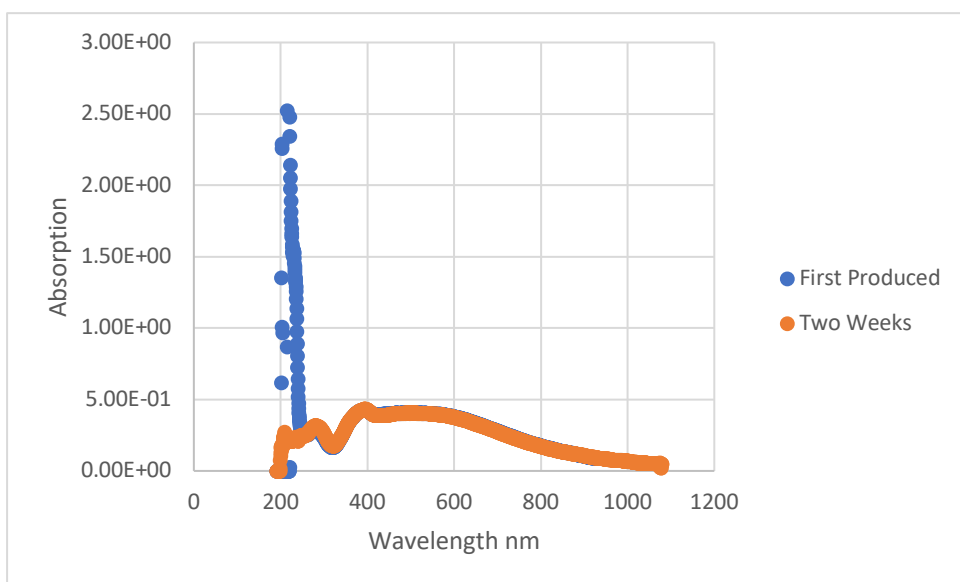


Figure Appendices II 11 Absorption of MNP 3 sample 1

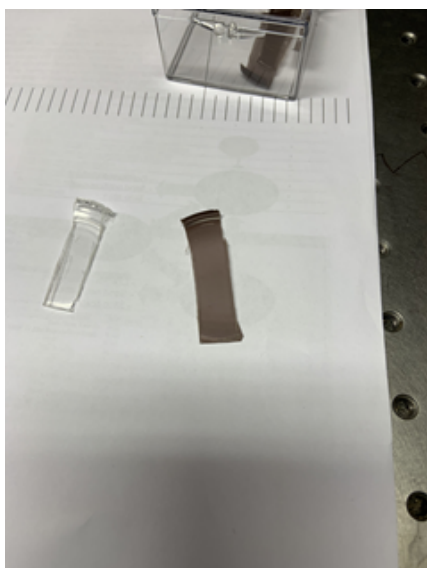


Figure Appendices II 12, MNP 3 sample 1

Sample 2

Thickness (mm) 0.472

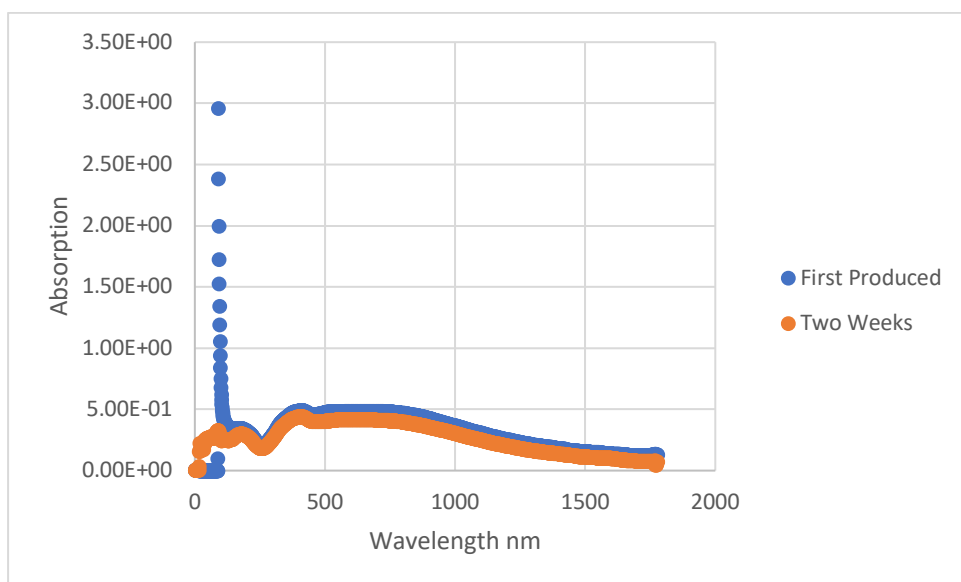


Figure Appendices II 13 Absorption of MNP 3 sample 2



Figure Appendices II 13, MNP 3 sample 2

Sample 3
Thickness (mm) 0.484

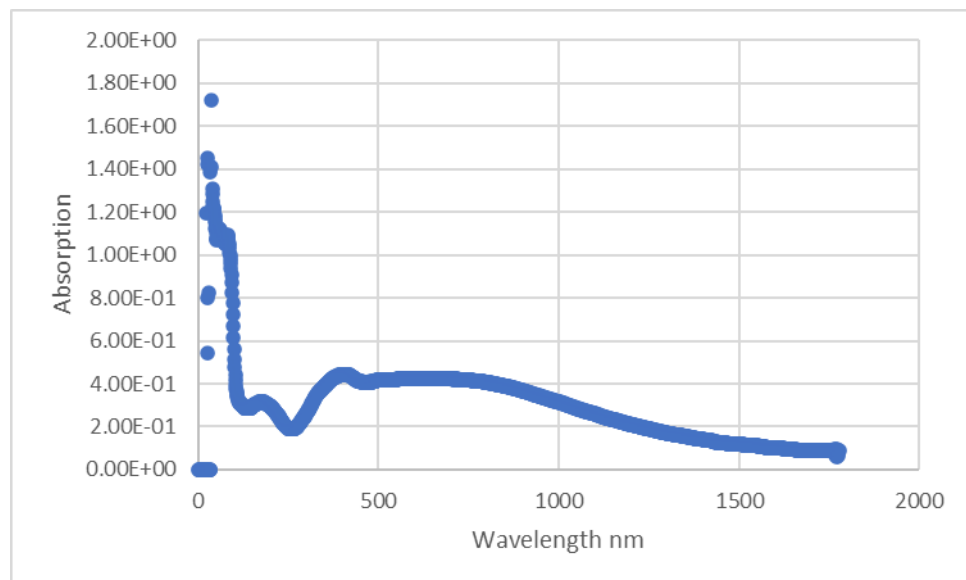


Figure Appendices II 13 Absorption of MNP 3 sample 3

MNP 4

Sample 1
Thickness (mm) 0.364

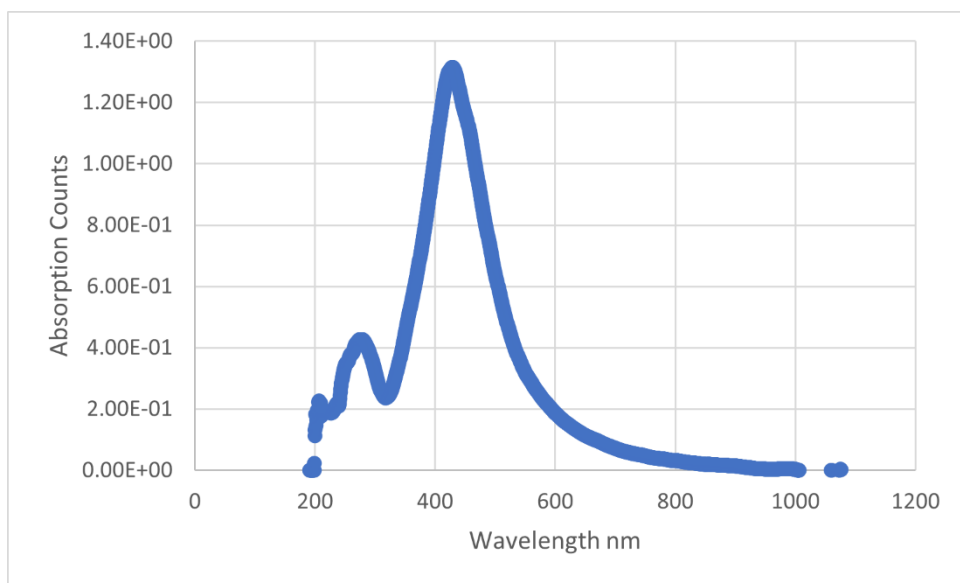


Figure Appendices II 14 Absorption of MNP 4 sample 1

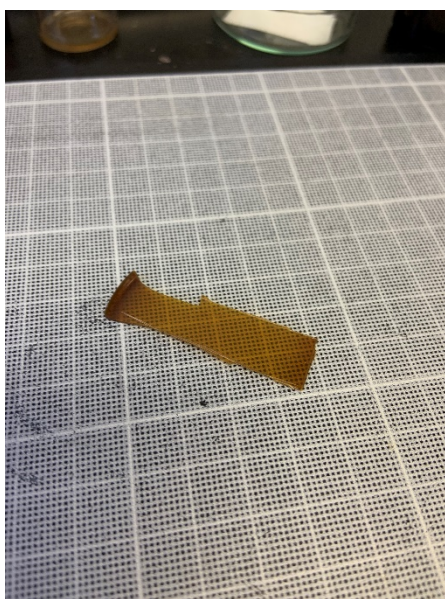


Figure Appendices II 15, MNP 4 sample 1

MNP 4 II
 Sample 1
 Thickness (mm) 0.321

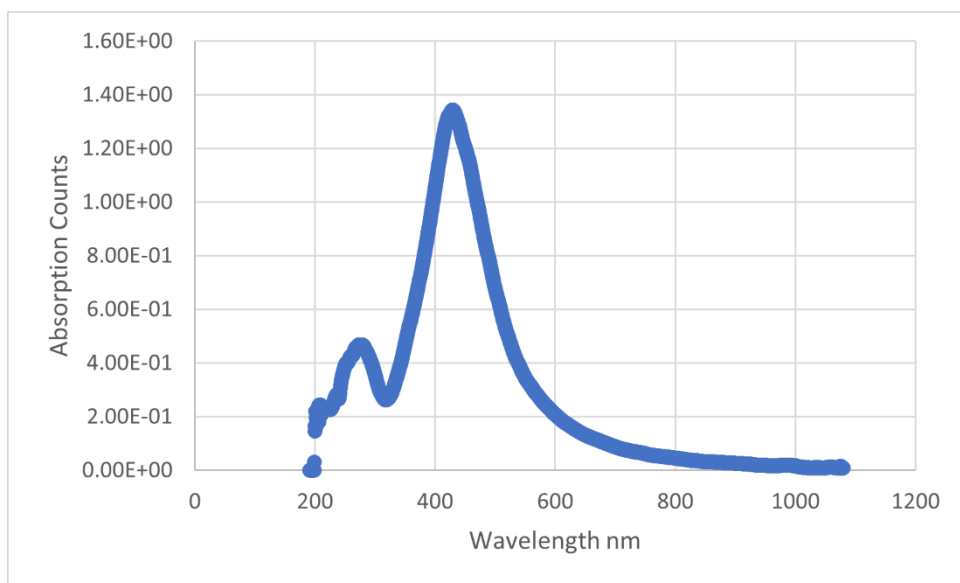


Figure Appendices II 16 Absorption of MNP 4 II sample 1

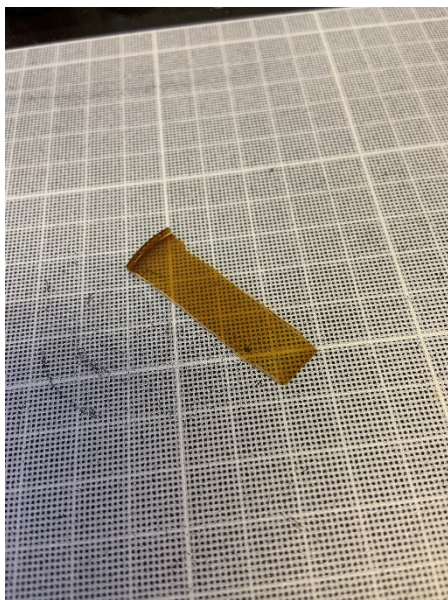


Figure Appendices II 16, MNP 4 II sample 1

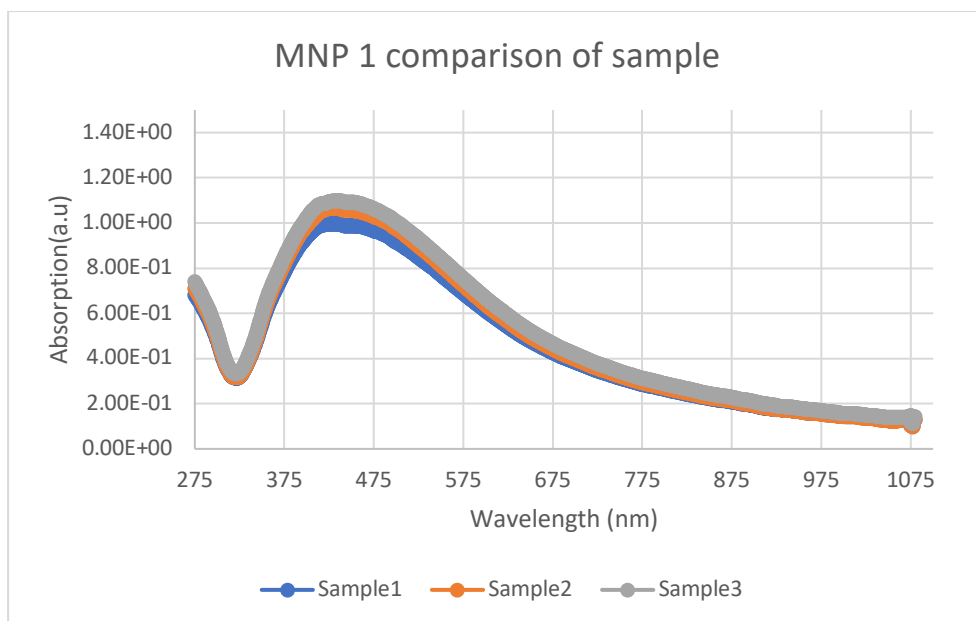


Figure Appendices II 17, MNP 1 Absorption comparison of samples

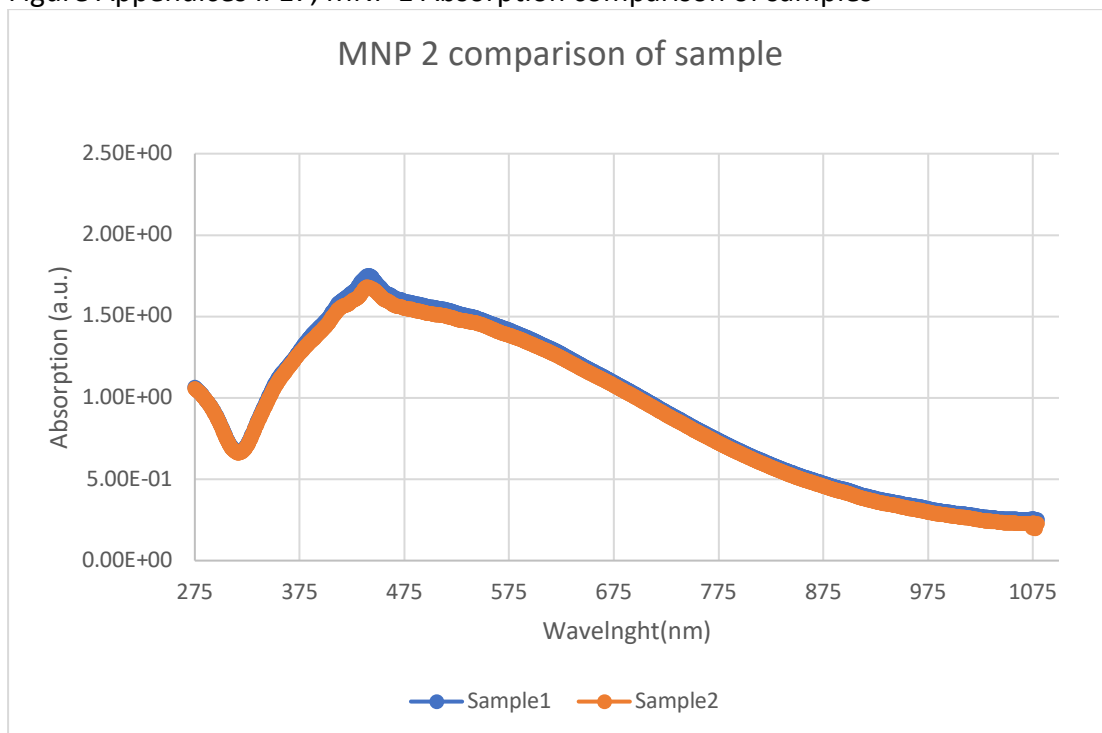


Figure Appendices II 18, MNP 1 Absorption comparison of samples