

Integration of Perovskite Solar Cells with Curved, Rigid, Carbon Fibre-Reinforced Polymer Composites

Timothy Thornber

Department of Physics & Astronomy

The University of Sheffield



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List of Publications

- 1 Elena J. Cassella, Emma L. K. Spooner, **Timothy Thornber**, Mary E. O’Kane, Thomas E. Catley, James E. Bishop, Joel A. Smith, Onkar S. Game and David G. Lidzey, *Gas-Assisted Spray Coating of Perovskite Solar Cells Incorporating Sprayed Self-Assembled Monolayers*, *Advanced Science*, 2022, 9, 14, 2104848. DOI: 10.1002/advs.202104848

As Chapter 4

- 2 **Timothy Thornber**, Onkar S. Game, Elena J. Cassella, Mary E. O’Kane, James E. Bishop, Thomas J. Routledge, Tarek I. Alanazi, Mustafa Togay, Patrick J. M. Isherwood, Luis C. Infante-Ortega, Deborah B. Hammond, John M. Walls and David G. Lidzey, *Nonplanar Spray-Coated Perovskite Solar Cells*, *ACS Applied Materials and Interfaces*, 2022, 14, 33, 37587-37594. DOI: 10.1021/acsami.2c05085

- 3 Elena J. Cassella, Emma L. K. Spooner, Joel A. Smith, **Timothy Thornber**, Mary E. O’Kane, Robert D. J. Oliver, Thomas E. Catley, Saqlain Choudhary, Christopher J. Wood, Deborah B. Hammond, Henry J. Snaith and David G. Lidzey, *Binary Solvent System Used to Fabricate Fully Annealing Free Perovskite Solar Cells*, *Advanced Energy Materials*, 2023, 13, 11, 2203468. DOI: 10.1002/aenm.202203468

- 4 Peter Claronino, Rahul Jayaprakash, Till Jessewitsch, Rachel C. Kilbride, **Timothy Thornber**, Alina Muravitskaya, Robert D. J. Oliver, Ullrich Scherf, Jean-Sebastien G. Bouillard, Ali M. Adawi and David G. Lidzey, *Organic copolymer lasing from single defect microcavity fabricated using laser patterning*, *Journal of Materials Chemistry C*, 2023, 11, 8204-8213. DOI: 10.1039/D2TC05360H

As Chapter 5

- 5 Onkar S. Game*, **Timothy Thornber***, Fernando Cepero-Mejias*, Luis C. Infante-Ortega, Mustafa Togay, Elena J. Cassella, Rachel C. Kilbride, Robert H. Gordon, Nic Mullin, Rachael C. Greenhalgh, Patrick J. M. Isherwood, J. Michael Walls, J. Patrick A. Fairclough and David G. Lidzey, *Direct Integration of Perovskite Solar Cells with Carbon Fiber Substrates*, *Advanced Materials*, 2023, 36, 20, 2209950. DOI: 10.1002/adma.202209950

*Authors contributed equally

- 6 Elena J. Cassella*, **Timothy Thornber***, Robert D. J. Oliver, Mary E. O’Kane, Emma L. K. Spooner, Rachel C. Kilbride, Thomas E. Catley, Onkar S. Game, Alexandra J. Ramadan, David G. Lidzey, *Ultrasonic Spray Deposition of a Passivating Agent for Spray-Coated, Methylammonium-Free Perovskite Solar Cells*, *Solar RRL*, 2023, 8, 2, 2300814. DOI: 10.1002/solr.202300814

*Authors contributed equally

- 7 Elena J. Cassella, Robert D.J. Oliver, **Timothy Thornber**, Sophie Tucker, Rehmat Goodwin, David G. Lidzey and Alexandra J. Ramadan, *Alumina nanoparticles enable optimal spray-coated perovskite thin film growth on self-assembled monolayers for efficient and reproducible photovoltaics*, Journal of Materials Chemistry C, 2024, 12, 13332-13342. DOI: 10.1039/D4TC01602E

- 8 Dominic Blackburn, Nathan S. Hill, Christopher J. Wood, Tamilselvan Velusamy, Balder A. Nieto-Díaz, Caitlin Woolley, Andy Brown, Loukas Zampelis, Trevor McArdle, Molly Worth, **Timothy Thornber**, Ibrahim Albariqi, Rachel C. Kilbride, Tingxiang Yang, C. Neil Hunter, Graham J. Leggett, George Koutsourakis, James C. Blakesley, Fernando A. Castro, David Beynon, Trystan M. Watson, Dumitru Sirbu and David G. Lidzey, *Back-Contact Perovskite Solar Cell Modules Fabricated via Roll-to-Roll Slot-Die Coating: Scale-Up toward Manufacturing*, ACS Applied Materials and Interfaces, 2025, 8, 4, 2219-2228. DOI: 10.1021/acsaem.4c02734

- 9 Joseph Baylay, **Timothy Thornber** and David G. Lidzey, *Characterising Power Generation by Model Photovoltaic Towers Located in a Simulated Urban Environment*, Energies, 2026

- 10 Yan Chen, Emmanouil Lioudakis, Tingxiang Yang, **Timothy Thornber**, Alexandra J. Ramadan, Andreas Othonos, C. Neil Hunter, Graham Leggett, David G. Lidzey and Kyriacos Georgiou, *Mapping Relaxation Pathways and Bottlenecks in 2D Perovskite Microcavities*, Journal of Materials Chemistry C, 2026

- As Chapter 6
- 11 **Timothy Thornber***, Ana Jurado-Estrada*, Fernando Cepero-Mejias*, Ibrahim A. Albariqi, Noor M. Alotaibi, Robert H. Gordon, Dinesh Behera, Samuel Furtado, Clara Polaco, Sajjad Ahmad, Onkar S. Game, Elena J. Cassella, Luke M. Jones, J. Patrick A. Fairclough, J. Michael Walls and David G. Lidzey, *Spray-Coated Perovskite Solar Cells Fabricated on Carbon Fibre-Reinforced Polymer Substrates*, Solar Energy Materials and Solar Cells, 2026
*Authors contributed equally

- 12 Nathan S. Hill, Freddie White, Sophia Baker, **Timothy Thornber**, Farshad Jafarzadeh, Jazib Ali, George Koutsourakis, James Blakesley, Jessica Walker, Trevor McArdle, Roderick Mackenzie, Dumitru Sirbu and David G. Lidzey, *Breaking Scalability Barriers: Fully Roll-to-Roll Coated Indium-Free Perovskite Modules*, Manuscript under submission [Energy and Environmental Science]

Conference Presentations

- 1 Oral Presentation - **Timothy Thornber**, James E. Bishop, Onkar S. Game, Elena J. Cassella, Mustafa Togay, Patrick J. M. Isherwood, Luis C. Infante-Ortega, John M. Walls and David G. Lidzey. *Through a Watchglass Darkly, or... Spray Coated Perovskite Solar Cells on Non-Planar Surfaces*. Supersolar/PVSAT 2021

Note on Thesis Format

This thesis has been submitted in the Alternative Format subject to the approval of the University of Sheffield.

Chapters 4 and 5 are comprised of published research articles which have undergone independent peer review. The contents of these are unchanged, however they have been reformatted to preserve stylistic continuity within the thesis for the benefit of the reader's sensibilities. However, should the reader be persuaded to view these articles in their published forms, the DOIs have been shared in the previous section. Chapter 6 comprises a manuscript of a research article which has been submitted for publication and therefore takes the same form as chapters 4 and 5.

The publications presented as chapters 4, 5, and 6 are collaborative endeavours with multiple coauthor contributions. In the cases of chapters 4 and 6, the majority of the experimental work, analysis, visualisation and writing of the manuscript was conducted by the author (Timothy Thornber) and all coauthors, listed below, have approved of this. In the case of chapter 5 this work was a joint collaboration in close proximity with Dr Onkar Game who is named as first author, in this case my specific contributions are detailed in the chapter foreword.

Onkar S. Game	Fernando Cepero-Mejias	Ana Jurado-Estrada
Elena J. Cassella	Rachel C. Kilbride	Ibrahim A. Albariqi
Mary E. O'Kane	Robert H. Gordon	Noor M. Alotaibi
James E. Bishop	Nic Mullin	Dinesh Behera
Thomas J. Routledge	Rachael C. Greenhalgh	Samuel Furtado
Tarek I. Alanazi	J. Patrick A. Fairclough	Clara Polaco
Mustafa Togay		Sajjad Ahmad
Patrick J. M. Isherwood		Luke M. Jones
Luis C. Infante-Ortega		
Deborah B. Hammond		
J. Michael Walls		
David G. Lidzey		

Abstract

In this thesis, we take an established roll-to-roll compatible solution deposition method, namely spray coating, and apply it to the fabrication of solar cells onto curved, load bearing structures. The aim is not to demonstrate the commercial viability of perovskite technologies as a low cost alternative to established technologies, which is being amply demonstrated already by legions of researchers, but to demonstrate the potential niche applications of the technology to which it is uniquely suited.

In the first experimental chapter of this thesis, we sought to investigate whether our assumptions that spray coating of perovskite devices onto curved surfaces were valid. Specifically, we needed to ascertain whether we could conformally coat a curved surface, without associated problems pertaining to solution run off. We first used flat surfaces held at a series of angles, where we established that solution run off was not an issue. Buoyed by this, we then fabricated curved devices with reasonable performance onto glass substrates.

In the second experimental chapter, we explored the fabrication of perovskite devices onto carbon fibre-reinforced composite materials. This is an important structural material finding applications in the aerospace and automotive industries, and thus an attractive target material for mobile power generation functionalisation. We found that mitigation of coefficient of thermal expansion mismatches was essential to successfully fabricate devices on these materials, however the study was limited to spin coated flat surfaces.

The final experimental chapter was an exercise in bringing the previous two chapters together to create spray-coated, curved, carbon fibre-reinforced polymer based perovskite photovoltaic devices. In this chapter, we improved our substrate materials to significantly reduce complexity and weight while retaining performance, yielding devices with stabilised specific powers up to 26 W g^{-1} , demonstrating the potential of such materials and manufacturing techniques for the realisation of self-charging electric vehicles and aircraft.

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Chapter 1

Introduction

1.1 Prologue

The amount of recoverable energy imparted upon our Earth *via* insolation annually is orders of magnitude larger than either the total anthropic energy consumption of the planet, or the recoverable annual yield of all other renewable energy sources *combined* with the *total* recoverable non-renewable reserves,¹ illustrating its potential as a means to mitigate against climate change.²⁻⁷ Indeed, when considering the reasonably assured recoverable reserves (RARR) of all energy sources over the next 30 years, solar photovoltaics could contribute over twice as much energy as all others combined (see **Figure 1.1**), despite conservative assumptions such as power conversion efficiencies of just 20%, zero off-shore deployment, and a maximum of 6 % continental land mass deployment (currently 38% of continental land area is used for agricultural purposes).⁸

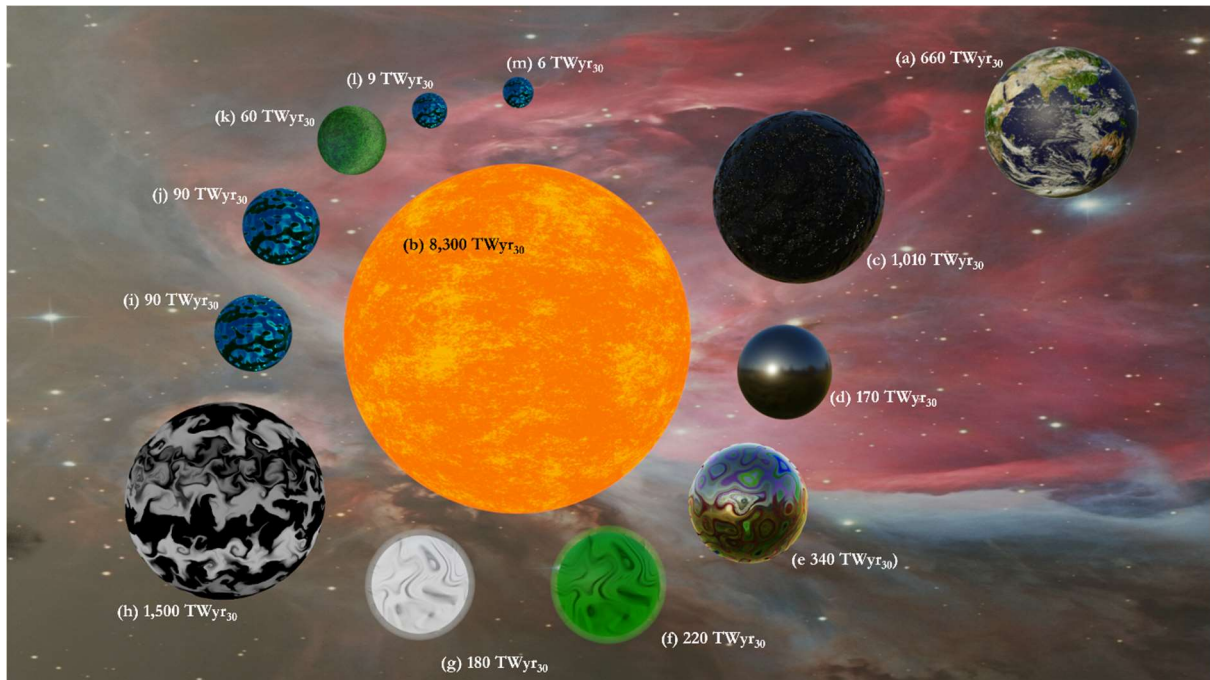


Figure 1.1: (a) Estimated total energy demand over the next 30 years, along with (b-m) RARR energy over the same time period for both finite and renewable energy sources where (b) is solar, (c) is coal, (d) is nuclear, (e) is petroleum, (f) is natural gas, (g) is geothermal, (h) is wind, (i) is oceanic thermal, (j) is hydroelectric, (k) is biomass, (l) is tidal and (m) is waves. Volume of each sphere is proportional to the RARR of each resource. Data extracted from reference [8].

The research focuses almost wholly on solar photovoltaics for stationary power generation, and for good reason. However, the vacuum presented must be filled and so we select the area of study which combines both mobile power deployment and solar photovoltaics – solar powered vehicles. The challenges which face mobile power applications are the same as those for stationary applications, but with the addition of further complications such as power to weight, or specific power, and seamless integration with body form. This is particularly the case where body form contributes to working surfaces, such as structural members or aerofoils.

Developed economies are already driving the adoption of electric personal vehicles, however, these are either hybrid or plug-in electric.⁹ While the former continues to make use of fossil fuels, the latter is only viable where charging infrastructure is readily available. For many economies the latter is unfeasible and infrastructural barriers to adoption must be reduced or ideally eliminated. Even developed economies must contend with the impracticalities of cable based charging, particularly when EV users do not have access to off-road spaces, as is the case in many urban environments where vehicles are parked on the highway.¹⁰ Here, solutions must be found to the trip hazard presented by charging cables, and such solutions must be installed and maintained so as to remain safe and protect other highway users from the dangers of, for example, electric shock.¹¹ Road electrification, whereby dynamic EV charging can be afforded by inductive coils buried beneath the asphalt continues to face significant technical challenges,¹² although test projects are ongoing.¹⁰ For electric propulsion to become the norm across the globe, including areas without the necessary infrastructure, the ability to self-charge would be a highly desirable trait for any electric vehicle. Integration of solar PV with vehicles is therefore an attractive proposition, albeit with the major drawback of additional weight, reducing operational range and potentially rendering the whole endeavour pointless.

1.2 Delocalised power generation

Solar photovoltaics have since their first practical applications always been ideally suited to delocalised energy generation. While they clearly have a role to play as fixed power sources, such as on buildings, car parks, and solar farms, amongst other renewable technologies they provide unique advantages for mobile applications. These include reliability,^{13,14} low mass,¹⁴ non-dependence on external infrastructure,^{15,16} zero tailpipe emissions,¹⁷ and the ability to operate in the absence of fuel or oxidising agents.¹⁸

Potential mobile applications include electric cars,¹⁹ unmanned aerial vehicles,²⁰ nautical superstructures,²¹ satellites, and military field operations.²² The most common technology,

crystalline Si, while almost ubiquitous for stationary PV is not ideally suited for mobile applications due to its indirect bandgap necessitating comparatively thick, heavy panels.²³ Currently, crystalline Si is low cost due to the high supply needed to adequately serve the wider semiconductor industry, and the high earth abundance of the element, overcoming the naturally expensive batch process Czochraslki method of fabrication.²⁴ III-V semiconductors like GaAs address the issue of poor absorption by exhibiting a direct band gap, but come with extremely high costs due to their manufacture *via* epitaxial growth.²⁵ This technology is typically limited to those exceptional applications, such as satellites, which demand the highest specific power available, at no expense spared. Unfortunately, due to the high temperature processes^{26,27} involved and/or strict substrate specifications,²⁵ neither crystalline-Si or GaAs respectively are suitable for direct fabrication on the lightweight materials essential for day to day mobile PV power generation.

Second generation, or thin-film, technologies such as CdTe, amorphous-Si, or CIGS, which also exhibit a direct band gap, are comparable to GaAs but can be mass-produced. Drawbacks here include materials with low earth abundance (e.g. tellurium),²⁸ low power conversion efficiency (e.g. amorphous-Si),²⁹ and high temperature processes (e.g. selenisation).³⁰ While it is possible to fabricate such devices onto polyimide based polymers, this material is more expensive and less suited for large scale adoption where high thermal resistance is not a necessary requirement for day to day performance.³¹

Emerging, or third generation, PV technologies provide a potentially low-cost avenue towards combining both high efficiency and low density with low cost. These technologies are especially attractive due to their low temperature fabrication processes, which allow them to be fabricated onto a wider variety of materials of interest.³² Dye sensitised solar cells make use of cheap materials, but demonstrate very low efficiencies,³³ while organic PV requires often expensive acceptor and donor materials.³⁴

However, since the early 2010s a another third generation technology, that of metal halide, or organic-inorganic hybrid, lead perovskites has emerged.^{35,36} These materials are composed of earth abundant elements,³⁷ further reducing costs, and demonstrate outstanding power conversion efficiencies.³⁸ Driven by a unique mixture of optoelectronic properties, specifically a direct band gap reducing absorber thicknesses to sub-micron scale,³⁹ high dielectric constant resulting in low exciton binding energies,⁴⁰ long charge carrier lifetimes⁴¹ and a seemingly eldritch resistance to defects,⁴² the current research scale efficiencies have reached a peak of 27.2 % at the time of writing.³⁸ Critically, further interest in metal halide perovskites is driven by the fact they demonstrate tuneable bandgaps based on composition, making them ideal candidates for tandem

photovoltaics.⁴³ Finally, but just as importantly, like other third generation materials, they can be fabricated *via* solution processing which, coupled with comparatively low temperature processing requirements, allows for a much wider variety of materials and shapes upon which devices can be fabricated.⁴⁴⁻⁵⁰

1.3 Solutions

Solution chemistry offers significant counterpoints to solid phase and gaseous phase chemistry. A good number of these are related to kinetics, however we are not particularly concerned with this and instead look to the ease of fabrication of thin films, or liquid deposition. Since prehistoric times, *homo* has been creating thin films *via* the solution phase.⁵¹ This in itself a demonstration of how feasible coating *via* the liquid phase is, we can find further evidence in the contemporary multi-billion dollar industries of decorative and protective coatings which predominantly find themselves deposited *via* a liquid medium.

Solution deposition of thin films at near-ambient conditions eliminates costs associated with high vacuum generation and high temperature dependant processes, while opening up possibilities to remove batch-to-batch fabrication in lieu of roll-to-roll. Of all the deposition techniques, however, spray coating is especially suited to rapidly conformally coating uniform films over 3D objects as evidenced by the multibillion dollar marine coating industry. The deposition of uniform semiconductor layers for nanometre scale PV devices demands precise control over film thickness. Unfortunately, while there are multiple methods to generate spray, these typically do not create a uniform droplet distribution size and therefore the resultant films have too great a degree of surface roughness. Ultrasonic spray coating is an outlier in this respect, creating uniform mists which are directed at their target by a shaping gas, and are capable of forming uniform submicron wet films.⁵²

Seamless integration for mobile power applications makes the ability to coat over complex surfaces (e.g. those which demonstrate curvature) the key point of difference. Rather than being restricted to flat surfaces, which would rule out many aerofoils and other working surfaces, or fabricating PSCs onto flexible substrates which could then be adhered to a working surface, direct fabrication *via* spray coating onto a surface of interest provides several benefits. Chief among these being the elimination of excess weight from both the adhesive layer and the extraneous substrate itself, yielding photovoltaic power generation where the only weight penalty is that of the electrodes and semiconductors which make up the device, thereby boosting specific power.

Finally, a note on working surface materials. Automobiles and aerial vehicles are increasingly made from composites.⁵³ Such materials are typically made from some sort of polymer matrix and reinforced by fibres. Combining high elastic modulus and strength with low density, these materials therefore offer extremely attractive strength to weight (specific strength) ratios.⁵⁴ A wide variety of matrix and fibre materials (and combinations thereof) can be used, but a typical example of a high performing composite are those using an epoxy matrix reinforced with carbon fibres. The demonstration of functionalised, curved carbon fibre-reinforced polymers (CFRP) therefore represents an important proof of concept which could pave the way towards further examples of directly integrated photovoltaics, and unlock a key potential niche market for perovskite semiconductors.

1.4 *Thesis Motivation*

The adoption of thin-film PV for mobile applications depends largely on the ability to successfully fabricate devices on arbitrary surfaces. These surfaces should be able to take any form or composition necessary to deliver the working surfaces and structural strength necessary for their primary purpose (e.g. aluminium aerofoils for flight). Clearly it is unfeasible to fabricate a thin-film device on every material and shape possible, therefore we aim to fabricate curved, rigid, devices on carbon fibre-reinforced polymer composite materials. We first seek to overcome the challenges associated with fabrication on curved shapes, electing to use evaporation and droplet based deposition techniques. Specifically, we elect to use ultrasonic spray coating where possible, to allow rapid deposition onto curved substrates. This technique has the benefit of reduced costs associated with manufacturing time, compared with other droplet based techniques such as inkjet printing. We then proceed to fabricate devices on our material of choice, *via* evaporation, and spin coating which is limited to flat substrates. Having demonstrated the ability to fabricate devices on curved, and carbon fibre-reinforced polymer, we look to merge both of the above strategies by fabricating curved carbon fibre-reinforced polymer composite substrates upon which high specific power devices have been directly integrated.

The aim of this thesis is therefore to investigate the feasibility of perovskite solar cell technology for the fabrication of directly integrated power generation on curved, CFRP surfaces. Here, the hypotheses we needed to test included whether spray-coated solution processed layers were able to produce even films on curved substrates, what degree of surface quality was required to successfully demonstrate curved devices, and what practical techniques would need to be developed in order to complete devices. These were all investigated in the first experimental chapter. Next, it was necessary to establish what, if any, processes were required to make CFRP

substrates suitable for thin-film solar cell fabrication, with respect to both roughness and electrical conductivity. Here, reference to electrical conductivity refers to both that of the bulk substrate, and that of the transparent coating oxide used to form the bottom electrode of the device. A suitable transparent top electrode would also need to be designed, and crucially, the completed devices would need to demonstrate competitive specific power output. These questions were investigated in the second experimental chapter of this thesis. With this having been carried out on flat CFRP, it was then necessary to establish protocols for the fabrication of curved CFRP with similar properties. Specifically, would CFRP substrates fabricated using moulds of the same quality as the glass substrates used in the first experimental chapter be of a suitable roughness, and what, if any, changes to substrate fabrication processes were required practically to ensure the targeted electrical conductivity requirements. Perhaps most importantly, we needed to identify what, if any, differences might be found when spray coating solution layers onto CFRP substrates, and how best to ensure uniform films across charge extraction pathways which must travel over exposed polymer regions, where wetting would likely be a significant problem. These devices are proposed to be load bearing, and therefore it would also be necessary to investigate whether such claims hold up under mechanical stress. Finally, as with the previous experimental chapter, the devices would need to demonstrate specific power outputs competitive with those found in the literature, and what degree of scope remained to improve would need to be assessed. We would also need to establish what, if any, intrinsic instabilities might exist with respect to our substrate choice, and device architecture, in comparison with devices fabricated onto ultrathin polymers, or glass. These areas of investigation would all be addressed in the final experimental chapter of the thesis.

1.5 *Thesis Overview*

Chapter 2 delves into the background theory associated with solid state materials, molecular orbital theory and bonding, and the properties of semiconductors. Included also will be a discussion of the physics of solar cells. Following on from this, an introduction to perovskites and the history of their study as an optoelectronic curio will be presented. Attention will then turn to matters pertaining to solution deposition techniques, in particular ultrasonic spray coating, along with an abridged history of the development of spray coated PSCs. Finally, a brief summary will be presented on thin film PV fabricated on non-standard substrates, high specific power PSCs, and curved, 3D, electronics.

Chapter 3 deals specifically with the experimental methods selected for the investigations presented later in this thesis. The chapter begins with a discussion of the materials used throughout, paying specific attention first to substrates, then to device architecture, and finally the specific materials

used throughout the device stack. Following this, a discussion of the fabrication techniques used through the course of investigations will be presented. To finish, an exploration of characterisation techniques used in this thesis will be presented, with discussion of the background physics of these where relevant.

Chapter 4 will be the first experimental chapter of this thesis. Here, we sought to fabricate curved, rigid perovskite solar cells *via* ultrasonic spray coating. To begin, we applied previously established protocols onto substrates held at a variety of inclination angles, with the aim being to establish the limits of our protocols *vis* wet adhesion and run-off under the effect of gravity. We then proceed to fabricate PSCs onto plano-convex optical grade lenses coated with indium tin oxide, thereby establishing the potential for coating non-planar surfaces *via* spray coating.

Chapter 5 is the second experimental chapter of this thesis. Here, we looked to demonstrate PSCs which had been fabricated directly onto CFRP composite substrates. First, we demonstrate a process for substrate manufacture which achieves an acceptable roughness for thin-film devices and also electrically isolates the subsequently deposited TCO from the underlying, conductive, carbon fibres. We next describe methods for overcoming issues pertaining to TCO adhesion and cracking due to an inherent coefficient of thermal expansion mismatch between the inorganic and organic materials. Having overcome this challenge, we then present spin coated PSCs which have been directly fabricated onto CFRP substrates.

Chapter 6 is the final experimental chapter of this thesis. Here, we aimed to fabricate spray-coated PSCs onto curved CFRP substrates. To create curved substrates we moved to woven CFRP substrates, finding this increased the thermal stability of our substrates. This allowed us to remove the crack prevention layers we introduced in Chapter 5, significantly reducing the mass of our device stack. We then fabricate devices *via* a combination of ultrasonic spray coating and spin coating onto both flat and curved substrates. Finally, we also present mechanical testing with *in-situ* optoelectrical testing where we demonstrate our devices to be robust with respect to fatigue testing.

Chapter 7 presents a summary of the results in this work. To finish, suggestions of further work to be undertaken to advance the adoption of CFRP composite integrated photovoltaics will be suggested. Here we will focus particularly on overcoming practical barriers to adoption for mobile power generation applications.

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Chapter 2

Theoretical Background

2.1 *Introduction*

In this chapter, we will cover topics concerning the conceptual bases which underpin semiconductors and photovoltaics. We will begin with an exploration of the physics of solid materials, molecular orbital theory and its relation to band theory, and semiconductors, drawing primarily upon the works of Atkins, de Paula and Keeler,¹ and Kittel.² We will then discuss the basics of photovoltaic device physics, drawn primarily from the work of Nelson.³ Subsequently, discussion will turn to organic-inorganic metal halide perovskites, their structure, and tunability. Also included will be a short treatise on the historical progress of perovskite based thin film photovoltaics since their initial demonstration. Emphasis on key developments in the broader field with respect to device architecture, perovskite composition and nucleation control techniques (and their importance) will be included here. This will be followed by an introduction to the physics of spray coating. Following this will be another history, this time concerning spray coated perovskite solar cells. The chapter will be rounded off by discussion of PV on various substrates, high specific power perovskite solar cells (PSCs), and finally a look into the fabrication of electronics onto curved, rigid substrates.

2.2 *Solids*

2.2.1 *Atoms & Atomic Orbitals*

The atom itself consists of a small, dense, nucleus surrounded by a cloud, or distribution, of electrons. The nucleus is made up of protons, which carry a positive charge, and neutrons which hold no charge. The electrons carry a negative charge. The protons and neutrons bear the same appreciable mass, which dwarfs that of the electron. The number of protons (Z number) in the nucleus governs the atom's element, and is equal to the number of electrons present in the atom.

Towards the tail end of the 19th Century, evidence was mounting that classical mechanics could not explain the behaviour of atoms or subatomic particles. The ultraviolet catastrophe, the tendency for the heat capacity of a given solid towards zero at low temperatures, and of course spectroscopy all imply that neither emitted radiation nor particles can hold arbitrary energy levels. Furthermore, the classical treatment of waves and particles as separate items collapses when electromagnetic radiation is shown to have particle-like properties *via* the photoelectric effect or

electrons are shown to have wave-like properties in the event a beam of them are directed at a crystal.

The solution to these apparent contradictions is found in the theory of quantum mechanics. Unlike the deterministic theory of classical mechanics, quantum mechanics is a probabilistic theory and can only tell us the likelihood of something happening. Here, both emitted electromagnetic waves, and particles, are postulated to hold only discrete energy levels, a concept known as energy quantisation. Furthermore, both electromagnetic radiation, and particles, are treated as both waves and particles simultaneously, giving rise to the concept of wave-particle duality. This allows for the expression of the dynamical properties of a particle in a quantum mechanical system using a wavefunction (Ψ). The wavefunction can be found by solving for the time-independent Schrödinger equation (**Equation 2.1**), treating both the kinetic and potential energy of the particle. The wavefunction can take both positive and negative values, which allows for constructive and destructive interference when two wavefunctions are brought into proximity, the importance of which will be highlighted later in this chapter.

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\Psi = E\Psi \quad \text{(Equation 2.1)}$$

Here, the first term is related to the kinetic energy of the particle, with $\hbar$ a simplification often used in quantum mechanics where $\hbar = h/2\pi$, h being Planck's constant. The term $V(x)$ is related to the potential energy of the particle.

The Born interpretation of the wavefunction states that the probability of finding a particle between x and $x+dx$ for a given value of Ψ at x , is proportional to $|\Psi|^2 dx$. This can be considered analogous to the square of the amplitude of an electromagnetic wave being interpreted as the probability (classically, the intensity) that a photon is present in that region. Here, it becomes apparent that Ψ is complex and can be thought of as a probability amplitude, and its square modulus as a probability density. It therefore follows that $|\Psi|^2$ is never negative, but can be zero where the wavefunction passes through a node or where it simply *is* zero.

The idea presented by Born imposes strict criteria as to what mathematical solutions to the Schrödinger equation are physically valid. Clearly, the solution cannot be infinite over a finite region, significantly reducing the number of acceptable solutions to the Schrödinger equation. There can only be a single value of $|\Psi|^2$ at any given point in the region, otherwise there would be multiple probability densities for the position of a single particle at that point. The wavefunction must be continuous, as the Schrödinger equation is a second-order differential equation and therefore relies on a continuous first derivative to be well defined. Finally, as the first derivative

is continuous, it follows that its slope must also be continuous. Due to these criteria, it becomes apparent that E cannot have an arbitrary value. It therefore follows that the energy of a particle must be quantised.

The quantisation of energy levels applies across three modes; the translational mode applies to movement in space, the vibrational mode pertains to harmonic oscillations, and rotational modes apply to angular momenta. The above modes can apply to molecules, atoms, and even subatomic particles such as electrons. As we are interested in building up an idea of the electronic structure of atoms, we are principally concerned with rotational motion of electrons around the atomic nucleus.

We can in the first instance consider the hydrogenic atom. Here, we assume an atom with just a single electron present. The potential energy of the electron, due to the coulombic force between the positive nucleus and the negative electron, can be stated as **Equation 2.2**.

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} \quad \text{(Equation 2.2)}$$

Here, Ze is the nuclear charge, the value r is the distance between the electron and the nucleus, and ϵ_0 is the vacuum permittivity. The Schrödinger equation for motion of an electron around the nucleus is given by **Equation 2.3**.

$$-\frac{\hbar^2}{2\mu} \nabla^2 \Psi - \frac{Ze^2}{4\pi\epsilon_0 r} \Psi = E\Psi \quad \text{(Equation 2.3)}$$

Here, μ represents the reduced mass, approximating towards m_e due to the large disparity between the mass of the nucleus with respect to the mass of the electron. As V is inversion symmetric, it is possible to split the wavefunction into radial and angular wavefunctions as per **Equation 2.4**.

$$\Psi(r, \theta, \phi) = R(r)Y(\theta, \phi) \quad \text{(Equation 2.4)}$$

We first deal with the angular wavefunction $Y(\theta, \phi)$. For simplicity, we will consider a particle travelling in 2D around a ring. Here, the potential energy is zero around the ring, with the inner and outer walls corresponding to an infinite potential, thus confining the particle to the ring. Clearly, as the wavefunction must be continuous, its value must be the same at a given origin, θ , and associated completion of the ring, 2π . **Figure 2.1** shows the circumference of a ring opened up into a line to demonstrate this.

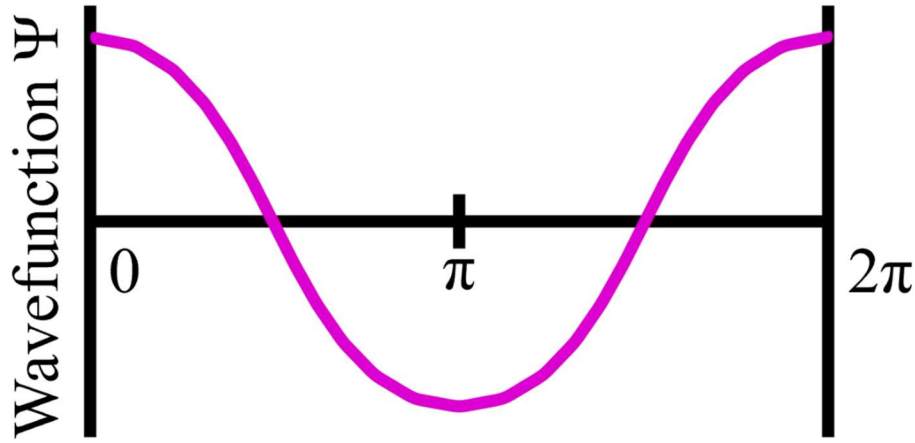


Figure 2.1: Circumference of a ring opened into a line, demonstrating a possible solution for the wavefunction of a particle bound to the ring.

Equation 2.5 details the energy levels for a particle on a ring. Note that this is dependent on an integer m_l , which acts as a quantum number. As the energy levels are quantised, so are the available angular momenta. As m_l increases in magnitude, more nodes are introduced to the cyclic wavefunction, corresponding to an increase in kinetic energy. Importantly, all values of $m_l \neq 0$ are doubly degenerate, and therefore are assigned $\pm$ signs. These signs govern the direction of the angular momenta.

$$E_{m_l} = \frac{m_l^2 \hbar^2}{2I} \quad m_l = 0, \pm 1, \pm 2, \dots \quad (\text{Equation 2.5})$$

For a particle travelling along the surface of a sphere, i.e. the above but in 3D, the particle must now satisfy two cyclic boundary conditions, a) the wavefunction must be continuous between the completion and commencement of a circuit around the equator, and b) the wavefunction must be continuous between the completion and commencement of a circuit through the poles. Conveniently, the spherical harmonic functions satisfy these, and are readily applicable to **Equation 2.6**.

$$E_{l,m_l} = l(l+1) \frac{\hbar^2}{2I} \quad l = 0, 1, 2, \dots \quad m_l = 0, \pm 1, \pm 2, \dots \quad (\text{Equation 2.6})$$

The consequence of this is that there are now two integer values, l , and m_l , acting as quantum numbers, where l is termed the *orbital angular momentum quantum number*, and m_l is termed the *magnetic quantum number*. Following Equation 2.6, l is solely responsible for the energy, however for each

quantised energy level there are $2l+1$ values of m_l , which each corresponds to a degenerate quantised z-component of the angular momentum.

Having found the quantum numbers which govern the angular wavefunction contribution to the total wavefunction, we can now address the radial wavefunction ($R(r)$) component. **Equation 2.7** details the potential energy term of the radial wave equation.

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2} \quad \text{(Equation 2.7)}$$

The first term is simply the Coulomb potential energy of an electron within the field of the nucleus. The second term is related to the angular momentum of the electron around the nucleus. When $l = 0$, clearly the only effective potential on the electron is the Coulomb potential, which is attractive at all values of r . If $l = 0$ then the angular momentum close to the nucleus is strongly repulsive, although it drops off exponentially as r increases. We can see, therefore, that close to the nucleus the two contributions are very different, however at appreciable values of r they look quite similar. We find that close to the nucleus the radial wavefunction is close to r^l and that far from the nucleus there is an exponential decay. Between these two regions lies a polynomial bridging function $L(r)$. This is shown below in **Equation 2.8**.

$$R(r) = r^l L(r) e^{-r} \quad \text{(Equation 2.8)}$$

Close to the nucleus, the value for e^{-r} becomes 1, and the polynomial is constant and therefore the wavefunction becomes proportional to r^l . Far from the nucleus the polynomial becomes proportional to r^{n-l-1} such that all wavefunctions for a given value of n become proportional to $r^{n-l-1} e^{-r}$ and therefore decay to zero regardless of the value of l . In actual fact, the value for n must be a whole positive integer, and this number, the *principle quantum number*, allows for an expression of the bound states of an electron in the hydrogen atom as described in **Equation 2.9**.

$$E_n = -\frac{\mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \times \frac{Z^2}{n^2} \quad \text{(Equation 2.9)}$$

Using the three quantum numbers we have determined above; we can begin to build up an image of the electronic structure of an atom. Here, the principal quantum number, n , relates to the energy level of an orbital and therefore also its size, and takes values of 1, 2, 3.... Orbitals with the same value for n are considered to share the same “shell”. For orbitals in a given shell, n , the number of spherical, planar, or conical nodes present are given by $n - l$.

The orbital angular momentum quantum number, l , relates to the shape of the orbital and takes values of $0, 1, 2 \dots, n - 1$. Here, $l = 0$ corresponds to an s orbital, $l = 1$ to a p orbital, $l = 2$ to a d orbital, $l = 3$ to an f orbital, continuing so in a now alphabetical fashion. The value of l denotes the “subshells” within a given shell.

The magnetic quantum number, m_l , relates to the orientation of the orbital, and takes values of $0, \pm 1, \pm 2 \dots, \pm l$.

It is immediately apparent that the range of m_l is governed by l , the maximum value of which is governed by n . These represent the allowable combinations of quantum numbers which satisfy the Schrödinger equation for the bound states of a hydrogenic atom and are summarised in **Table 2.1**.

Quantum number	Allowed values
Principle quantum number, n	$n = 1, 2, 3 \dots$
Orbital angular momentum quantum number, l	$0 \leq l \leq n - 1$
Magnetic quantum number, m_l	$-l \leq m_l \leq +l$

Table 2.1: Summary of the three quantum numbers we have encountered thus far, and their allowable values.

Figure 2.2 depicts the shape of subshells with l values of $0 - 2$, along with their various orientations in space, given by the available magnetic quantum numbers.

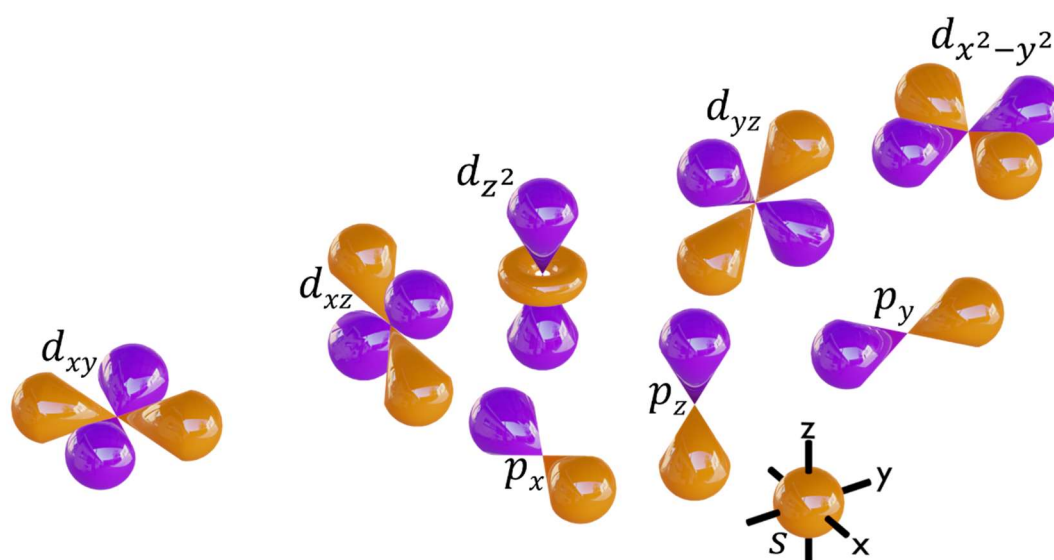


Figure 2.2: Representations of hydrogenic s, p, and d orbitals, along with their various orientations in space.

Hitherto, we have only focused on the hydrogenic atom, with a single electron. Of course, we must actually concern ourselves with polyelectronic atoms. This creates additional complications with respect to the orbital picture we have built up above, due to electron-electron interactions. In this instance, the Schrödinger equation becomes much too complex, certainly for our purposes. Therefore, we shall take advantage of the orbital approximation. Here, we omit electron-electron interactions, and instead treat each orbital as hydrogenic, but with the nuclear charge modified by all other electrons present.

With this caveat in place, we can proceed to discuss how additional electrons would occupy our atomic orbitals. We can first turn to the Pauli exclusion principle which states that no two fermions can occupy the same quantum state. This would suggest that each orbital, having been described as above by their 3 quantum numbers can only be occupied by a single electron. As it happens, there is one more quantum number we need to consider, that of the electron's intrinsic spin. This is termed the *spin magnetic quantum number*, m_s , and can take values of $\pm 1/2$. It follows therefore that there is room within each orbital for 2 electrons, provided they hold opposite intrinsic spin. Electrons occupy orbitals progressively from the lowest energy upwards, as per the *aufbauprinzip*, but also following Hund's rule that in degenerate orbitals electrons of the same spin magnetic quantum number fill first, this is depicted in **Figure 2.3**.

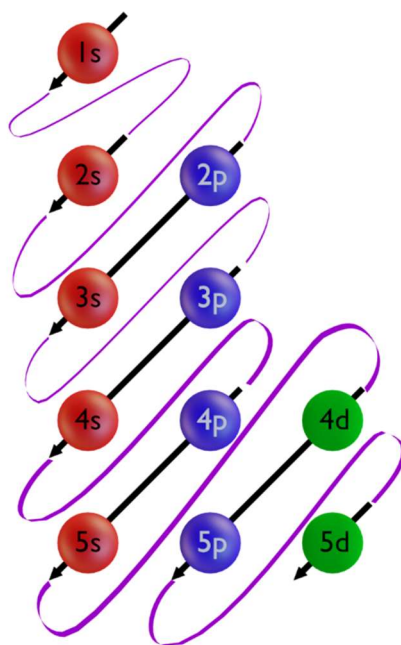


Figure 2.3: Representation of the order in which orbitals are filled with electrons as per the Aufbau principle and Hund's rule. Note, in actual fact, this representation is flawed and there are numerous exceptions above elements with $Z = 20$.

2.2.2 Molecular Orbitals & Band Structure

When two atoms are brought into close proximity, the potentials acting upon a single electron now comprise the two attractive nuclei-electron interactions and a single repulsive nuclear-nuclear interaction. The wavefunctions obtained by solving the Schrödinger equation for this system yields the two atom molecular orbitals. Here, the electron probability density is spread out over the whole of the molecule, rather than localised to a particular bond as per valence bond theory. With the addition of further atoms, the Schrödinger equation begins to get unwieldy. For such polyatomic systems, it instead becomes more practical to find the overall wavefunction *via* a superposition of the individual atomic orbitals.

$$\Psi_{\pm} = N_{\pm}(\Psi_A \pm \Psi_B) \quad \text{(Equation 2.10)}$$

Here, we can take the wavefunctions for each atom and add them using a linear combination of atomic orbitals as per **Equation 2.10**. Here, N is a normalisation factor and Ψ_A and Ψ_B are, in the case of the hydrogen molecule ion, the 1s orbitals for the two atoms A and B . $\Psi_{\pm}$ is positive when the wavefunctions are added together, and negative when the wavefunctions are subtracted.

$$\psi_+^2 \propto \psi_A^2 + \psi_B^2 + 2\Psi_A\Psi_B \quad \text{(Equation 2.11)}$$

$$\psi_-^2 \propto \psi_A^2 + \psi_B^2 - 2\Psi_A\Psi_B \quad \text{(Equation 2.12)}$$

When added together, the newly formed molecular orbital is considered a bonding orbital, with the bonding probability density shown in **Equation 2.11**. Here, the last term is the overlap density and takes a positive value. This suggests that the bonding orbital will exhibit increased electron density between the two nuclei. In this case, the newly formed molecular orbital takes a lower energy than the two atomic orbitals. When subtracted from each other, the newly formed orbital is considered an anti-bonding orbital, and the overlap density here is reduced (see **Equation 2.12**). The anti-bonding orbital takes a higher energy than the atomic orbitals.

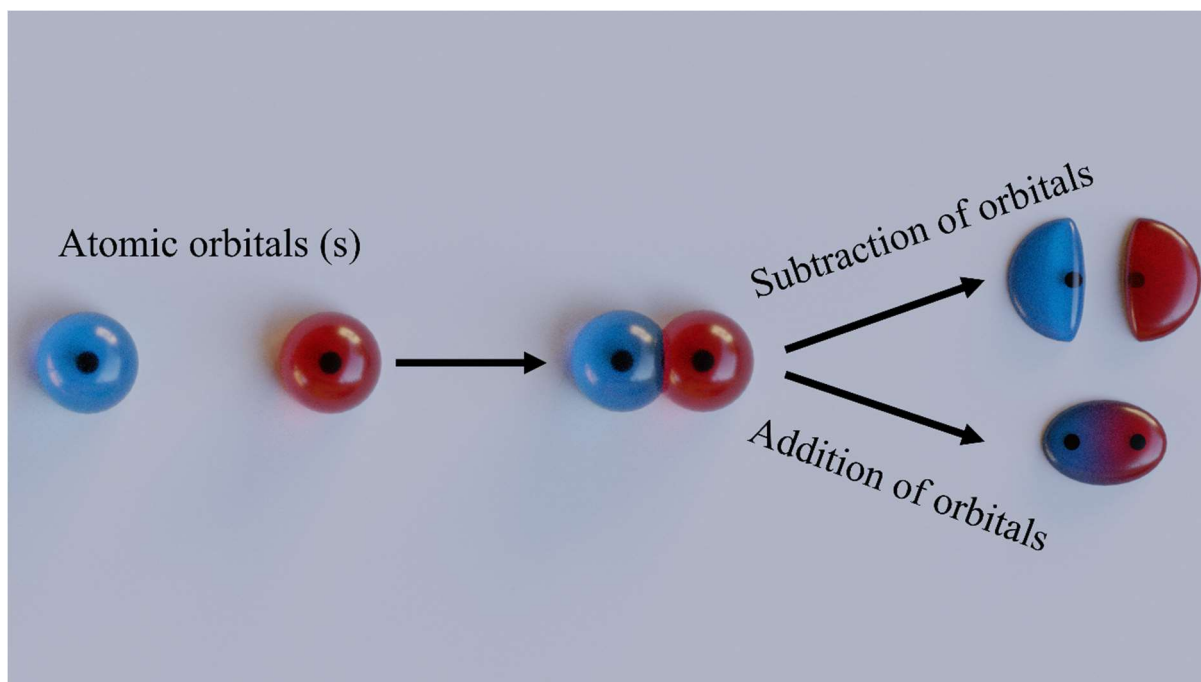


Figure 2.4: Depiction of hydrogen 1s atomic orbitals mixing to form bonding, via addition, and anti-bonding, via subtraction, molecular orbitals.

Figure 2.4 demonstrates how addition and subtraction of atomic orbitals yields bonding and anti-bonding orbitals. As can be seen, the anti-bonding orbital introduces an internuclear nodal plane perpendicular to the bond axis. Importantly, the total energy of the two molecular orbitals must be equal to the total energy of the two atomic orbitals which formed them, therefore there is a splitting in energy levels, resulting in the bonding orbital having a reduced energy and the anti-bonding orbital having a higher energy. This is illustrated in **Figure 2.5**.

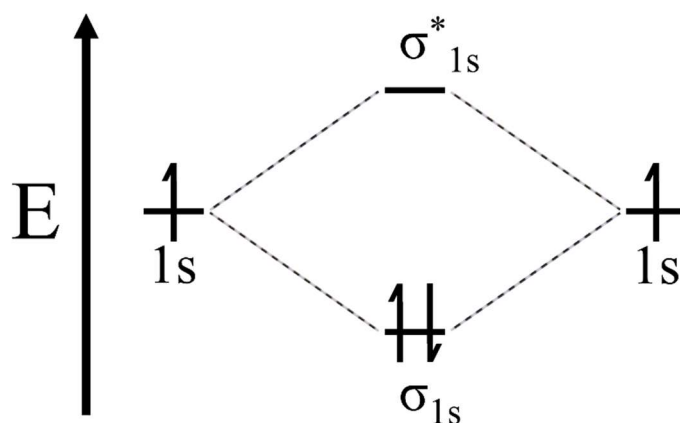


Figure 2.5: Formation of bonding and anti-bonding molecular orbitals formed by addition and subtraction of 1s orbitals in a hydrogen atom.

We have now treated a homonuclear diatomic molecular ion containing a single electron and found that there is an associated splitting between bonding and anti-bonding molecular orbitals. It is not

necessary for our purposes to inspect much deeper into this, although there are of course many complexities regarding, for example, the number of electrons, what valence orbitals are interacting with what other valence orbitals, atoms of different Z-number to name but a few. We are primarily interested in the idea of a crystalline material, and therefore we can attempt to consider what happens to the energy diagram as in **Figure 2.6** when we begin to add more and more atoms into proximity with each other.

What we can determine, is that as more atoms are brought into proximity, more energy level splitting occurs, and more states associated with bonding and anti-bonding are formed. Eventually, with enough states lying close enough to each other, the distinction between such states is blurred into a continuum. Here, we effectively have what can be termed bands, within which electrons may reside. Figure 2.6 demonstrates this idea, here the valence band is made up of the bonding orbitals associated with mixing of valence atomic orbitals, and the conduction band is that of the delocalised anti-bonding molecular orbitals associated with destructive interference of the same valence atomic orbitals.

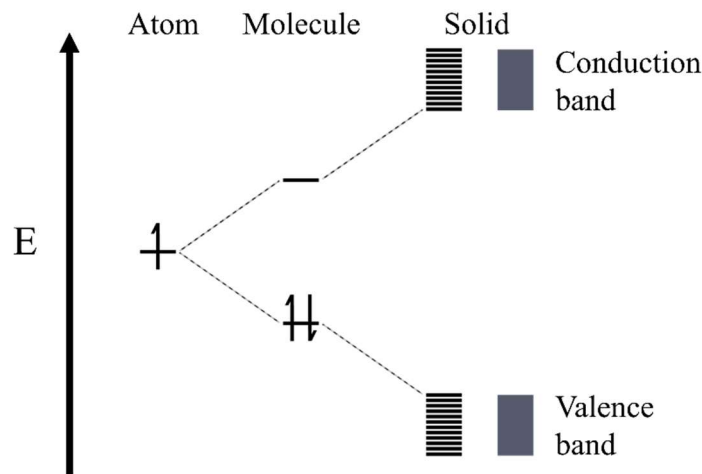


Figure 2.6: One representation of how bands form in semiconductors, here, as the number of atoms increases, atomic orbitals split into molecular orbitals. As more atoms are brought into proximity, eventually the number of split energy states merge into continuous bands.

We have discussed band formation with a focus on molecular orbitals; however it is important also to consider how bands might form from a solid state physics perspective in crystals. To begin, we consider the free electron model in 1D. Here, the energy of an electron is related to its momentum by **Equation 2.13**.

$$E = \frac{p^2}{2m_0} \quad (\text{Equation 2.13})$$

Here, $p = \hbar k$ and therefore Equation 2.13. can be rewritten as **Equation 2.14**.

$$E = \frac{\hbar^2 k^2}{2m_0} \quad (\text{Equation 2.14})$$

We can now plot E of the electron as a function of its wave vector, k , where we find a parabolic relationship. The wavefunctions for the free electron must satisfy the form shown in **Equation 2.15**, and are represented as travelling waves.

$$\Psi_k(r) = e^{ik \cdot r} \quad (\text{Equation 2.15})$$

Of course, in an actual 1D lattice we have a linear periodic array of atoms existing in real space, each holding a nuclear charge which perturbs the relationship in Equation 2.15. This is demonstrated in **Figure 2.7**.

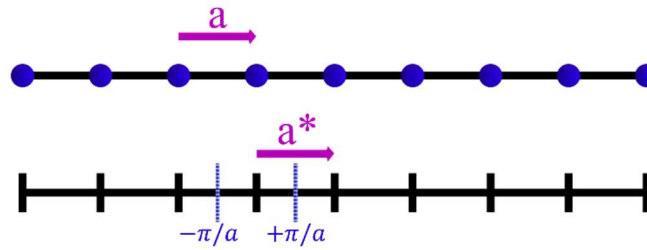


Figure 2.7: Schematic representation of, above, a 1D atomic lattice with nuclear potentials represented by blue spheres. Here, we find the primitive vector a , along which we can travel to an identical point in the lattice. Below, the reciprocal lattice in momentum space. Here, we have the primitive vector a^* , the point exactly midway along this vector is the edge of the Brillouin zone.

The linear array has an associated primitive vector a . Travelling from an atom along this vector brings us to a point in the lattice identical to where we started. In momentum space, we have the reciprocal lattice with an associated primitive vector a^* , defined as **Equation 2.16**.

$$a^* = \frac{2\pi}{a} \quad (\text{Equation 2.16})$$

We define the Brillouin zone as the area in reciprocal space between $-\pi/a$ and $+\pi/a$ as demonstrated in Figure 2.7. At $k = \pm\pi/a$, the wavefunction is travelling equally left and right, and the waves are Bragg reflected. As such, we have the formation of two standing waves at the edges of the Brillouin zones given by the **Equations 2.17**.

$$\begin{aligned} \psi(+) &= e^{i\pi x/a} + e^{-i\pi x/a} = 2 \cos(\pi x/a) \\ \psi(-) &= e^{i\pi x/a} - e^{-i\pi x/a} = 2i \sin(\pi x/a) \end{aligned} \quad (\text{Equations 2.17})$$

Here we can see the waves are out of phase, and therefore each wave has an electron probability density at different points relative to the position of the atomic nuclei. Here, Ψ_+ has the highest probability density of electrons at $0, a, 2a, \dots$ while Ψ_- has the highest probability density at $\pi/a, 2\pi/a, 3\pi/a, \dots$. This is the origin of the band gap, and means that at values of π/a , i.e. at the edge

of the Brillouin zone, relative to the travelling wave Ψ_+ has a lower potential energy, and Ψ_- has a higher potential energy.

We can treat this array as being infinite, and therefore we can consider an infinite periodic array of atomic potentials acting upon an electron. It therefore follows that the probability distribution $|\Psi|^2$ will also be periodic, and we assume this is so in accordance with the lattice periodicity. Bloch's theorem (**Equation 2.18**) allows for the creation of a Bloch wavefunction, which satisfies the Schrödinger equation for this set of boundary conditions.

$$\Psi_k(r) = u_k(r)e^{ik \cdot r} \quad \text{(Equation 2.18)}$$

Here, the wavefunction is made up of two separate parts, $u_k(r)$ describes the periodic potential, and $e^{ik \cdot r}$ is a plane wave delocalised across the crystal. **Figure 2.8** maps the bands onto the first Brillouin zone to give a band structure diagram. Here, the gap between the highest energy of a lower band and the lowest energy of a higher band is defined as the band gap, as states pertaining to these energies are forbidden. The highest occupied band is the valence band, and the lowest unoccupied band is the conduction band, delocalised across the whole crystal.

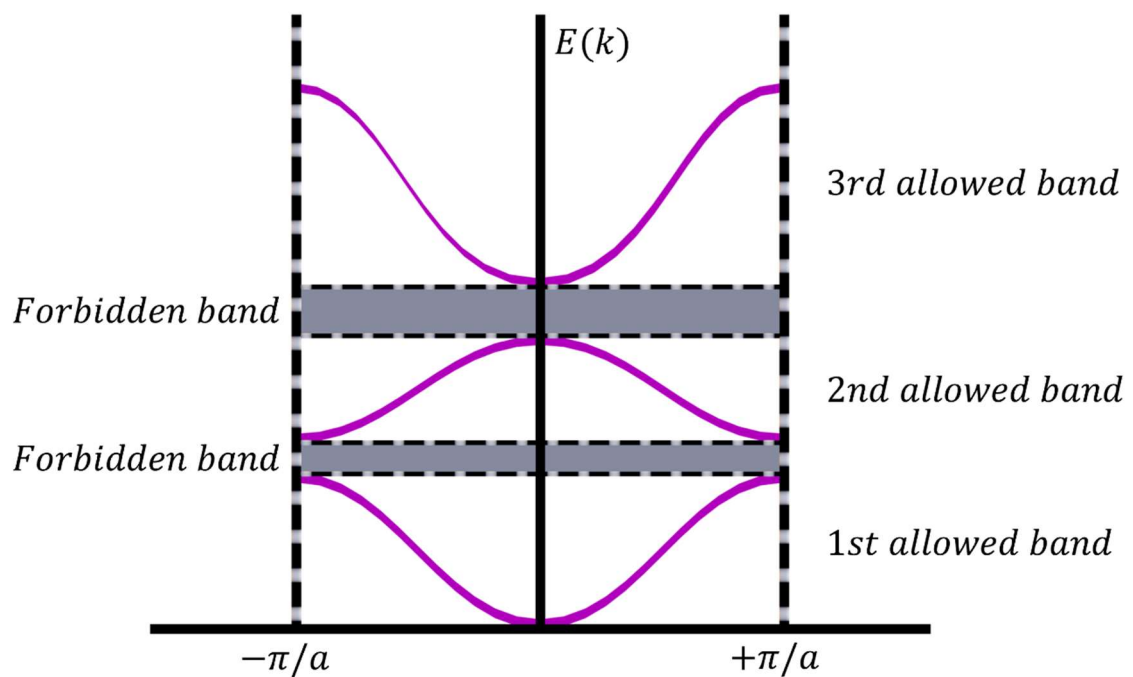


Figure 2.8: Reduced Brillouin zone demonstrating energy bands as a function of k and forbidden states, or band gaps.

2.2.3 Semiconductors

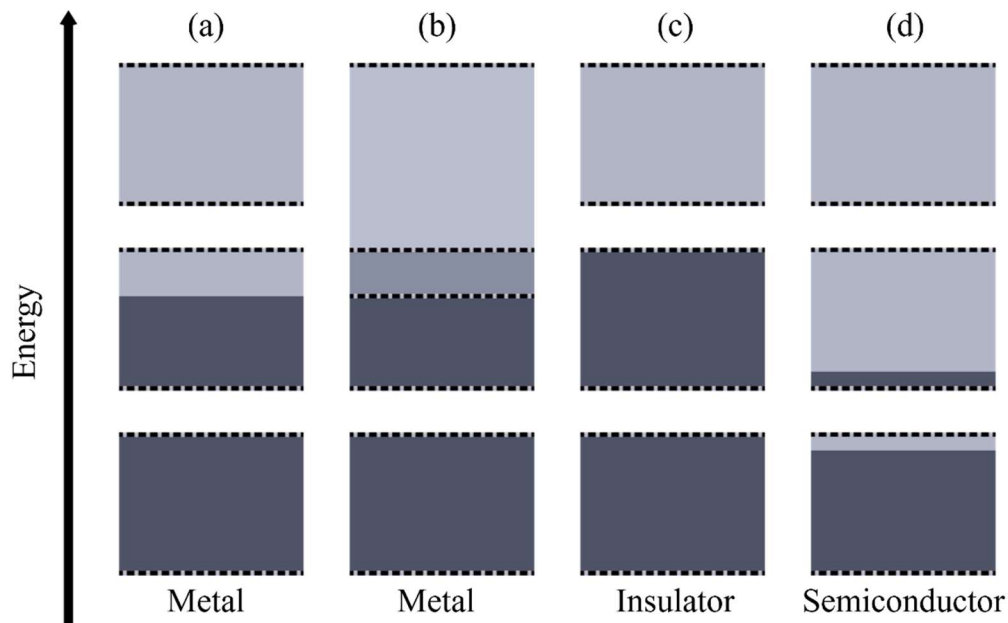


Figure 2.9: Schematic diagram of bands and filling of (a,b) metals, (c) insulators and (d) semiconductors. Here, dark grey is used to indicate the presence of electrons filling states within the bands, light grey represents unfilled states. In the case of (b), there is an overlap of valence and conduction bands, with electrons able to easily move between, represented by a middling grey colouration.

First, let us define the term “semiconductor”. If the valence band is partially unfilled, a current can flow through it *via* the movement of holes (**Figure 2.9a**). If the valence band and the conduction band overlap, then electrons in the valence band can easily hop into delocalised states and again, a current can flow (**Figure 2.9b**). Materials with either or both of these characteristics are considered metals. However, in the case where there is an appreciable gap between the valence and conduction bands, we find that a current can only flow if there are some electrons present in the conduction band. If the band gap is large, then electrons cannot be thermally excited into the conduction band, current cannot flow, and we have what is termed an insulator (**Figure 2.9c**). If, however, the band gap is small enough, then it is possible for electrons to occupy states in the conduction band due to thermal excitation, or indeed, photoexcitation, and we have what is termed a semiconductor (**Figure 2.9d**). Typically, materials exhibiting band gaps of 0.5 – 3 eV are considered semiconductors, those with band gaps less than 0.5 eV are considered semimetals, and those with band gaps above 3 eV are considered insulators. We are primarily interested in semiconductors because these present the potential for light-matter interactions, necessary for the PV effect.

The effect of light on a semiconductor increases its conductivity, and effect called photoconductivity, as free carriers are promoted into the conduction band under irradiation. This is useful, but does not generate power as the effect still requires an external bias to manifest.

We have referred to occupied and unoccupied orbitals or bands occasionally so far, and noted the valence and conduction bands. As described previously, due to the Aufbau and Pauli exclusion principles, electrons fill states with the lowest energy first. This gives rise to the idea of the Fermi energy level, E_f . In a neutral solid at 0 K states are filled progressively and completely until all electrons are accounted for, with the energy level of the highest filled state being equal to E_f . As temperature is increased, some electrons can be thermally excited into higher states, leaving behind holes. In this situation E_f is considered to be the energy at which there is a 50 % chance that an electron occupies that energetic state. This probability, $f(E)$, is related by the Fermi-Dirac distribution shown in **Equation 2.19**.

$$f(E) = \frac{1}{e^{(E-E_f)/k_B T} + 1} \quad \text{(Equation 2.19)}$$

Clearly, if $E = E_f$ then the exponential reduces to 1, and therefore $f(E)$ must be equal to 0.5. As per the ideas discussed above, the Fermi level in a metal is found within the valence band, however in semiconductors or insulators the Fermi level is found somewhere within the band gap.

In the previous section we were able to produce a band diagram as a function of wavevector, k , in 1D. Clearly, an actual semiconducting crystal would exist in 3D, and therefore if the crystal structure contained heteroatoms, or different lattice constants in different directions, the band gap properties would not be uniform in all dimensions. To demonstrate the band gap properties of a 3D crystal, it becomes useful to consider points of symmetry based on Brillouin zones for a given crystal structure. For example, in a face-centred-cubic (fcc) crystal, the Brillouin zone is identical to the Wigner-Seitz cell in a body-centred-cubic (bcc) crystal. Here, we can follow the wavevector from the origin, Γ , to the centre of a square face, X , to the vertex of the square and hexagonal face, W , to halfway along the line between hexagonal faces, K , or halfway along the line between hexagonal and square faces, U , then either back to Γ or to the midpoint of the hexagonal face, L , before returning back to Γ . These paths are demonstrated in **Figure 2.10a**, and a depiction of the band structure for a fcc structured lattice is given in **Figure 2.10b**.

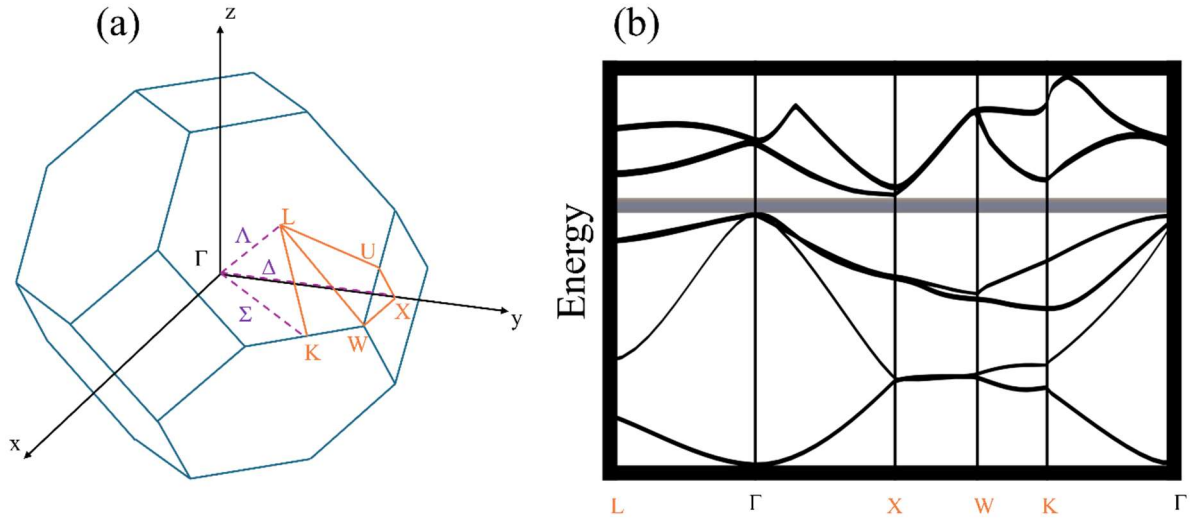


Figure 2.10: Schematic representations of (a) 3D Brillouin zone for a face-centred cubic lattice and (b) a stylised band diagram for a face-centred cubic semiconductor, here, the grey region represents the band gap made up of forbidden states, note the valence band maximum and conduction band minimum are separated in k -space, making this an indirect semiconductor.

We have already defined our band gap as the forbidden states between the valence band maximum and the conduction band minimum. However, while previously we found that these were aligned in k -space (Figure 2.8), in Figure 2.10b we do not find this to be the case. When these two points occur at the same value of k , then the band gap is considered direct, as electrons can be promoted across the band gap without any change in crystal momentum. If these two points do not share the same value of k , then the band gap is considered indirect, and for an electron to be promoted a certain amount of momentum must be supplied. This is important for solar PV, as photons carry a negligible amount of momentum, and therefore for absorption to occur in an indirect semiconductor, e.g. c-Si, momentum must be supplied by a lattice phonon. This means in comparison to thin-film technologies, indirect semiconductors used for PV must be considerably thicker, increasing their weight and therefore reducing specific power.

2.3 Photovoltaic Device Theory

First observed by Edmund Bequerel in 1839,⁴ the photovoltaic effect can be defined as the conversion of electromagnetic energy into electrical energy *via* the absorption of a photon and subsequent production of an electron-hole pair dissociated under an asymmetric electric field. The extraction of excited electrons produces a potential difference equal to their additional energy, which can then drive an external circuit. The key point of difference here, vis previous discussion on photoconductivity, being the presence of an inbuilt asymmetry providing the spontaneous generation of a current under illumination.

Bequerel made his observations using silver-plated platinum electrodes immersed in an electrolyte solution, forming a photoelectrochemical cell not dissimilar to a modern Grätzel cell operationally. Solid-state photovoltaics were first attested to by William Adams and Richard Day in 1876 while working on the photoconductivity of selenium, furthered in 1894 by Charles Fritts. These devices were based on metal-semiconductor rectifying junctions. The first semiconductor-semiconductor, or p-n, junction devices were produced at Bell labs in 1954 with such devices famously used for extraterrestrial purposes in the subsequent decade. In this section we will discuss the mechanisms at work in a p-i-n junction photovoltaic device, starting with a discussion of the solar source and ending with a brief overview of the operating principle of a PV device.

2.3.1 Helios

Light reaching the Earth comes from a well-known source which we call the Sun, and it bears close resemblance to the spectrum of a black body at 5,778 K. In addition to spectral characteristics the irradiance, or power per unit area, is important to note. Outside the Earth's atmosphere this is around $1,350 \text{ W m}^{-2}$ and is defined as the solar constant.

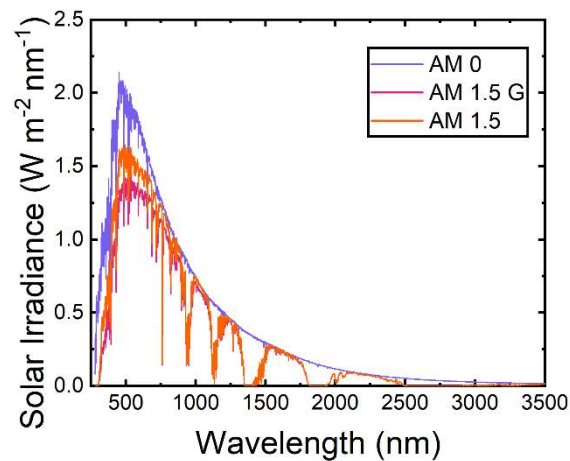


Figure 2.11: Solar spectrum at the surface of the atmosphere, AM 0, and at the surface of the earth, demonstrating overall attenuation and sharp absorption bands related to various atmospheric components.

The sunlight falling upon the Earth's crust is not the same as that falling upon its atmosphere. The atmosphere itself attenuates irradiance at any given point in the spectrum, particularly where certain components strongly absorb. This gives rise to the concept of air mass (AM) which is essentially the amount of atmosphere the light must travel through to reach the surface. Rays falling perpendicular to the surface travel the shortest distance through the atmosphere, defined as AM 1.0, reducing total solar irradiance to around 1000 W m^{-2} . Ozone, O_2 , water vapour and CO_2 are responsible for strong absorption bands in the spectrum. Rayleigh scattering is responsible

for attenuation across higher wavelengths, giving rise to the blue colour of the sky, and the yellow colour of the Sun as viewed from the terrestrial surface.⁵ Mie scattering across all wavelengths due to particulate matter contributes to total attenuation and gives rise to the white colour of clouds.⁶

For rays to fall perpendicular to the crust, depending on the time of year the location must be somewhere in the tropics. However, due to the historical prevalence of PV research conducted in mid latitude regions (e.g. Murray Hill, Bell Labs, has a latitude of 40.7 °N), and the need to standardise a solar spectrum for testing purposes, an AM 1.5 spectrum was settled upon. Here, the air mass corresponds to a solar zenith angle of 48.2 °, or solar elevation angle of 41.8 °. At the Earth's surface, the average intensity of the AM 1.5 spectrum is found to be 900 W m⁻², however, if measured on a panel tilted towards the sun at 37 ° (the average latitude of the contiguous United States) this increases to 1000 W m⁻². This spectrum is given the designation AM 1.5 G and this spectrum and intensity is the global standard for PV testing (strictly speaking, we use an AM 1.5 spectrum, with the intensity boosted to 1000 W m⁻²). A comparison of AM 0, AM 1.0 and AM 1.5 G is given in **Figure 2.11**. Here, the sharp absorption bands relating to the atmospheric components mentioned above are apparent in both the AM 1.0 and AM 1.5 G spectra.

2.3.2 Absorption & The Detailed Balance Limit

PV devices take the energy of a photon, and transfer it to an electron allowing it to cross the band gap of the semiconductor and enter the conduction band. The energy of a photon is given by **Equation 2.20** where h is Planck's constant, c is the speed of light in a vacuum, λ is the wavelength of the photon and ν is its frequency. Provided the energy of the photon is greater than or equal to the band gap energy, the photon can couple to an electron in the valence band, transfer its energy to the electron, and allow the electron to jump into the conduction band. If the energy of the photon is insufficient to do this, the photon is simply not absorbed by the semiconductor.

$$E = \frac{hc}{\lambda} = h\nu \quad \text{(Equation 2.20)}$$

A semiconducting material with a negligible band gap will therefore absorb nearly all photons incident upon it. However, while this is the case, the only energy which can be extracted from said photons will be proportional to the energy of the band gap. Conversely, if one used a wider band gap material, many photons would simply pass through the material such that only very few, albeit high energy, photons will be captured. Clearly, then, there is a balance which needs to be struck regarding the ideal band gap for a PV semiconductor, and this is intrinsically related to the spectral characteristics of the incident electromagnetic radiation. This concept is known as the detailed balance limit.

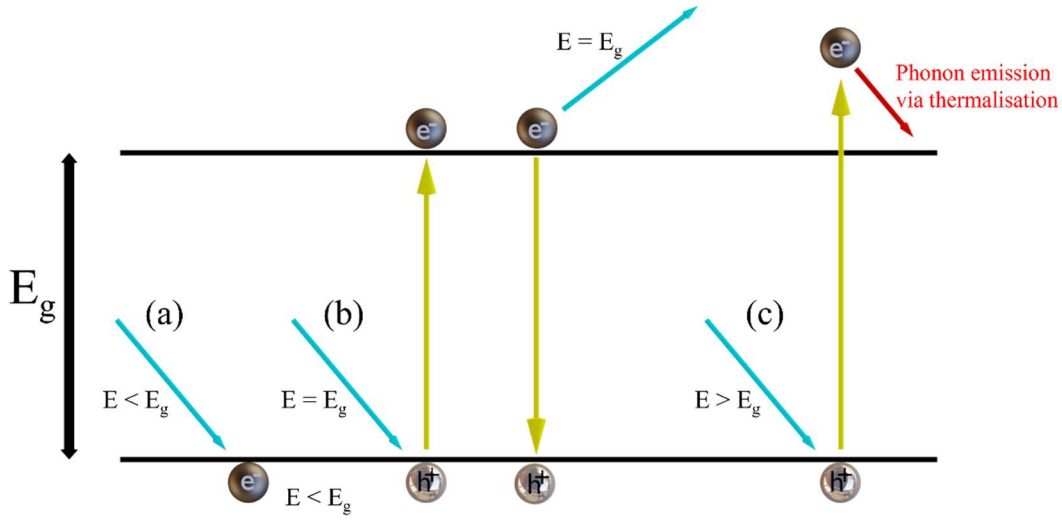


Figure 2.12: Schematic representation of possible absorption events, (a) energy of the incident photon is insufficient to excite an electron across the band gap and is not absorbed, (b) energy of the photon is equal to the band gap and an electron is excited into the conduction band. If not extracted, eventually the electron may radiatively recombine with a hole in the conduction band and emit a photon of the same energy as the band gap, (c) a photon carrying energy above the band gap excites an electron above the conduction band, where it rapidly thermalises down to the conduction band minimum, an analogous process can occur with holes.

There are three considerations at play here. First, the concept of thermalisation, whereupon photons of $E > E_g$ are absorbed (**Figure 2.12c**), but rapidly lose energy in the form of heat until they reach the conduction band minimum edge. Secondly, losses from transparency towards photons whose $E < E_g$, whereupon no energy is captured (**Figure 2.12a**). Thirdly, intrinsic radiative recombination losses due to electron hole annihilation prior to extraction (**Figure 2.12b**).

When the above is taken into account, it becomes possible to chart the maximum theoretical efficiency limits for the AM 1.5 G spectrum as a function of band gap, where we find the theoretical most efficient band gap to be between 1.3 – 1.5 eV, as depicted in **Figure 2.13**.

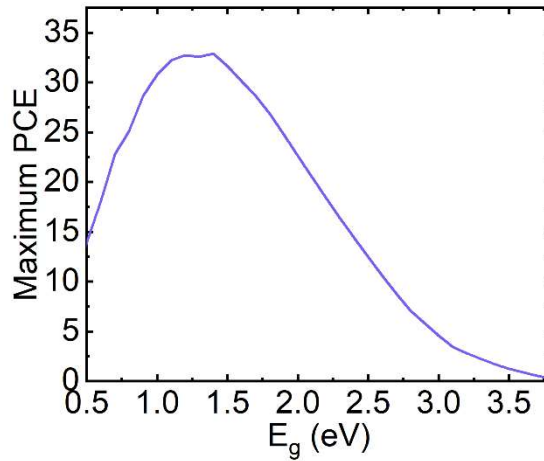


Figure 2.13: Representation of the radiative efficiency limit of a semiconductor as a function of band gap under AM 1.5 G solar spectrum.

2.3.3 Recombination

There are three mechanisms for electron hole annihilation, or recombination. First is the aforementioned radiative recombination, then there is trap-assisted recombination, and finally there is Auger recombination.

Radiative recombination can be considered as the opposite of absorption. Here, as opposed to the promotion of an electron to the conduction band and formation of a hole in the valence band due to absorption of a photon, the excited state electron recombines with a hole in the valence band resulting in the emission of a photon, the energy of which is equal to the band gap. It is possible that this photon will be reabsorbed, however it might also be lost if emitted near the surface of the semiconductor. This process is shown in Figure 2.12 in the previous section. Radiative recombination is the dominant form of recombination for direct semiconductors.

Trap-assisted recombination occurs where so called trap states are present, and is non-radiative. These traps can be formed due to defects in the lattice, or the presence of impurities. They are particularly prevalent at interfaces, where managing them often requires passivation techniques. Here, the trap states are electronic states which exist within the band gap. Either holes or electrons can be trapped and re-emitted. However, it is also possible that an electron or hole could become trapped, and then in a second step move into an empty valence or conduction band state respectively. This is presented schematically in **Figure 2.14a**. Trap assisted recombination is the dominant recombination mechanism for indirect semiconductors, as the impurities can cushion differences in momentum between the two carriers.

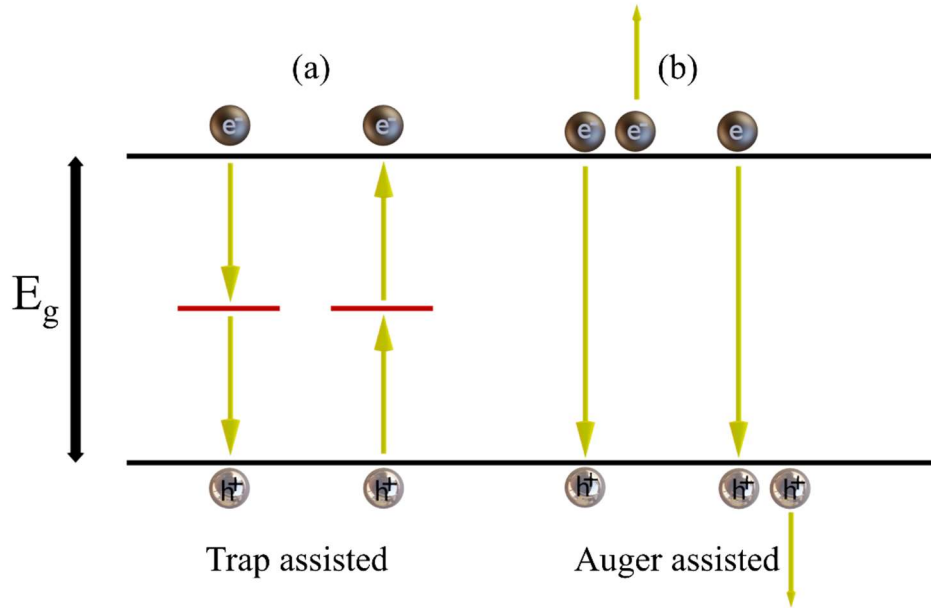


Figure 2.14: Schematic representation of non-radiative recombination events, (a) monomolecular trap assisted recombination and (b) trimolecular Auger recombination.

Auger recombination occurs when an electron in the conduction band recombines with a hole in the valence band, but instead of photon emission, instead the energy is transferred to a neighbouring electron in the conduction band. This promotes the second electron to some energetic state, usually within the conduction band, where it then undergoes thermalisation to release the energy in the form of lattice phonons. This is shown in **Figure 2.14b**. The process can also occur for two neighbouring holes in the valence band and a single electron in the conduction band. Auger recombination only typically becomes dominant at high carrier concentrations, for example, in heavily doped c-Si. For further discussion on doping of semiconductors, and the operating principles of p-n junctions, please see Appendix A.

2.3.4 Operation of Perovskite Solar Cells, and Quasi-Fermi Level Splitting

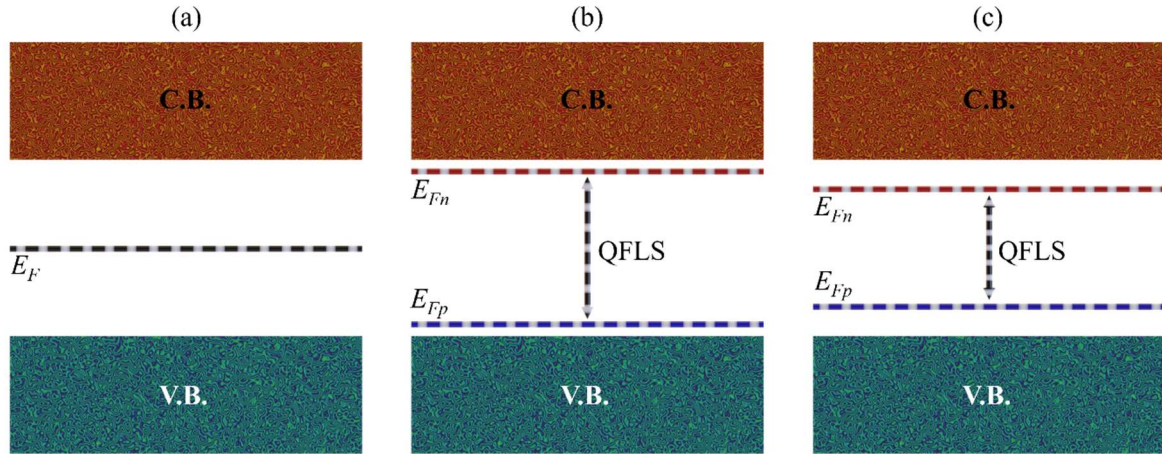


Figure 2.15: Schematic representation of a direct semiconductor held at V_{OC} , (a) at thermal equilibrium where the Fermi level is centred within the band gap, (b) under illumination, whereby electrons and holes experience their own quasi-Fermi levels, and the quasi-Fermi level splitting (QFLS) defines the maximum open circuit voltage, and (c) the same as part (b) but with a lower radiative efficiency, reducing maximum QFLS.

In perovskite solar cells, the absorber layer is an intrinsic semiconductor, i.e. not doped. We will first discuss the intrinsic semiconductor held at V_{OC} (or, for example, the semiconductor *sans* device stack) such that any generated charge carriers cannot be extracted. When the semiconductor is in the dark and held at thermal equilibrium the Fermi level will sit in the middle of the band gap, as discussed previously. In addition, *via* the principle of detailed balance, a semiconductor in thermal equilibrium must necessarily have an equal rate of emission and absorption.

Under illumination, the semiconductor now absorbs additional incident radiation, however as per detailed balance must continue to emit an equal amount of energy to that which it absorbs (recall, in our scenario no charges are being extracted to do useful work). The semiconductor does this *via* thermalisation of energy from photons with $E > E_G$, radiative recombination and non-radiative recombination (also generating heat). Of the non-radiative recombination mechanisms, Auger recombination is not of particular concern to us as the perovskite layer is undoped and this regime is unlikely to be entered into (outside of solar concentrating optics). Unfortunately, however, we must consider the presence of non-radiative trap mediated recombination centres, which serve to reduce the radiative efficiency (i.e. the ratio of emitted photons to those absorbed) of the semiconductor. It is within the device engineer's gift to reduce the number of traps *via* good device engineering and *via* the inclusion of defect passivating treatments, however the rate of unavoidable

radiative recombination is largely material and charge carrier density dependent, and thus outside the hands of the device engineer.

We can imagine that under illumination, with charges not extracted, the generation of electrons and holes can give rise to the concept of conduction band and valence band Fermi levels. Indeed, as the system is not exactly at “equilibrium” we call these *quasi*-Fermi levels and typically refer to them as electron or hole *quasi*-Fermi levels. Here, the idea is that as electrons are excited into the conduction band, they rapidly thermalise down to the band edge at a rate much faster than that of recombination, thus creating a *quasi*-steady-state picture we can use (an analogous process occurring with holes). We can then describe electrons and holes as having separate *quasi*-Fermi levels. The splitting between the two, is termed the *quasi*-Fermi level splitting (QFLS). The degree of QFLS of photogenerated charge carriers governs the total electromotive force that can be extracted by the solar cell and therefore governs maximum V_{OC} . In turn, the maximum QFLS is governed by the inevitable radiative recombination rate, with the splitting increasing with illumination intensity until this rate equals that of charge carrier generation. This concept is demonstrated in **Figure 2.15a,b**. Further, the effect of non-radiative recombination serves to reduce the QFLS, thus limiting the maximum achievable V_{OC} and this is demonstrated in **Figure 2.15c**.

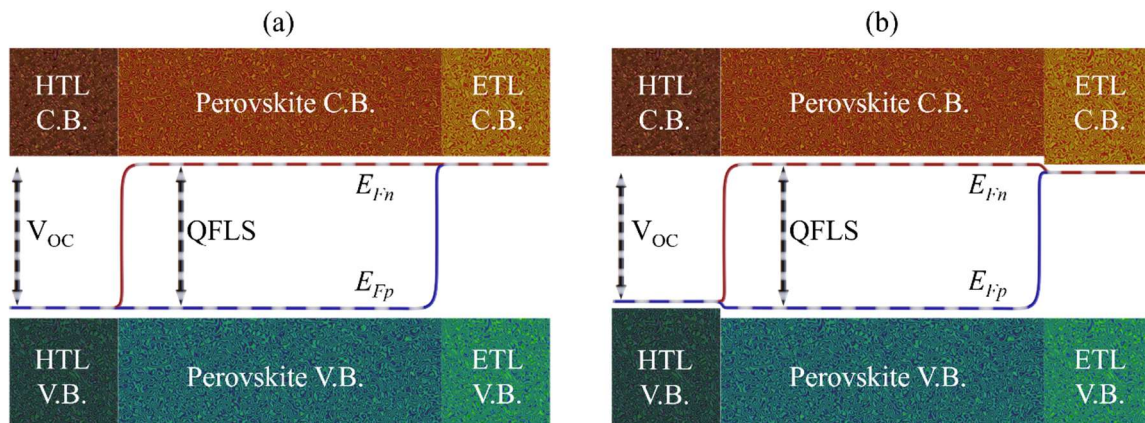


Figure 2.16: Schematic representation of a perovskite device with (a) perfect interfaces between perovskite layer and charge transport layers, note here, the V_{OC} is identical to the QFLS, (b) where imperfect, or lossy, interfaces result in the V_{OC} being diminished in comparison to the QFLS.

Finally, we must consider what all this means when the perovskite layer is incorporated into a device stack. Here, the device is considered a p-i-n junction, and mechanistically operates differently to a more conventional p-n junction. Under illumination the electron and hole *quasi*-Fermi levels split according to the degree of radiative and non-radiative recombination within the

perovskite, and charges can be extracted when the device is operating at its maximum power point. Assuming a perfectly lossless interface between the CTLs, the QFLS is maintained all the way through to the external circuit, and the device experiences no further losses in V_{OC} . However, such interfaces are notorious for having significant non-radiative recombination centres. As such, the device engineer might employ surface passivating techniques, or otherwise try to engineer superior contact between the perovskite layer and the transport layer in question. In the event that there is a “lossy” interface, this further reduces the QFLS and therefore reduces the attainable V_{OC} of the device. This is depicted in **Figure 2.16**. The final step is extraction of the carriers, which occurs due to the electric field across the absorber layer created by p- and n-type charge transport layers. These must be energetically aligned to minimise losses by maintaining the quasi-Fermi levels of the selected carriers.⁷

2.3.5 The Equivalent Circuit

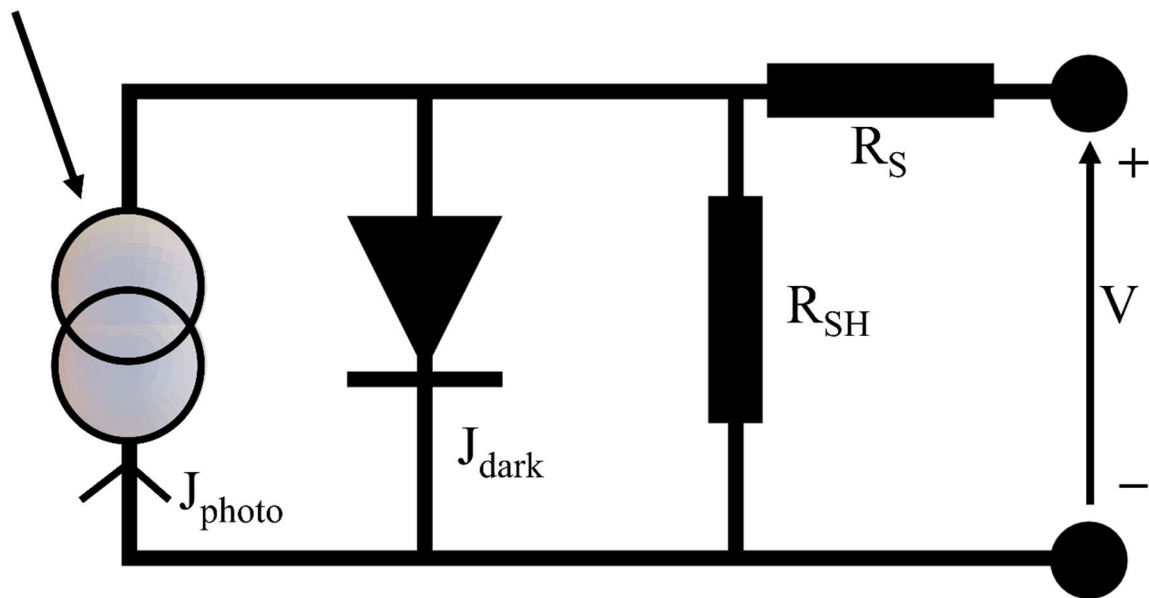


Figure 2.17: Schematic representation for the equivalent circuit of a solar cell. Here, a current source is in parallel with a diode.

Figure 2.17 demonstrates a useful concept for the modelling of a solar cell. Here, we have what is termed the equivalent circuit. Due to the built in field, the solar cell behaves akin to a diode, but can at the same time be considered as an ideal current generator. Therefore, we can model the solar cell as a current generator in parallel with a diode. The equivalent circuit can be described using the following equation.

$$J = J_{SC} - J_0 \left(e^{\frac{q(V+JAR_S)}{nk_bT}} - 1 \right) - \frac{V+JAR_S}{R_{SH}} \quad \text{(Equation 2.21)}$$

Here, J_{SC} is the short circuit photocurrent density, J_0 is the dark saturation current density, q is the fundamental charge, V is the bias voltage, J is the current density, A is the area of the cell, n is the diode ideality factor ranging between 1 – 2, k_b is Boltzmann's constant, T is the operating temperature, R_S is the series resistance and R_{SH} is the shunt resistance.

The photocurrent generated will, at short circuit, flow entirely through the load, however it will have no appreciable power as there will be no voltage across the load. Consequently, if the resistance of the load is increased, a greater potential difference will manifest across it. Clearly, a balance must be struck to maximise current and voltage to generate the most power. At some point, the voltage across the load will switch on the diode, and current will begin to decrease through the load, instead now being directed through the diode. Eventually, a voltage will be reached where the dark current is matched by the photocurrent, and no current will flow, this is termed the open circuit voltage (V_{OC}).

We can also use the equivalent circuit to model the ideas of series, and shunt resistances. These are theoretically extrinsic loss mechanisms, but are in reality always present. Here, a low shunt resistance results in current leakage, and manifests as a linear loss of photocurrent immediately as the load is increased, as the current bypasses the diode and runs contrary to the photocurrent, depleting it. The series resistance derives simply from increased resistance from all materials within the circuit. This includes bulk, and/or sheet, resistance of materials/electrodes in the stack, non-radiative recombination at interfaces, charge build up, and associated resistances in the measurement system. High series resistance acts to reduce the voltage at which the photocurrent begins to diminish as the load is increased.

2.3.6 Solar Cell Testing

As discussed previously, for testing solar cells we use a simulated AM 1.5 solar spectrum, with a calibrated intensity of 100 mW cm^{-2} (P_{in}). To simulate the load across a variety of resistances, we can simply vary the voltage across the device. This generates a current density versus voltage (JV) curve from which we can extract certain key parameters. Current density, J , is used instead of current, I , to account for the area of the device.

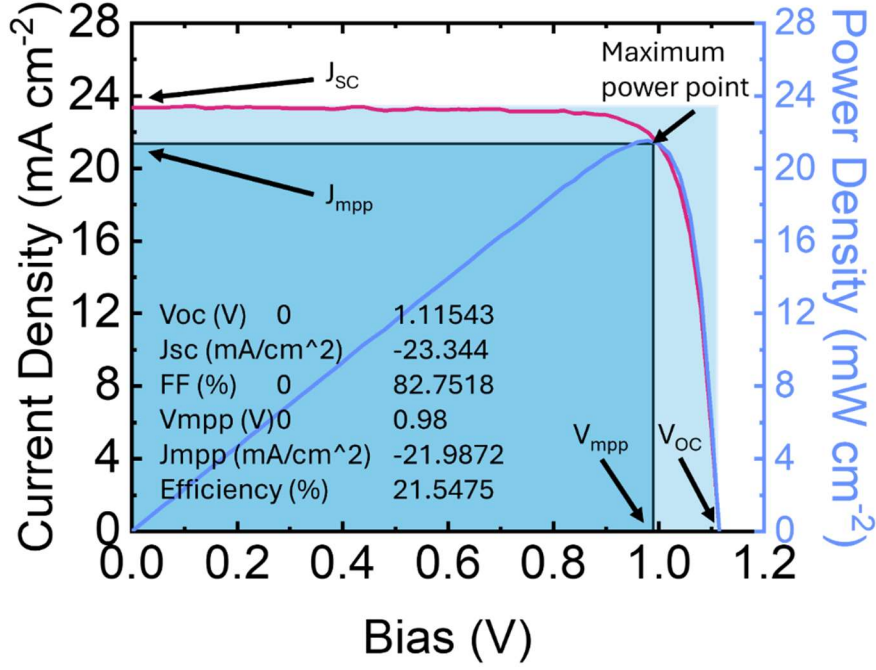


Figure 2.18: Current density vs Voltage characteristics of a solar cell.

In **Figure 2.18** data are presented for a spray coated perovskite solar cell which has been tested as per the above description.

The blue line represents the JV characteristic of the device. The J_{sc} is the maximum current density and is found at a bias voltage of 0 V, here there is no power generated. As the bias voltage is increased (analogous to an increasing resistance across a load), the photocurrent density initially remains level, however around 0.7 V this begins to reduce, as the dark current begins to manifest. There follows the expected exponential behaviour predicted by the diode equation as the photocurrent rapidly begins to diminish and travel towards 0 mA cm⁻². At this point, the device is at V_{oc} and the photocurrent and dark current are matched. Here, there is no longer power generated by the PV cell.

The purple line represents power density in units of mW cm⁻² as a function of applied bias, and illustrates the above. This is simply J multiplied by V , and climbs linearly as the voltage increases without significant drop in photocurrent density. However, as the photocurrent density begins to fall, there comes a point, the *maximum power point* (P_{out}), where the power curve must begin to trend down. Associated with the maximum power point is a maximum power point voltage (V_{mpp}) and maximum power point current density (J_{mpp}).

Efficiency of the solar cell can be defined in **Equation 2.22**. Here, η is the power conversion efficiency (PCE), with P_{out} the maximum power supplied by the solar cell under illumination and

P_{in} incident power density of the simulated solar spectrum. As P_{out} is equal to J_{mpp} multiplied by V_{mpp} , we can rewrite this equation as **Equation 2.23**.

$$\eta = \frac{P_{out}}{P_{in}} \quad (\text{Equation 2.22})$$

$$\eta = \frac{J_{mpp}V_{mpp}}{P_{in}} \quad (\text{Equation 2.23})$$

In Figure 2.20 are two shaded rectilinear boxes, the larger of the two represents the intersection of J_{sc} and V_{oc} . The smaller box of the two represents the intersection of J_{mpp} and V_{mpp} . Here, the ratio of the area of the smaller box to area of the larger box gives rise to the concept of fill factor (FF) and can be described as the “squareness” of the JV curve. FF is related to the quality of the device vis parasitic losses as discussed in the previous section. We can write this relationship as **Equation 2.24** and substitute it into Equation 2.23 to yield **Equation 2.25**.

$$FF = \frac{J_{mpp}V_{mpp}}{J_{sc}V_{oc}} \quad (\text{Equation 2.24})$$

$$\eta = \frac{J_{sc}V_{oc}FF}{P_{in}} \quad (\text{Equation 2.25})$$

Here, we find that the PCE is made up of 3 key performance metrics, short circuit current density, open circuit voltage, and fill factor. It becomes the device engineer’s task to optimise these as best as possible.

2.4 Perovskite Solar Cells, Spray Coating, Wacky Substrates, High Specific power, and Non Developable Electronics; A Review

2.4.1 An Introduction to Perovskites

Gustav Rose is credited with the 19th century discovery of the perovskite crystal structure (of the form ABX_3) from samples sourced in the Ural Mountains, naming them for the contemporary statesman and mineralogist Count Lev Perovski,⁸ but it wasn’t until Goldschmidt in the 1920s and subsequently Moller in the 1950s that they were studied in more detail.^{9,10} The first perovskites as characterised by Rose were made up of $CaTiO_3$ and for decades research into perovskites was based primarily on inorganic metal oxides. Over the years, driven by the electro-ceramics industry, many different perovskites have been studied for their ferroelectric,¹¹ piezoelectric,¹² dielectric,¹³ and pyroelectric¹⁴ properties. Some compositions demonstrated limited semiconducting properties, including even the PV effect, here as a result of ferroelectric polarisation.¹⁵ The wide variety of different perovskites, indeed this crystal structure makes up the majority of all mineral structures found in the Earth’s crust, and their various applications makes it necessary to

distinguish the type of perovskite being discussed at any one time. For PV purposes, the most interesting are those known as organic-inorganic metal halide perovskites.

Organic-inorganic lead halide perovskites have been the focus of intense interest in the PV community for their exceptional optoelectronic properties, including but not limited to their strong solar absorption coefficient¹⁶ derived from an intrinsic band gap,¹⁷ low exciton binding energies,¹⁸ long charge carrier diffusion lengths,¹⁹ and associated high carrier mobilities.²⁰ Significantly, they are low temperature solution processable,²¹ and their ease of fabrication has considerably aided research efforts.²² A unique combination of low energy fabrication techniques and the high efficiencies demonstrated creates a technology with potential for very low energy payback times.²³ Prior experience within the thin film PV community in dye sensitised solar cells (DSSCs) and organic solar cells (OPVs) have largely contributed to the realisation of certified PCEs within a decade and a half of up to 27.2 %.²⁴

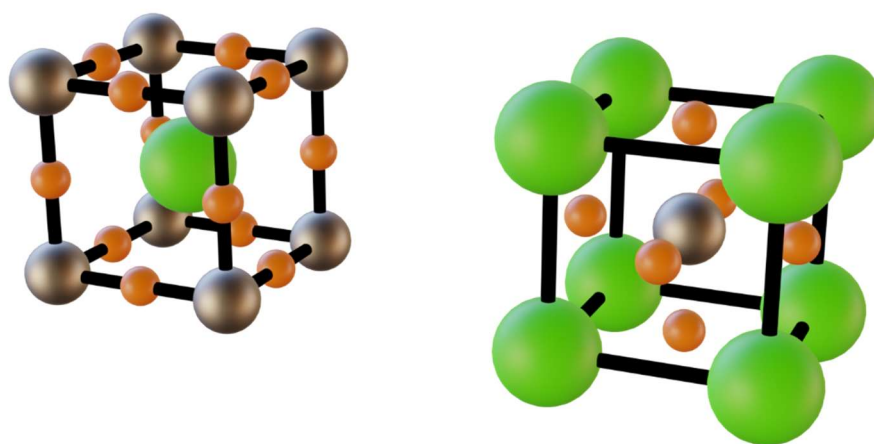


Figure 2.19: Ball and stick representations of the ideal cubic perovskite crystal structure. Here, the large green spheres represent the monovalent A-site cation, the silver spheres represent the divalent B-site cation and the small orange spheres represent monovalent X-site anions.

Organic-inorganic metal halide perovskites are made up of a monovalent organic or inorganic cation, typically methylammonium (MA), formamidinium (FA), ethylammonium, caesium, or even rubidium situated in the A position. In instances where this cation is organic, the resultant perovskite is termed hybrid, or organic-inorganic, whereas when the cation is a metal they are simply considered inorganic. The B position consists of a smaller, divalent, cation, typically Pb although Sn has also found use. The X anion is a halide, with iodide, bromide and chloride all possible such ions. The ideal perovskite crystal structure (see **Figure 2.19**) is made up by corner octahedra of BX_6 , arranged around the A site cation, and adopts a cubic symmetry. The unit cell

can also be considered as having A cations at the corner position, with X anions at each face and the B cation body centred.²⁵

The Goldschmidt tolerance factor, t , is a useful means to predict the phase stability of a perovskite. Here, the ratio in a solid sphere model of the distances between the A and X site ions, along with the ratio between the B and X site ions as per **Equation 2.26**, where R is the ionic radii of the subscript indicated ion gives a value for t .¹⁰ As can be inferred from the equation, this tolerance factor increases as the A site cation increases in size, and decreases as the B site cation increases in size.

$$t = \frac{R_A + R_X}{\sqrt{2(R_B + R_X)}} \quad \text{(Equation 2.26)}$$

Cubic symmetry perovskite structures are typically formed between tolerance factors of 0.9 – 1.0. Between 0.76 and 0.9 orthorhombic structures occur due to distortion and tilting of the BX_6 octahedra.^{25,26} Further decreasing the tolerance factor yields even lower symmetries such as trigonal (*ilmenite*) phases.²⁶ Conversely, tolerance factors greater than 1.0 typically yield hexagonal photoinactive perovskite phases.²⁶ As hybrid perovskites often contain organic A site cations, their non spherical nature demands modifications to the tolerance factor, as expounded by Kieslich et al.²⁷ Heavier halides such as iodide demonstrate increased covalent character in metal halide bonds, reducing the validity of the solid sphere argument in such cases.²⁸ For this reason, the tolerance factor becomes less useful when considering hybrid halide perovskites, with its ability to predict cubic phases accurately in only 74 % in a total of 576 cases.²⁹

Within the relative confines of the tolerance factor, any combination of A site, B site and X site ions can be used to make up the perovskite structure. This is particularly important to improve phase stability and to tune the band gap. The band gap is related to both the crystal structure and the electronic structure of the perovskite. DFT studies on $MAPbI_3$ and $MAPbBr_3$ have indicated that the top of the valence band is predominantly composed of iodine 5p (bromine 4p) with minor contributions from lead 6p and 6s states, whereas the bottom of the conduction band is composed mainly of lead 6p with some contributions from iodine 5p (bromine 4p) states.³⁰ Thus, the nature of the divalent metal, the halides, and their proportions if mixed, can be used to control the band gap *via* manipulation of electronic structure. The halides, in particular, are thought to significantly impact on the electronic structure due to the degree to which they provide shielding. As the halide ionic radius reduces from iodide to bromide, there is a reduction in shielding, leading to shorter, stronger, more ionic bonds, thus increasing the band gap.³¹

The monovalent cation was not found to significantly contribute to states surrounding the band gap, however in other studies changes in band gap as a function of the A site cation have been observed. This is likely due to changes in the lattice structure. For example, changing from the relatively bulky FA to the smaller MA increases the band gap due to lattice contraction, and an increase in BX₆ octahedra tilt.^{32,33}

2.4.2 *Advances in Perovskites*

Metal halide perovskites were first reported by Wells in the 1890s,³⁴ but surprisingly, the first reports of hybrid organic inorganic perovskites predate Wells, with reports from Topsøe as early as 1884.³⁵ However, interest in such materials was not revived until 1978 when Weber conducted a series of crystallographic studies into them.³⁶ These hybrid perovskites demonstrated significant structural tunability, with the incorporation of bulky A site cations allowing for the formation of 2D perovskites. Such 2D materials were investigated at IBM by Mitzi et al and demonstrated potential for use in transistors and LEDs.^{37,38} The poor stability of tin based perovskites and a disinclination to work with toxic lead slowed this research, although even at this stage it was proposed that such materials might be useful for PV applications.^{22,38}

It wasn't until 2009, when Kojima et al fabricated a lead containing hybrid perovskite using a traditional DSSC structure, demonstrating a PCE of 3.8 % that interest was revived. Here, the device was made up of a thick mesoporous n-type TiO₂ scaffold layer of around 8-12 μm which was then infiltrated with MAPbI₃ perovskite solution, before being completed with a lithium halide/halogen redox couple acting as a hole transport layer (HTL).³⁹ Unfortunately, the device rapidly deteriorated due to the liquid electrolyte dissolving the perovskite sensitizer material. A few years later, in 2012, Lee et al and Kim et al separately overcame this issue by incorporating a solid state HTL, yielding PCEs of 10.9 % and 9.7 % respectively.^{40,41} Lee et al demonstrated devices made from a mixed halide perovskite, MAPbI₂Cl, illustrating compositional tuneability even at this early stage, employed here to improve stability in air. Significantly, Lee et al also demonstrated the use of an inert Al₂O₃ scaffold, demonstrating the perovskite was effective at both separating charge and transporting electrons, indeed more so than the typically employed TiO₂ scaffold.⁴⁰ It is fair to say that with the publication of these two studies, the floodgates were well and truly opened, and research into inorganic organic metal halide perovskites went supernova.

The mesoporous scaffold architecture was initially favoured due to its prevalence within the DSSC community. As the dye sensitizers used in DSSCs were excitonic in nature, it was necessary to use a high surface area n-type junction to efficiently separate bound electron hole pairs, such that they could be used to perform electrical work.⁴² Perovskites, on the other hand, have high dielectric

constants, and excitons formed are quickly dissociated *via* thermal energy. As such, Ball et al in 2013 demonstrated a planar architecture PSC, eliminating the need for a bulk heterojunction, significantly reducing the processing temperature of the TiO₂ electron transport layer (ETL) such that polymer substrates became an option, and achieving a PCE of 12.3 %.⁴³ Within a few years, almost all research into PSCs moved onto the less complex, easier to fabricate, planar architecture.

Control of perovskite crystallisation is of utmost importance to make high efficiency PSCs. Two step depositions were initially explored, whereby the perovskite would be formed by first coating a layer of lead halide, before dipping the film into, or spin coating, a solution of MAI.^{44,45} A major breakthrough came when Jeon et al pioneered the “antisolvent quench” technique. This allowed for the deposition of a perovskite precursor solution in one step, before inundating the drying film with an orthogonal solvent. This antisolvent would dislocate the true solvent, inducing supersaturation and the formation of a dense network of nuclei. When the film was thence annealed, a uniform polycrystalline film would form, yielding PCEs of up to 16.2 %.⁴⁶ In 2015, the same group reported PCEs of up to 20.2 % using intramolecular exchange of DMSO in PbI₂-DMSO complexes with FA, along with the antisolvent quench, to form a FAPbI₃ perovskite layer.⁴⁷

Complex coordination techniques to inhibit crystal growth and promote nucleation as per the above study were explored in 2016 by Lee et al. They found that electron pair donors, or Lewis bases, coordinate preferentially with PbI₂, termed Lewis base adduct theory. Conveniently, the most commonly used solvents such as DMSO, DMF and GBL all manifest this effect, containing as they do, lone electron pairs. By removing DMSO from MAPbI₃ solutions, they demonstrated the subsequent perovskite films yielded poor surface coverage and acicular crystallites due to rapid crystallisation. When incorporating thiourea into FAPbI₃ solutions, they found the reverse effect, improving film morphology. The conclusion was that the presence of a Lewis base adduct resulted in the dissociation of the adduct becoming the rate limiting step with respect to crystallisation, allowing time for both formation of nuclei, and the organic cations to intercalate prior to annealing.⁴⁸

The antisolvent drip technique is well suited to spin coated films, but requires a degree of operator skill and consistency, and liberates high volumes of often toxic solvents. Li et al, in 2016, found that it was possible to induce supersaturation *via* exposure of an as spun perovskite precursor film to a vacuum. This rapidly removed free solvent, and, in the presence of a Lewis base adduct allowed for the homogeneous nucleation of the perovskite layer without the aforementioned

disadvantages. They were able to demonstrate impressive PCEs of up to 20.5 % from relatively large 1 cm² devices.⁴⁹

In addition to the anti-solvent and vacuum post processing techniques, in 2019 Ding et al demonstrated the use of an air knife to induce supersaturation. Simply put, a lamellar flow of nitrogen was run across a perovskite precursor wet film which had been dripped onto a substrate. The gas flow first controlled the film thickness, and then acted to quickly remove free solvent and induce nucleation. They were able to demonstrate devices with PCEs over 20 %, but importantly while sharing the benefits of vacuum treatment compared to antisolvent quenching, here there is no need to generate a vacuum, the air knife technology is well known in industry, and the technique is fully compatible with R2R processing.⁵⁰

In 2016 Saliba et al produced the first demonstration of what would become known as the “triple cation” composition, here caesium was incorporated into a mixed MA/FA perovskite. Aimed at mitigating against the poor phase stability of FA based perovskites, the too wide band gap of Cs based perovskites, and the low thermal stability of MA based perovskites, they fabricated devices which achieved stabilised PCEs of 21.1 %. Remarkably, these devices continued to operate above 18 % after 250 hours, highlighting their improved stability.⁵¹

TiO₂ is inherently unstable in the presence of UV light and O₂, as well as having relatively low electron mobilities. For these reasons, research was conducted into the replacement of this layer with SnO₂, which demonstrates a wider band gap and far superior electron mobilities. While there are a number of methods to deposit planar SnO₂ films, including chemical bath deposition (CBD), and atomic layer deposition (ALD), among others, one particularly facile solution based method includes using SnO₂ nanoparticles (np-SnO₂). Anaraki et al and Jiang et al, both in 2016, developed this technique. While Anaraki et al synthesised their own nanoparticles and compared spin coated np-SnO₂ with ALD and spin coated np-SnO₂/CBD films, Jiang et al used a commercially available nanoparticle solution. Since then, most high performance n-i-p PSCs have used a SnO₂ ETL.^{52,53}

So far, all devices discussed have taken the form of either mesoporous or planar n-i-p architecture. However, there is also a vast wealth of p-i-n architecture research, with the first such devices arriving in 2013.⁵⁴ These devices used a PEDOT:PSS HTL, and a PC₆₀BM/BCP ETL. Since then, a variety of other HTLs have seen use, including NiO_x, PTAA among others. In 2019 Al-Ashouri et al first made use of carbazole based phosphonic acid materials, dubbed self-assembled monolayers (SAMs) as an HTL material.⁵⁵ These materials do self-assemble, but in the timescales typically associated with spin coating this is likely not occurring in the normal sense of the terminology. The devices fabricated demonstrated PCEs above 21 %, with no additives or

passivation techniques employed. SAMs have been included in a variety of optoelectronic devices, and in the field of perovskite PV are noted for excellent performance and stability.⁵⁵ Indeed, at the time of writing the current world record single junction PSC utilises a p-i-n structure incorporating a NiO_x/SAM HTL and demonstrates a champion PCE of 27.2 %.⁵⁶

2.4.3 Ultrasonic Spray Coating

Running parallel to efforts improving and further understanding PSCs using facile but non scalable techniques such as spin coating, a considerable body of research pertaining towards scale up has emerged. Both chemical⁵⁷ and physical⁵⁸ vapour deposition techniques have been explored, however these require the formation of a high vacuum and thus have associated additional costs. As hybrid metal halide perovskites are solution processable, there are a variety of alternative solution based deposition techniques available to the device engineer. Meniscus coating techniques such as slot die coating,⁵⁹ blade coating,⁶⁰ and bar coating⁶¹ have all been explored, as have non-meniscus techniques such as screen printing,⁶² inkjet printing,⁶³ and spray coating.⁶⁴ A key advantage of solution based deposition techniques over vapour based techniques are the much higher throughputs achievable. Of the above techniques, the fastest is spray coating, with web speeds of 12 m min⁻¹ attainable for roll to roll (R2R) perovskite deposition.⁶⁵ Another important advantage of spray coating is the ability to rapidly coat surfaces curved in more than a single dimension.⁶⁶

The spray process first demands atomisation of a liquid phase, and can be created by forcing a liquid through a small aperture at high pressure, such that shear forces break it up into droplets.⁶⁷ This creates a high velocity spray characterised by a wide particle size distribution, non-ideal for the spray coating of uniform nanometre to micron scale films for electronic purposes.⁶⁸ Ultrasonic spray coating, however, uses a piezoelectric tip vibrating at kHz frequencies to atomise solutions at low pressure, generating a uniform mist with very low velocity.⁶⁹ This allows for fine control of the mist using a shaping gas to direct it towards the target substrate. Upon arriving at the substrate, the droplets wet the surface and coalesce into a wet film, eventually forming a dry film as solvent evaporates.⁷⁰

$$D_{0.5} = 0.34 \left(\frac{8\pi\sigma}{\rho f^2} \right)^{\frac{1}{3}} \quad \text{(Equation 2.27)}$$

Equation 2.27 accounts for the median particle diameter ($D_{0.5}$) as a function of solution surface tension (σ), solution density (ρ) and the frequency (f) with which the piezoelectric tip vibrates.⁶⁹ As the droplets travel towards the substrate, some solvent evaporation occurs, altering the final

wet-film concentration.⁶⁷ The effect of this is governed by the individual boiling points of each component of the solvent system, along with the surface area of the mist as generated. For the creation of a conformal, uniform, thin-film it is essential that the droplets wet the surface adequately and coalesce into a wet-film. A number of factors must be considered here, including the substrate surface energy, substrate temperature, substrate roughness, droplet temperature, droplet velocity, solution density and solution surface tension.^{70,71}

With the substrate of interest typically fixed, there is little control of surface energy that can be had. An important technique to address this is the introduction of interlayers, such as Al₂O₃ nanoparticles, demonstrated to significantly improve wetting onto low surface energy charge transport layers (CTLs).⁷² Plastic materials also have low surface energies, making solution wetting over the etched areas of polymer substrates particularly challenging. Here, the deposition of a conformal oxide film such as SiO₂ *via* electron beam can help to mitigate such issues. Manipulation of the substrate temperature affords some control of solution surface tension after it arrives at the substrate, with an increase in temperature serving to decrease surface tension and thus aid wetting.⁷³ Care must be taken to ensure that increased temperatures do not drive solvent away before the droplets have had time to coalesce, however.⁷⁴

A greater degree of control may be found in the solutions themselves. The simplest method to alter solution surface tension is to use a lower surface tension solvent. Unfortunately, this is not always trivial, as many of the salts typically used to fabricate hybrid perovskites require polar solvents, which demonstrate appreciable dipole-dipole interactions thus making their surface tension relatively high. Another route involves the use of surfactants, which can act to reduce the surface tension of a solution, although these can introduce various effects as they remain in the final dry film where they can inhibit optoelectronic properties and environmental stability.⁷⁵ The use of solvent systems incorporating miscible solvents with contrasting boiling points and surface tensions can act to distribute a solution more evenly across a substrate *via* the Marangoni effect.⁷⁶ Here, as a lower boiling point, lower surface tension solvent preferentially evaporates, a surface tension gradient is formed pulling the bulk solution towards it. This effect is exacerbated by the additional cooling effect of the lower boiling point solvents' evaporation, further increasing the surface tension and thus the gradient.⁷⁷

The parameter space for optimisation of spray coating is multidimensional. The rate at which solution flows through or onto the head, the height of the head with respect to the substrate, the velocity with which the head or substrate moves, the temperature of the substrate, the temperature of the ink, the tip vibrational frequency, ink concentration and solvent system all impact on film

deposition, thickness and morphology.⁶⁸ Repeated passes of the spray head causes additional complexities, exacerbating artefacts, and producing uneven films where freshly sprayed wet films overlap dry film regions. Fluctuations in substrate temperature as solvent evaporates must also be considered as this can result in non-reproducible results. For these reasons, wherever possible it is preferable to complete depositions in a single pass.^{71,72}

2.4.4 *Spray Coating of Perovskite Solar Cells*

Our group here in Sheffield can take the credit for the first demonstration of a PSC containing a spray coated perovskite layer. Barrows et al in 2014 built upon previous work spraying organic semiconductor layers, depositing *via* ultrasonic spray coating a MAPbI_{3-x}Cl_x perovskite onto an indium tin oxide (ITO)/PEDOT:PSS substrate. The device was completed with a PCBM ETL and a Ca/Al back electrode to produce a p-i-n device with PCEs of up to 11 % demonstrated, comparable with spin cast analogues. Lateral head speed and substrate temperature were both systematically investigated here, along with subsequent annealing temperature. Surface coverage initially improved with increasing substrate temperature, however at a certain point this began to deteriorate as solvent evaporation occurred prior to wet film coalescence. DMF and DMSO were both studied as solvent choices, however the increased surface tension and boiling point of DMSO resulted in significant dewetting on the hydrophobic organic HTL. Champion devices here were based on DMF inks, sprayed onto substrates held at 75 °C prior to a 90 min anneal at 100 °C.⁷⁴

Das et al spray-coated the same perovskite in 2015 but in n-i-p architecture, reporting 13 % efficiency. They also demonstrated devices on flexible PET/ITO substrates. Processing differences compared to Barrows et al included a shorter 60 min annealing time, and the use of an IR lamp for photonic curing of the TiO₂ ETL, chosen to overcome difficulties associated with sintering of TiO₂ on the PET substrates. The IR lamp was also used for annealing of the perovskite on PET.⁷⁸ Tait et al, in 2016, used a twin feed system to spray coat devices and simultaneously map the perovskite compositional space. Here, DMF based solutions of MAPbICl₂ and MAPbIAc₂ were fed at different rates to yield different ratios of chloride to acetate in the final films. They were able to fabricate devices with PCEs up to 15.7 % from the 75 % acetate perovskite. Using similar methodology, they also explored varying bromide and iodide stoichiometry, demonstrating the ease with which the band gap could be varied. All fabrication here was conducted in a nitrogen filled glovebox, reducing the deleterious effects of humidity and oxygen.⁷⁹

That same year, Huang et al utilised a two stage process. First, lead iodide was sprayed from DMSO and force dried prior to infiltration *via* a second pass of MAI dissolved in IPA with the

lead iodide film held at 80 °C. The films were then washed in IPA and annealed at 100 °C for 2 h yielding PCEs up to 16.0 %.⁸⁰ Heo et al demonstrated devices with PCEs as high as 18.3 % by using a continuous spray process. Here, the substrate was held at high temperature, and the solution flux was balanced with evaporation rate to slowly grow, *via* continuous redissolution and recrystallisation, perovskite crystals to a micron scale. The major drawback here is of course that the process is much slower than that typical for spray coating.⁸¹

Post deposition processing to induce crystallite nucleation was not explored in spray coated perovskite films until 2018 by Uličná et al. Here, they took an as sprayed film and dipped it into diethyl ether for 45 s, achieving PCEs of 17.3 % despite the process being conducted in air.⁸² Drawing on work produced by Yang et al,⁸³ they used NMP as a cosolvent to lengthen the processing window for antisolvent dipping due to its elevated boiling point compared to DMSO. The same year, Bishop et al adapted the vacuum assisted processing method to initiate nucleation of an as sprayed triple cation perovskite solution. Here, the solvent system chosen was a 4:1 blend of DMF:DMSO and the solution was sprayed onto ITO/TiO₂ substrates held at 40 °C prior to being transferred into a vacuum chamber and pumped down for 5 min. The films were then annealed under nitrogen with processed films demonstrating much smoother finishes compared to those which were annealed immediately post deposition. The processed films accordingly demonstrated improved performance properties and delivered devices with PCEs up to 17.8 %.⁸⁴

In 2020, Su et al sprayed a triple cation perovskite precursor solution from DMF:NMP making use of the same antisolvent dip technique established by Uličná. Post dip, the samples were annealed at 100 °C for 30 min and demonstrated peak efficiencies of 18.5 %.⁸⁵ Cai et al, from the same group, went further with the demonstration of devices with PCEs up to 20.6 % by optimising film thickness and dip duration.⁸⁶ In the same year, Rolston et al demonstrated a plasma processed spray coating technique conducted in air. As the spray head traversed the substrate, immediately following was a plasma afterglow at atmospheric pressure. The plasma acted as both post deposition processing and anneal, significantly increasing throughput and reducing stresses associated with substrates subjected to high annealing temperatures. The speed demonstrated here was 12 m min⁻¹, the fastest known perovskite deposition technique. Completed devices demonstrated PCEs up to 18 %.⁸⁷

Gao et al in 2021 achieved PCEs of 18.2 % in air using L- α -phosphatidylcholine to reduce the width of grain boundaries and improve the crystallinity of spray coated FA_xMA_{1-x}PbI_{3x}Br_{3(1-x)}. They also incorporated KI which was found to increase grain sizes and passivate defects.⁸⁸ In 2022, the same group replaced KI with C₇H₇OBF₃K, finding that the BF₆⁻ moiety formed

hydrogen bonds with MA/FA in the perovskite, stabilising them with respect to formation of cation vacancies. This boosted device performance from 18.2 % to 19.5 %, remarkable for devices fabricated in air.⁸⁹

In 2023, Cassella et al demonstrated the first example of a spray coated passivation layer. Here, n-i-p devices were fabricated, using a $\text{Cs}_{0.15}\text{FA}_{0.85}\text{PbI}_{2.85}\text{Cl}_{0.15}$ perovskite. Post deposition, this layer was processed using an air knife, prior to spray coating of i-BABr from IPA solvent. The champion device here demonstrated a PCE of 21 %, and was the first demonstration of scalable interfacial passivation.⁹⁰ The following year, the same group demonstrated that the use of Al_2O_3 nanoparticles could overcome the hydrophobicity of an Me-4pacz SAM layer to produce p-i-n devices. Importantly, the effect enabled the spraying of DMF:DMSO based inks, allowing for compositions containing Cs, such as the triple cation perovskite. The spray coated triple cation devices demonstrated PCEs up to 20.4 %.⁷² The current world record for a spray coated perovskite solar cell was achieved in 2024 by Xu et al. Here, FAPbI_3 was deposited from a triple solvent system containing DMF, NMP and IPA as an additive. The resultant n-i-p devices demonstrated PCEs up to 22.4 %, however they required an antisolvent bath treatment, potentially limiting this process with respect to scalability.⁹¹

Until now, we have only discussed devices where the perovskite was the sole layer spray coated. The first attempts to spray coat all solution processable layers were in 2016 by Mohamad et al. Here, p-i-n devices were fabricated with a spray coated PEDOT:PSS HTL, perovskite absorber, and PCBM ETL. To improve the wetting of the PEDOT:PSS solution onto ITO, this was diluted with IPA and EtAc. To ensure rapid evaporation of the solvent sprayed onto the perovskite layer, the PCBM layer was cast from a 1:1 solvent system of CB:CF. The devices here demonstrated PCEs up to 9.9 %.⁹² The following year, Bishop et al fabricated mesoporous devices, a compact TiO_2 layer was first deposited *via* spray pyrolysis onto FTO coated substrates. A mesoporous TiO_2 scaffold layer was then sprayed from EtOH and sintered at 450 °C. A $\text{MAPbI}_{3-x}\text{Cl}_x$ precursor solution in DMF was then sprayed and annealed without a post processing step. Finally, a spiro-OMeTAD HTL was sprayed from a 1:1 CB:CF solvent prior to completion of the devices with a Au back contact. The devices fabricated demonstrated PCEs up to 10.2 % for small area cells, and 6.6 % for 1.5 cm² cells.⁹³

Smith et al optimised a spray coating process for deposition of np- SnO_2 , eliminating the necessity for high temperature sintering processes. By taking a commercially available aqueous solution of np- SnO_2 and heavily diluting it, they were able to produce devices with PCEs greater than 19 %. The substrate would only need to be held at 30 °C during spraying, and the subsequent anneal was

at 150 °C for 30 min, far reduced from the 450 °C necessary for TiO₂ sintering. The perovskite and HTL layers were, however, spin-coated.⁹⁴ The same year, Bishop et al brought together various aspects of the above studies, spray coating the np-SnO₂ layer as per Smith, utilising the previously demonstrated vacuum processing of a sprayed triple cation perovskite, and finishing the devices with the previously demonstrated spiro-OMeTAD layer from a CB:CF. The finished devices demonstrated a significant improvement on the previous fully sprayed record holder, demonstrating a champion PCE of 19.4 %.⁹⁵

An interesting approach to the spray coating of np-SnO₂ is to use biomaterials to construct nanostructures. Kumar et al in 2023 used a virus, M13 bacteriophage, added to the np-SnO₂ solution to create a mesoporous SnO₂ ETL. The subsequent devices demonstrated PCEs up to 22.1 %, compared to 20.1 % for the standard planar np-SnO₂ ETL. It should be noted that here, the devices were completed *via* spin coating.⁹⁶ In 2025 Su et al incorporated a sodium salt of L-aspartic acid to reduce aggregation of np-SnO₂ in spray-coated films. They found that the carboxylic acid group stabilised Sn⁴⁺, stabilising the colloidal dispersion and reducing oxygen vacancies. Spin coated devices on spray coated np-SnO₂ films yielded PCEs up to 24.3 %.⁹⁷

In 2022, Cassella et al fabricated p-i-n devices *sans* spin coating *via* the spray coating of an MeO-2pacz SAM layer, followed by spray coating MAPbI₃, with the rest of the device layers evaporated. Here, the hydrophobicity of the SAM was overcome *via* a combination of washing the SAM layer after deposition, and the use of 2-methoxyethanol as the majority solvent in the precursor ink. The devices demonstrated PCEs up to 20.8 %.⁹⁸

2.4.5 Thin Film PV on Atypical Substrates

Thin film PV typically pertains to those technologies which have historically been considered scalable, thus precluding c-Si and gallium arsenide (GaAs). Such technologies include amorphous silicon (a-Si), cadmium telluride (CdTe) and copper indium gallium selenide (CIGS), with these materials typically requiring a support structure upon which carrier transport and/or photoactive layers are grown.³ More recently, third generation thin film technologies include DSSCs, OPVs and PSCs. Here, we briefly discuss the substrate types on which high quality devices can be fabricated, typically dictated by the processing temperatures involved.

A-Si is relatively cheap, and owing to relatively low temperature deposition processes is viable on a variety of substrates including metals, glasses and polymers. Methods used to fabricate films include chemical vapour deposition, sputtering and plasma decomposition of silane.⁹⁹ Polyimides, PET and PEN¹⁰⁰ are examples of polymers where this technology has been demonstrated,

however in recent years devices have also been fabricated on photo-paper¹⁰¹ and paper.¹⁰² Unfortunately, the outright efficiency of a-Si puts it at a disadvantage compared to perovskite absorber materials.

CdTe can be fabricated from a variety of different techniques including magnetron sputtering,^{103,104} electrodeposition,¹⁰⁵ close-spaced sublimation,¹⁰⁶ and physical evaporation,^{107,108} and even screen printing of a CdTe paste.¹⁰⁹ Historically the most common substrate used is soda-lime glass, with all the above techniques compatible with this material. CdTe paste requires very high temperature sintering, and is thus unsuited to substrates other than glass. Physical vapour deposition has been realised on both rigid and flexible metals where flexible metal based devices demonstrated PCEs of up to 5.3 %, ¹⁰⁷ as well as polyimide substrates.¹⁰⁸ Here, steps must be taken to improve transparency of the polyimide, such that their high temperature stability can be taken advantage of without optical losses, however, such polyimide based devices only demonstrated PCEs up to 11.4 %. Close-spaced sublimation requires temperatures in excess of 400 °C and is therefore only suitable for metal or glass substrates with groups having demonstrated films fabricated onto Mo foil.¹⁰⁶ Electrodeposited CdTe significantly reduces waste and demonstrates low temperature requirements, applicable to metals and metal foils such as stainless steel,^{110,111} or molybdenum.¹¹² Unfortunately non-glass based devices fabricated *via* electrodeposition demonstrate extremely low PCEs.¹¹³ Glass,¹⁰⁴ Mo foil,¹¹⁴ and polyimide films coated first with Mo¹¹⁵ have all been used to fabricate CdTe devices *via* sputter coating. Here, the polyimide/Mo based devices demonstrated PCEs up to 6.5 %.¹¹⁵ Flexible willow glass has also seen use, with CdS first sputtered onto this followed by close-space sublimation of CdTe to complete the devices. Here, the ultrathin 100 – 200 µm thick glass easily survives the high temperature sublimation process and demonstrates PCEs up to 16.4%.¹¹⁶

Similar to CdTe, CIGS have most commonly been deposited onto glass *via* either sputtering or evaporation under high vacuum.¹¹⁷ A significant body of literature pertains to low vacuum deposition processes including electrodeposition,¹¹⁸ particulate based processes such as screen printing, electrospray and doctor blading,¹¹⁹ and even solution processes such as spray pyrolysis,¹²⁰ and spin coating.¹²¹ Solution based processes require hydrazine based precursors whether spray or spin coated.¹²² Unfortunately, spray pyrolysis requires substrate temperatures ranging between 360 and 420 °C.^{120,123} Spin coated analogues require annealing around 500 °C.^{121,124} This severely limits substrate options, especially with respect to polymers, with only polyimides potentially suitable. Polyimide based CIGS have been demonstrated using a low temperature sputtering process prior to a high temperature selenisation process, demonstrating PCEs up to 9.3 %, ¹²⁵ but this was subsequently bettered by coevaporation techniques which yielded PCEs up to 20.4 % by

2013.¹²⁶ In 2017 a CIGS device was fabricated *via* spray coating onto a polyimide substrate held at 300 °C and annealed at 350 °C, however the efficiency of the subsequent devices was only as high as 1.4 %.¹²⁷

The advent of the DSSC broadened options significantly due to the lower processing temperatures associated with their fabrication. OPVs similarly can be processed at relatively low temperatures, making them suitable for polymer substrates also.

Early DSSCs required mesoporous TiO₂ scaffolds onto which the sensitisers are adsorbed. Unfortunately, the deposition of compact and mesoporous TiO₂ *via* spray pyrolysis typically required substrates to be held at temperatures between 400 and 500 °C, severely limiting substrate options. As a result of this, for some time DSSCs were not truly low temperature processable, limiting substrates to just glass or metals. By 2005, however, a variety of techniques for fabrication of the TiO₂ layers had been successfully demonstrated, including compression of TiO₂ pastes,¹²⁸ electrophoresis and exposure to microwaves,¹²⁹ control of pH to induce flocculation of colloidal TiO₂ solutions,¹³⁰ and cold isotactic pressing.¹³¹ Nanocrystalline titania pastes which could be effectively “sintered” at room temperature entered the field in 2007,¹³² and between all these techniques many new substrate materials were unlocked, including but not limited to PET, PEN and even paper.¹³³ Unfortunately, the highest recorded PCE for a DSSC is only 13 %, making this technology less suited to high specific power applications.²⁴

Early work into OPVs demonstrated devices could be fabricated from simply sandwiching a p-type organic material between two different metals, or a metal and a TCO coated glass.¹³⁴ This architecture is not especially dissimilar to the planar arrangements found in modern OPV stacks but noticeably requires no high temperature processes. Modern OPVs are formed using a bilayer, or more commonly a bulk heterojunction of acceptor and donor molecules, situated on top of a TCO coated substrate. While depending on material choice there are some processes involving heat, none of these are of especially high temperatures and therefore OPVs have been produced on glass,¹³⁵ polymer and metal substrates.¹³⁶ Polymer substrates include polyimides,¹³⁷ PEN,¹³⁸ and PET.¹³⁹ Currently, PET based OPVs demonstrate PCEs up to 17.5 %, ¹⁴⁰ and parylene based OPVs demonstrate up to 16.9 %.¹⁴¹ Other substrates include newspaper and elastomers such as PDMS.¹⁴²⁻¹⁴⁴ As with OPVs, PSCs also require low temperature processes, and therefore devices have been demonstrated on rigid and flexible glass,¹⁴⁵ metals,¹⁴⁶ polycarbonate,¹⁴⁷ polyimide,¹⁴⁸ PEN,^{149,150} PET,¹⁵¹ PES,¹⁵² paper,¹⁵³ cellophane,¹⁵⁴ and even transparent wood.¹⁵⁵

The ability to fabricate onto polymers is advantageous as these materials are low density and therefore mass can be reduced. Another advantage of using polymers is that they can be made

highly flexible, and thus compatible with R2R production techniques, however this is not a prerequisite for structurally integrated PV. Instead, for integrated PV, mechanical properties must be different, closer to the qualities provided by metals. Clearly, this presents a dichotomy, heavy, strong metals vs light, structurally unsound polymers. Carbon fibre-reinforced polymer (CFRP) composites are used widely in many high performance industries for their exceptional strength to weight ratios. There is no literature to the author's best knowledge of PSCs fabricated directly onto CFRP substrates, although several groups have fabricated devices onto individual carbon fibres. Commercially, there are companies which offer CFRP based PV, however these are simply CFRP panels upon which c-Si PV has been adhered.

2.4.6 High Specific Power Perovskite Solar Cells

The successful demonstration of high specific power devices should create mobile power applications uniquely suited to PSCs, and indeed there is a wide body of literature on the topic. Kaltenbrunner et al pioneered this field in 2015 with the demonstration of flexible PSCs (f-PSCs) fabricated onto 1.4 μm thick PET substrates. The devices were fabricated using a PEDOT:PSS HTL acting also as a transparent conducting film (TCF). Onto this, MaPbI_3 was deposited *via* spin coating and the devices were completed either by vacuum deposition of N,N-dimethyl-3,4,9,10-tetracarboxylic perylene diimide (PTCDI) or spin coated PCBM, prior to back contact deposition. Importantly, here a Cr layer which rapidly oxidised to Cr_2O_3 was used to protect the back contacts from deleterious reactions with halides in the perovskite material. They reported a specific power of 23 W g^{-1} and demonstrated a small solar plane powered by several such f-PSCs. In the same study, they also fabricated PSCs onto elastomeric substrates which had been pre-stretched. These elastomeric PSCs (e-PSCs) could in theory be wrapped around 3D surfaces.¹⁵⁶

In 2019, Kang et al demonstrated f-PSCs fabricated onto 1.3 μm PEN substrates. In this study, they used Ag nanowires (AgNWs) to create a TCF. Both randomly oriented AgNWs and orthogonally oriented AgNWs were investigated. To create a good contact between the PEN and AgNWs, the PEN surface was first amine functionalised by spin coating of poly-L-lysine. It was found that orthogonal AgNWs were far superior to randomly oriented AgNWs, which were prone to aggregating leading to poor surface coverage and increased roughness. AgNW films were fabricated *via* capillary printing prior to sequential spin coating of PH 1000 and AI 4083 PEDOT:PSS to form a HTL. A $\text{MAPbI}_{3-x}\text{Br}_x$ perovskite absorber layer was then deposited *via* two step spin coating prior to solvent vapour annealing. PC_{61}BM was then spin coated and the devices were completed with the thermal evaporation of Al back contacts. The f-PSCs created

demonstrated PCEs up to 12.9 % corresponding to a specific power of 29.4 W g^{-1} and were lightweight enough to be supported by a bubble.¹⁵⁷

In 2022 Wu et al fabricated f-PSCs onto $3 \mu\text{m}$ parylene-C substrates *via* lift off fabrication. Here, a $3 \mu\text{m}$ parylene-C film was fabricated *via* chemical vapour deposition onto glass. This was then flip over transferred to another glass support, to expose a clean, flat parylene-C surface. A Zr, Ti, Ga doped In oxide TCO was then fabricated *via* sputter coating directly onto this surface. A PTAA HTL was then spin coated and functionalised *via* spin coating of phenyl ethyl ammonium iodide. Onto this surface a triple cation perovskite absorber layer was spin coated using the antisolvent quench technique. PCBM and BCP were then sequentially spin coated to create an ETL and the devices were completed *via* the thermal evaporation of Cu back electrodes. The f-PSCs here demonstrated remarkably high PCEs of 20.2 %, corresponding to a specific power of 30.3 W g^{-1} , and retained 96 % of their initial PCE after 50 bending cycles around a 1 mm radius.¹⁵⁸

In 2024 Hailegnaw et al, from the Kaltenbrunner group, fabricated f-PSCs onto $1.4 \mu\text{m}$ PET substrates. Here, they first deposited *via* atomic layer deposition a 100 nm thick blocking layer of amorphous Al_2O_3 , aimed to reduce moisture and O_2 permeability through the thin polymer layer. A PEDOT:PSS layer was then deposited *via* spin coating to create a TCF with hole transporting properties. Using methyl benzyl ammonium iodide as a bulky cation, a quasi-2D perovskite absorber layer, $\text{MBA}_2(\text{Cs}_{0.12}\text{MA}_{0.88})_6\text{Pb}_7\text{I}_{22}$, was deposited *via* spin coating and antisolvent quench. The devices were completed *via* spin coating of a PCBM ETL, spin coating of a TiO_2 sol-gel interlayer and either thermally evaporated Au, Cr/Au, or Al back contacts. The champion f-PSC demonstrated a PCE of 20.1 % corresponding to a specific power of 44 W g^{-1} . Larger, 1 cm^2 , devices yielded PCEs up to 16.3 % corresponding to a specific power of 35.2 W g^{-1} and such devices were used to power a small quadcopter drone dubbed *Solar Hopper*. Here, 4 banks of 6 individual 1 cm^2 PSCs are used to power the drone, with each device consisting of 1/400 the total weight of the drone. After various supporting structures and electronics, including tapes, wires and a laser cut balsa wood frame, are added this becomes 1/25 of the total weight. It is not clear what the effective specific power is after these additions, but the addition of solar power generation extended the drone's flight time under a simulated solar spectrum by 6 % from 119 s to 225 s. As with the 2015 Kaltenbrunner paper, pre-stretched devices were also fabricated, with these in principal capable of being adhered to surfaces curved in more than a single dimension.¹⁵⁹ Later in the same year, Jia et al fabricated what are to date the highest specific power f-PSCs. Here, $1.5 \mu\text{m}$ thick polyimide substrates were fabricated onto PDMS and cured at a low enough temperature (280°C) to yield colourless polyimide substrates which remained capable of higher temperature

processing than PET or PEN. PSCs were then fabricated onto these substrates demonstrating PCEs up to 22.13 % corresponding to a specific power greater than 50 W g⁻¹.¹⁶⁰

For context, at the time of writing, the highest specific power demonstrated for c-Si is 9.3 W g⁻¹,¹⁶¹ for a-Si this falls to 8.3 W g⁻¹.¹⁶² The highest reported III-V is only 3.8 W g⁻¹,¹⁶³ WSe₂ achieves only 4.4 W g⁻¹,¹⁶⁴ and CIGS only manages 3.3 W g⁻¹.¹²⁶ Quantum dot based solar cells achieve 15.2 W g⁻¹,¹⁶⁵ and OPVs reach 32.1 W g⁻¹.¹⁶⁶ Note that flexible solar cells would need to be mounted onto a surface of interest, which would introduce additional weight in the form of adhesives, substrates, and rear encapsulation, all of which would serve to reduce effective specific power.

2.4.7 *Thin Film Electronics on Curved, Rigid, Substrates*

There are significant hurdles which must be overcome when it comes to fabrication of electronics onto arbitrary non-developable surfaces. Such surfaces cannot conformally be wrapped with a 2D plane without stretching, compressing, or folding and is the root of the cartographer's single greatest headache. For a surface to precisely match another surface, they must be identical at all points, giving rise to the idea of developable and non-developable surfaces. A plane, for example, is developable and can be curved into a cylinder, and a cylinder can in turn be turned out into a plane. This is because they share the same Gaussian curvature, K , given by **Equation 2.28**.¹⁶⁷

$$K = \kappa_1 \kappa_2 \quad \text{(Equation 2.28)}$$

Here, κ_1 and κ_2 are the principle curvatures of the surface. For a 2D plane both are 0 and therefore $K = 0$. For the cylinder, there is only one principle curvature and therefore $K = 0$. However, as soon as both κ_1 and κ_2 take values, positive or negative, K is no longer 0 and no developable surface can intimately take its form.¹⁶⁷ It follows, therefore, that curvature of such a surface is an intrinsic property, such that it becomes impossible to wrap a 2D plane around a 3D globe without stretching it.¹⁶⁸

The obvious solution is to just go ahead and fabricate the desired electronic structure (e.g. a circuit) onto a stretchable planar substrate, and apply it to the curved surface.¹⁶⁹ Provided, of course, the designer accounts for stretching of certain elements, either by using intrinsically stretchable electronics or designing stretchable geometries for materials which are mostly rigid. A simple example of the latter would be a spring, which compared to a straight rod of the same gauge and material stretches much further. Alternatively, the planar substrate could be pre-stretched, the design applied, and then left to relax, forcing the design to either compress or take on compressible geometries (here, the hypothetical rod is squeezed such that it buckles into a spring like shape).¹⁷⁰

Another option would be to mould the stretchable substrate to the non-developable surface (e.g. by curing PDMS resin on the surface of interest), then pre-stretch it until it is planar, apply the desired electronic structure to it, and then release it such that it returns to its original form. This can then be replaced back onto the non-developable surface.¹⁷¹ Alternatively, the electronic structure could be fabricated onto a thermoplastic 2D planar substrate. This could then be heated up such that it softens, and then applied to the non-developable surface and allowed to cool and harden. Of course, here, the components making up the structure would need to be thermally stable.¹⁷² Tattoo electronics makes use of structures applied to ultrathin stretchable substrates adhered to a flexible layer which can be dissolved in a solvent (usually water) of choice. This can then be applied to the non-developable surface, and in the presence of the chosen solvent the stretchable electronic is transferred like a temporary tattoo. This technique has been used to mount biosensors to skin, but in principle could be applied to any surface.¹⁷³ All the stretching techniques described here may adversely affect electrical performance, are limited to relatively simple geometries, store stresses and may be easily damaged due to the softness of the substrates used. Compared to direct fabrication, they also introduce substrate weight, and where used, adhesive weight. Stretching techniques have been used to fabricate optoelectronic devices including both electroluminescent devices,¹⁶⁹ and solar cells.¹⁷⁴ Here, the PV devices fabricated were OPVs with estimated PCEs of 0.36 %.

Another potential route to creating electronics on non-deformable surfaces is to use non-stretchable substrates which can be folded, or cut and folded, such that they closely adhere to the shape of interest. Here, we are essentially advocating the use of advanced origami and kirigami techniques, as well as Miura folds and flexible strips (gores). Devices are fabricated on the flat areas of the inextensible sheets, and electrical connections between flat areas go through the folded lines. Alternatively, rigid faces and flexible hinges might be used. Here, the main disadvantages are the intricate designs required which often require computational methods to achieve efficiency, low conformity with the underlying shape desired which could, for example, disturb lamellar flow over an aerofoil, and limited versatility. However, it is clear how planar devices might easily be integrated into such designs, and there is potential to use high conductivity metals as substrates or as connections between faces. While PV devices have not been demonstrated in this manner, a number of groups have fabricated other optoelectronic devices, including electroluminescent devices,¹⁷⁵ and photodetectors.¹⁷⁶

3D printing is another route towards conformal electronics on rigid curved surfaces. Here, if the object of interest can be fabricated *via* 3D printing, then the electronics can be printed at the point of part manufacture. Alternatively, printing directly onto a surface of interest can also be

performed, and with the use of orthogonal solvents multilayer architectures can be realised. 3D printing can also be used to print masks to enable other deposition techniques. It is necessary to maintain both nozzle angle and distance when printing over curved surfaces, this can be achieved either by being programmed into the control software, or *via* the use of algorithmic feedback loops. Drawbacks to 3D printing are relatively slow process speeds, compatibility only with simple surfaces due to the head proximity and bulk, and limited scalability. 3D printed optoelectronic devices include quantum dot LEDs deposited directly onto the surface of a lens.¹⁷⁷ Child et al have even 3D printed a variety of interesting desktop friends, including a ladybird media controller, a slug clicker, an isopod desk pet, and a MIDI instrument in the form of a cartoonish toadstool.¹⁷⁸

Transfer printing represents yet another route towards non-deformable electronics. One such technique is hydrodynamic printing, whereby the desired structures are printed onto a water soluble 2D substrate, with this then placed into a container of water. Here, the target surface of choice has already been submerged below the waterline. The dissolution of the substrate then leaves the structure floating on the surface of the water. The target surface can then be either raised through the water/pattern/air interface, or the water level can just be reduced. The patterned structure then conformally wraps around the target surface.¹⁷⁹ It should be noted that we are still ultimately wrapping a 2D structure around a complex shape, and therefore there will be some degree of stretching involved here. Another method for transfer printing includes that which uses some form of stamp. This can take the form of a soft, compliant and elastomeric pad, which picks up a 2D pattern and predictably conforms to the shape of interest.¹⁸⁰ Importantly, judicious use of orthogonal solvents should mean that multilayered patterned devices are feasible *via* stamp printing. For especially high curvatures, the soft pad can be replaced by some sort of compliant inflatable balloon.¹⁸¹ Optoelectronic devices fabricated *via* transfer printing include arrays of Si PV,¹⁸¹ photodetectors,¹⁸² and electroluminescent devices.¹⁷⁹ Individual Si based PV cells within the array demonstrated PCEs up to 2.56 %.¹⁸¹

Another technique that has applications on curved substrates is that of nanolithography. Here, standard photoresist methods can be used however it is often more useful to use flexible, stretchable photomasks.¹⁸³ In this case, the process is termed soft lithography. As surfaces get larger or more curved, application of masks becomes more difficult, and distortions become greater. Other routes to target include directly writing masks onto the surface of interest,¹⁸⁴ or using mask free techniques such as holographic lithography.¹⁸⁵ These processes are extremely complex, time consuming and require expensive, bespoke equipment. Using nanolithography, devices including photodetectors and photoconductors have been demonstrated on curved surfaces.^{186,187}

Spray coating has also been demonstrated in the manufacture of various optoelectronic devices on non-developable surfaces. In 2018, Carey et al successfully spray-coated a mixture of graphene nanoparticles and PEDOT:PSS from ethanol onto the inner surface of two half spheres of PMMA to create TCFs. By combining both half spheres to form a sphere with the inside coated in TCF, and attaching Cu tape to the outside, they were able to create what was essentially a capacitive transparent touch sensor.¹⁸⁸ Other groups have fabricated heaters *via* spray coating of silver nanowires onto complex shapes, or circuits using stretchable masks.¹⁸⁹ Hanton et al have used a combination of 3D printing to embed electrodes into 3D shapes *in situ*, followed by spray coating of subsequent layers to yield electroluminescent films with defined shapes on curved surfaces.¹⁹⁰

Notably, in 2014, Kramer et al fabricated colloidal quantum dot (CQD) solar cells wherein a solution of CQDs was sprayed *via* airbrush in a so called spray layer deposition (sprayLD). Here, sprayLD is claimed to deposit extremely thin layers approaching monolayers, with multiple passes used build up the photoactive layer. The curved devices here were fabricated using optical grade lenses, coated at 350 °C *via* sputtering with ITO, and subsequently a TiO₂ ETL. PbS CQDs were fabricated and treated with CdCl₂, diluted in octane. A single “pass” of the sprayLD consisted of a layer of CQDs, followed by a layer of mercaptopropionic acid sprayed *via* airbrush, a rinse layer of methanol again from airbrush, and finally a dry air airbrush. CQD devices required between 65 and 85 sprayLD passes. Devices were completed *via* thermal evaporation of MoO₃ and ebeam deposition of Au back contacts. The curved devices were fabricated onto hemispherical lenses and exhibited champion PCEs of 5.0 %, commensurate with spin coated analogues.⁶⁶

In 2022, Feng et al fabricated a perovskite photodetector onto hemispherical substrates *via* a combination of evaporation and spray coating. Here, 0.8 cm diameter hemispherical lenses were first coated with Cr by thermal evaporation. Onto this a solution of PEDOT:PSS diluted in EtOH was spray coated at a 45 ° angle with the lens rotating. After each layer a N₂ stream was directed at the sample to assist in solvent removal. When 125 nm of PEDOT:PSS was achieved, the sample was annealed at 100 °C. Subsequently, a solution of PEA₂FA₃PbI_xBr_{13-x} 2D perovskite was spray coated from a DMF:ACN solvent system. A 3D FA_{0.92}Cs_{0.08}PbI_yBr_{3-y} perovskite was then sprayed onto the 2D perovskite prior to annealing at 170 °C. The resultant film was then mechanically polished before evaporation of C₆₀, BCP and a semi-transparent Cr top electrode. The authors also fabricated n-i-p devices using spray coated np-SnO₂ and PTAA. The fabricated detectors were able to perform lens free imaging at angles approaching 180 ° when patterned into arrays. Perovskite films on a variety of 3D shapes were also demonstrated, suggesting that spray coating of perovskite active layers onto arbitrary surfaces is indeed feasible.¹⁹¹ This study was published a

couple of months after the work presented in Chapter 4 was published, demonstrating the increasing interest in spray-coated perovskite semiconductors on non-developable surfaces.

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Chapter 3

Experimental Methods

3.1 Introduction

This chapter concerns itself primarily with a discussion regarding the experimental methods, both with respect to fabrication of samples and their characterisation, used throughout the rest of this thesis. In each experimental chapter, precise experimental methods will also be included, with this chapter acting as an overview of the necessary procedures and any relevant background physics which may not have been covered in the previous chapter. First, consideration will be given to the materials used throughout the subsequent investigations. Next, a discussion of the fabrication techniques employed herewith. Finally, a variety of device and thin-film characterisation techniques will be discussed.

3.2 Materials

Information regarding material purity and provenance can be found in the relevant experimental chapters, and are typically specific to that investigation.

3.2.1 Substrates

A variety of substrate materials have been used in this thesis, ranging from low-cost, mass-manufactured laboratory watch glasses to commercially available high-quality quartz coated glass and even self-prepared, curved carbon fibre-reinforced polymer (CFRP) substrates. All substrates used for PV device fabrication were coated with an indium tin oxide (ITO) transparent conducting oxide (TCO).

Throughout the course of all investigations, 15 x 20 mm ITO coated soda lime glass substrates were used to perform experiments upon which initial findings could be drawn from. Once processes were established on these substrates, they would then be applied to others, with varying degrees of success. The 15 x 20 mm ITO substrates come in two forms, prepatterned 8-pixel or unpatterned plain. Here, patterning refers to areas of the substrate where the ITO layer was chemically etched to expose bare glass, electrically isolating 8 fingers from the active area. This acts to significantly reduce opportunities for electron hole recombination on the pathway out of the device, which would appear as a reduction in shunt resistance and

negatively impact on device performance. The ITO coating on these substrates was of a nominal 100 nm thickness, with a sheet resistance of $20 \Omega/\square$.

Typically, in instances where film characterisation of samples fabricated on ITO were of interest unpatterned substrates were used, with the 8-pixel substrates reserved for devices. In cases where unpatterned substrates were used to fabricate devices, an etching step was necessary to pattern the substrates for the same reasons as those mentioned above. Manually etching the samples was performed using a 4 M solution of hydrochloric acid (HCl), in combination with zinc (Zn) powder. Here, Kapton tape was used to mask off roughly two-thirds of the substrate area, along the short axis. A light dusting of Zn powder was then applied to the exposed ITO, before HCl solution was added dropwise *via* pipette. The metal-acid (M-A) etch technique for TCOs has a long tradition and is well understood.¹ Here, the reaction between Zn and HCl forms ZnCl and elemental, or active, hydrogen (H^0). The produced H^0 can then reduce the Sn^{4+} present in SnO_2 to form elemental Sn^0 . The H^+ ions formed here do not cause any appreciable dissolution of Sn over the timescale of the etch, and therefore this reaction does not contribute to the formation of further H^0 .² Etching in this method does not provide a fine line etch, due to undercut of the TCO beneath the masked area, however for our purposes this is not critical. The etching process ultimately is brought to a halt *via* quenching under running tap water. It ought to be noted that for 6-pixel designs, in fact only the middle four pixels were ever tested to eliminate edge effects along the long axis of the substrate.

In addition to the commercially available substrates discussed above, for Chapter 4 it was necessary to use curved, transparent substrates. ITO coated curved substrates are not readily available for purchase, therefore it was necessary to procure curved substrates which could then have ITO deposited upon them. In the first instance, laboratory grade soda lime watch glasses were used, followed by polymer (CR-39) optical lenses and finally borosilicate glass optical lenses. In all cases, ITO was deposited by our collaborators at Loughborough University. Here, a 200 nm thick ITO film was deposited onto the curved substrates *via* magnetron sputtering at a power of 155 W, using an argon (Ar) flow rate of 7 SCCM, with the substrates held at room temperature. The ITO deposited *via* this method demonstrated a sheet resistance of $20 \Omega/\square$, but had a slightly lower transmission than the commercially obtained coatings. Prior to device fabrication, the substrates were etched as per the above described M-A method.

CFRP substrates were necessary for Chapters 5 and 6. Detailed discussion of their fabrication is reserved for later in this chapter, with further discussion of their properties reserved for Chapters 5 and 6. Substrates were fabricated here in Sheffield initially by our collaborators in the Department of Mechanical Engineering and subsequently by the author. Substrates were either unidirectional (Chapter 5), or woven (Chapter 6), with respect to the orientation of the carbon fibres. While Chapter 5 deals exclusively with flat substrates, Chapter 6 introduces curved CFRP substrates, necessitating the use of woven fibres. All substrates utilised a planarization layer, used to electrically isolate the fibres from the bottom TCO and reduce roughness to that conducive for thin film device fabrication. As one might expect, all CFRP substrates were opaque, removing the necessity for a transparent bottom contact. In any case, we elected to use a TCO due to their inherent stability and blocking properties.^{3,4} Here, to create the bottom electrode, ITO was deposited using the same process as that described above. For device fabrication, substrates were either etched *via* the same M-A technique described above, or an SiO₂ insulating layer was deposited *via* e-beam evaporation to electrically isolate top and bottom contacts.

Finally, where thin film characterisation in the absence of a TCO was appropriate, ultra-flat quartz coated commercially available 15 x 20 mm glass substrates were used.

3.2.2 *Device Stack Materials*

As discussed in the previous chapter, perovskite solar cells (PSCs) typically come in two distinct flavours. On the one hand we have *n-i-p* architecture, whereby light entering the cell comes into contact first with an n-type charge transport layer (CTL). On the other hand, we have *p-i-n* architecture, whereupon light entering the cell first encounters a p-type CTL. It must be noted, however, that while devices are always deposited onto a substrate, whether light first enters that substrate governs its configuration. Where the substrate is the first material encountered by light the device is considered in superstrate configuration. If light first encounters the back electrode, the device is in substrate configuration (see **Figure 3.1**).⁵

As a large amount of research into thin-film solar cells occurs on transparent substrates, illuminated through the substrate (i.e. in superstrate configuration), typically the first CTL deposited onto the TCO in either an *n-i-p* or *p-i-n* stack is n-type or p-type respectively. This can lead to a general assumption that the optical architecture (i.e. orientation with respect to light) of the device is always the same as the fabrication architecture (i.e. orientation with respect to CTL deposition order). However, this need not always be the case; in the example

of a device fabricated onto an opaque substrate, with a transparent back (or top) electrode (i.e. in substrate configuration), the light clearly must enter the final CTL deposited onto the substrate and thus the optical architecture is the opposite of the fabrication architecture.

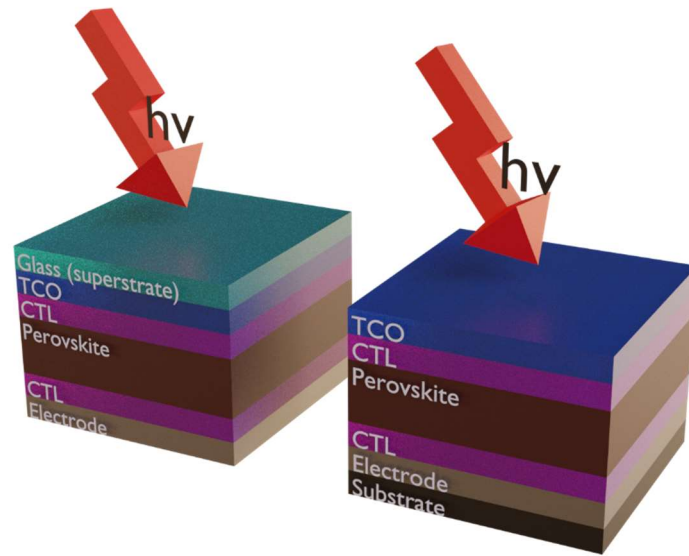


Figure 3.1: Schematic representation demonstrating left, superstrate vs right, substrate architecture.

Thus, it seems prudent to ignore the fabrication architecture entirely, as it ought to be largely irrelevant from a characterisation point of view and serves only to confuse matters. Simply reporting the optical architecture and the configuration should serve to give a complete picture to the reader. However, for our purposes it becomes more sensible to refer to the fabrication architecture as we are primarily interested in the processes for the successful fabrication of devices, in either configuration and/or optical architecture. For example, in Chapter 4 we demonstrate superstrate configuration, *n-i-p* optical architecture devices, but in Chapter 5 we employ the same device stack (bar some minor differences) now in substrate configuration, reversing the optical architecture but largely retaining the same engineering challenges.

For *n-i-p* architecture devices, the electron transport layer (ETL) employed was SnO_2 . SnO_2 is an ideal material to act as the n-type layer in PSCs, thanks to its wide band gap (3.6 – 4.2 eV),⁶ deep conduction band and high electron mobility.⁷ The SnO_2 ETLs were fabricated *via* deposition of an aqueous nanoparticle solution (np- SnO_2).⁸ This material exhibits several advantages, being solution processable and thus suitable for a variety of solution-based deposition techniques, requiring relatively low temperature post deposition processing, and the self-passivating nature bestowed upon it by the presence of potassium hydroxide stabilisers.⁹

In this thesis, np-SnO₂ was deposited either *via* spin coating, or spray coating, with the only difference between deposition techniques being the degree to which the colloidal solution was diluted by water. The hole transport layer in this architecture was doped spiro-OMeTAD. The dopants used are lithium and *tris*(2-(1H-pyrazol-1-yl)-4-*tert*-butylpyridine)cobalt salts of *bis*(trifluoromethane)sulfonimide both initially dissolved in acetonitrile, alongside 4-*tert*-Butylpyridine (*t*BP).¹⁰ The salts were added to improve conductivity, with morphological improvements benefitting from the inclusion of *t*BP.¹⁰ Doped spiro-OMeTAD was deposited either *via* spin coating or spray coating from solutions of either chlorobenzene or a mixture of chlorobenzene and chloroform respectively. Importantly the spiro-OMeTAD layer was left to oxidise in a dark dry-box overnight to boost conductivity prior to the deposition of a Au back electrode contact.¹¹

3.3 *Fabrication techniques*

3.3.1 *Deposition techniques*

3.3.1.1 *Solution processed*

As previously mentioned, there are a variety of different solution deposition techniques, however in this thesis we focus on only two, spin coating and ultrasonic spray coating.

3.3.1.1.1 *Spin coating*

Spin coating is a commonly used thin film deposition technique which is ideally suited to small scale research. Highly repeatable, and offering the ability to finely control film thickness simply and easily,¹² spin coating is by far the most commonly used deposition technique for PSCs in the literature. Furthermore, the so-called anti-solvent drip method of initiating perovskite nucleation is especially well suited for integration with this particular deposition technique (see **Figure 3.2**).

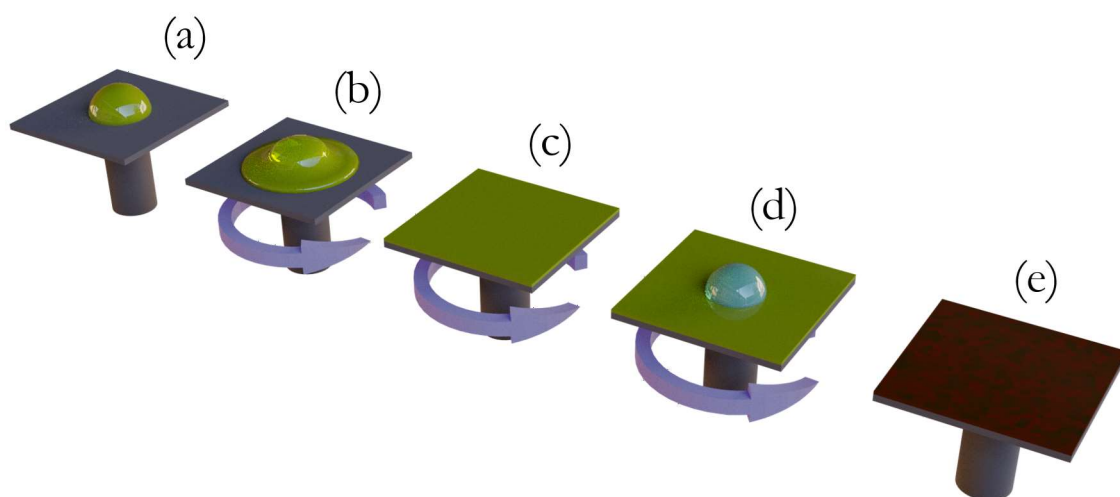


Figure 3.2: (a) admission of solution onto substrate, (b) hydrodynamic spreading and thinning of the wet film, (c) evaporative thinning of the wet film, (d) admission of antisolvent to induce perovskite nucleation, (e) resultant nucleated film.

Here, the substrate of choice is mounted onto a chuck, housing an appropriately sized recess, or held in place by a vacuum. Subsequently, a small amount of solution (10-120 μL) is admitted onto the surface of the substrate, typically *via* pipette. The substrate may or may not already be rotating during the admission stage, termed *dynamic* or *static* spin coating respectively. The solution is spread *via* the centripetal force evenly across the substrate, albeit with the majority (upwards of 90 %) of the solution flung off the edges. During this initial stage, film thinning is driven primarily by a combination of hydrodynamic and radial forces. The wet thin-film then continues to thin as solvent evaporates from the spinning substrate, eventually leaving a thin film of the non-volatile solute.¹² Typically, the angular frequency (ω) is of an order of hundreds to thousands of revolutions per minute, with the spinning time anywhere between 20 – 50 sec. Film thickness is governed by a variety of factors, including angular frequency of the substrate, solution concentration, density and viscosity, and evaporation rate of the solvent or solvent system.¹³

Spin coating, while quick and facile does have some drawbacks. As mentioned above a high degree of material wastage is associated with the technique which damages economic viability when looking to deposit expensive materials such as spiro-OMeTAD, or other bespoke organic molecules. However, perhaps more importantly an inherent limit on scale up exists,

requiring higher and higher spin speeds as the substrate area increases, and an incompatibility with roll-to-roll manufacturing set ups. Finally, of especial importance to the work carried out in this thesis is a non-compatibility with anything barring gently curved or planar substrates, thus rendering even more complex geometries entirely unsuited to this technique.¹²

3.3.1.1.2 Ultrasonic spray coating

As discussed in the previous chapter, there are many forms of spray coating. However, of these, the vast majority rely on pressure based techniques to atomise droplets. Ultrasonic spray coating (USC) however is an outlier in this regard and generates uniform particle size distribution mists, ideal for micron scale wet film coating.¹⁴

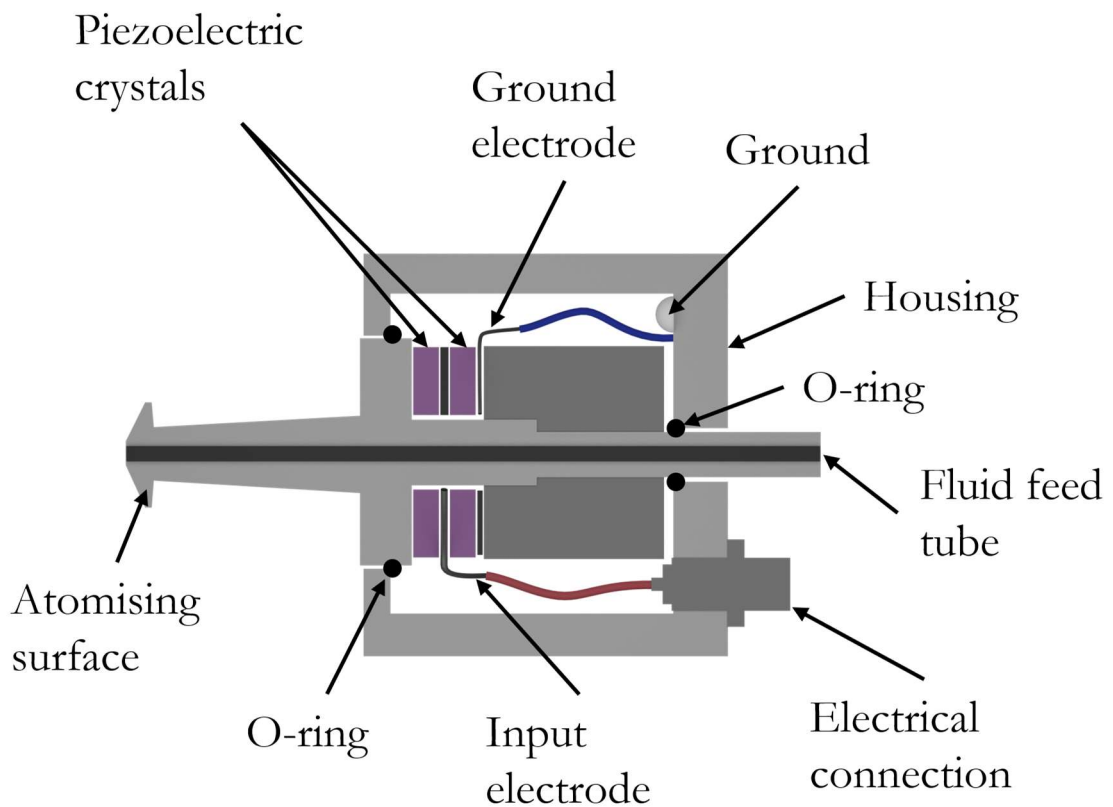


Figure 3.3: Schematic representation of a Sono-Tek ultrasonic spray head, adapted from reference [16].

USC is a relatively recent advancement in spray coating methodology, first developed by Harvey L. Berger, founder of Sono-Tek, for atomising fuel more efficiently during the 1970s energy crisis.¹⁵ Here, a piezoelectric transducer is used to vibrate a tip through which a solution which is pumped (see **Figure 3.3**), or deposited onto, at low pressure. The action of the vibrating tip is to atomise the solution being ejected. The velocity of the generated spray is

two orders of magnitude lower than those produced by pressure based spray processes, eliminating problems associated with overspray. In addition to this, because there is no requirement for a small orifice to generate shear forces, the orifice in an ultrasonic nozzle can be anywhere between 0.6 – 6.4 mm in diameter, significantly reducing potential for clogging and reducing fluid flow rates such that abrasive erosion is nearly eliminated.¹⁶

One of the key attributes of USC is that very low flow rates can be achieved, allowing for the fine metering and control of critical tolerances necessary, for example, in the semiconductor industry. The maximum flow rate is dependent on the size of the atomising surface, and the nozzle aperture size. The minimum flow rates achievable are around 20 % of the maximum flow rate, which is governed by the size of the nozzle aperture and the atomising surface. Lower than this flow results in a non-continuous flow of liquid to the atomising surface, resulting in variable spray plumes. If flow rate is too high for a given nozzle aperture and shape, then atomisation can be inhibited by either ejection of a stream of liquid in the extreme case, or simply too much fluid coating the atomising surface. Therefore, it is critical to choose the correct nozzle size and atomising surface area.¹⁶

The size of a USC nozzle is inversely related to the operating frequency desired. As the particle size decreases with increasing frequency, this means that for a smaller particle size, the nozzle itself must also be scaled down. For microelectronics this is ideal, as it means the 20 % lowest flow rate limit will have a lower absolute value, providing for even finer control. The geometric shape of the atomising surface controls shape of the generated mist. If the surface is flat the mist will take a cylindrical shape, and if the surface is conical the mist will take a conical shape. Control of the shape of this cone is directly related to the angle of the conical atomising surface. Amplitude control is another critical factor, too low results in no atomisation as not enough energy is transferred into the liquid to create capillary waves, too high results in cavitation resulting in large globules being spit from the nozzle.¹⁶

Unlike pressure based spray coating techniques, little directionality is afforded by USC, the mist created simply left to fall howsoever it feels. As such, it is necessary to include a so-called “shaping gas”. This is typically either in the form of a shroud or a jet of inert gas such as nitrogen, and guides the mist towards its intended target.

Spray coating also introduces several process parameters which require careful optimisation to form uniform dry films of the desired thickness. These include solution concentration, spray-

head height and velocity, solution flow rate, number of passes, shaping gas pressure, and tip frequency.¹⁷

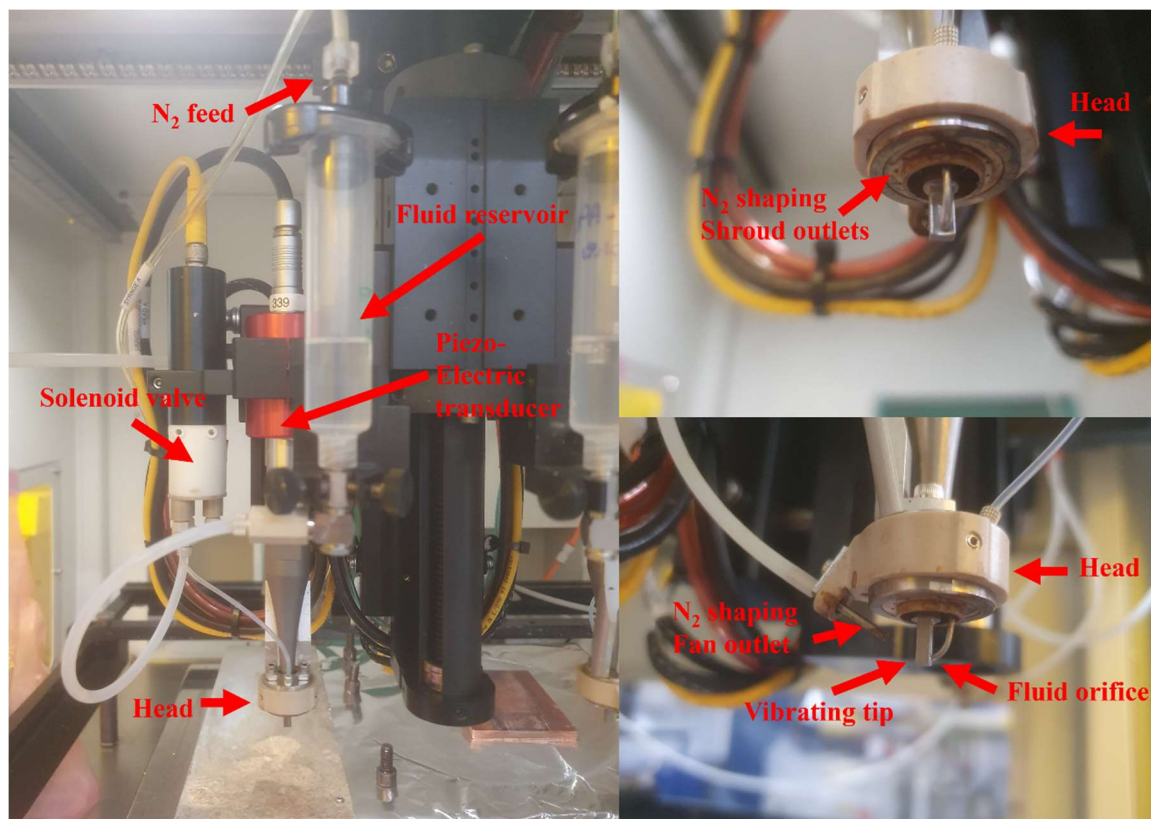


Figure 3.4: Photographs of PRISM system.

Throughout this thesis, a grand total of two ultrasonic spray coaters were used. One of these was a PRISM Ultra-Coat 300 (Ultrasonic Industries) (see **Figure 3.4**). This spray coater was housed in an enclosure to ensure local exhaust ventilation, meaning that solutions were sprayed in the presence of air. The system contains two fluid reservoirs, and two spray heads, all mounted onto a computer controlled motorised gantry. Beneath this, a large hotplate for controlling substrate temperature acts as the primary stage. Solutions to be sprayed were stored in their respective fluid reservoir, with flow rate controlled by N_2 gas fed into the reservoirs at a controllable pressure. The solution was then fed *via* a tube onto a tip being vibrationally driven at 30 kHz by a piezoelectric crystal, which would then shear the solution into a mist as discussed previously. Either a shaping gas fan, or shroud, was then used to control the shape of the sprayed solution as it travelled vertically downwards towards the substrate. This system was typically used for spray coating CTLs, as these are less sensitive to O_2 and moisture than perovskite solutions, and the relatively short distance from the reservoir to the tip meant reduced wastage of expensive small organic molecules such as spiro-OMeTAD.

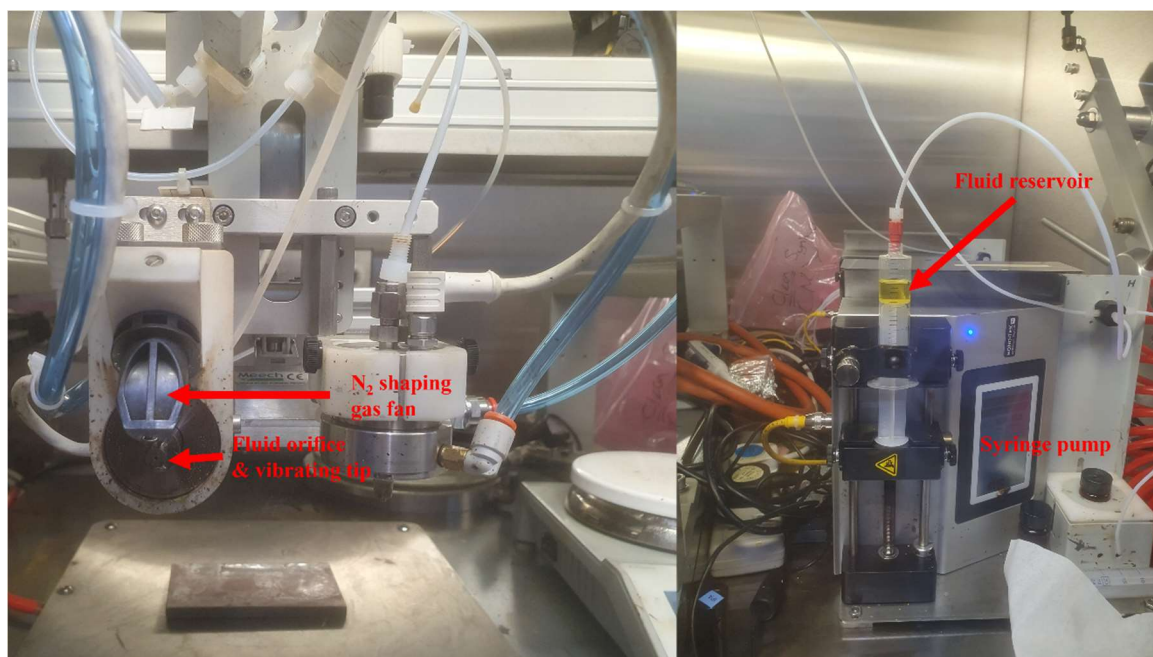


Figure 3.5: Photographs of Sonotek system

The other ultrasonic spray coater used in this thesis, solely for spraying of perovskite solutions was a Sono-Tek Exactacoat (Sono-Tek) ultrasonic spray coater (see **Figure 3.5**), housed in a N₂ filled glovebox. This system was equipped with a so called Impact (Sono-Tek) head. As with the PRISM system, the head was mounted onto a computer controlled motorised gantry, however in this case the fluid reservoirs were instead syringes, with fluid flow rate determined by a syringe driver. This system utilises a nozzle which is driven vibrationally by a piezoelectric crystal, as opposed to the simpler tube and tip set up found on the PRISM. Here, the solution is pumped at low pressure through this vibrating nozzle, generating a mist. Unlike the PRISM system, here the power delivered to the piezo crystal can be controlled, allowing for fine tuning of the average particle size. The impact head only has a single shaping gas configuration, creating a fan directed towards the substrate, however the pressure can be determined by the user.

3.3.1.2 Vacuum processed

Several materials used in this thesis were deposited under high vacuum conditions *via* physical vapour deposition (PVD). In such techniques, a material is heated under vacuum, liberating it from the solid phase where it then travels through the vacuum before condensing upon a substrate. The mean free path is the average distance a gaseous molecule travels before colliding with another molecule. At atmospheric pressure this distance is of an order of hundreds of Angstroms. By reducing pressure, and generating a high vacuum, a longer mean

free path can be created, allowing for particles to travel much greater distances without collisions. This means that the distance between the evaporative source and the substrate can become longer, thus allowing for a significant temperature difference, in turn allowing for materials to condense onto the substrate. Additionally, the generated vacuum removes atmospheric impurities which could be incorporated into the subsequent films, and allows for plasma generation and/or mass flow into the chamber.¹⁸

The vacuum chambers used in this thesis were all fitted with either turbomolecular pumps or cryopumps. Such pumps are capable of creating exceptionally clean vacuums, either by inducing a preferred direction for molecular motion through collisions with a rapidly rotating multi-stage turbine or *via* condensation of gases onto vanes cooled to cryogenic temperatures by a refrigerant.¹⁸ In all cases, chamber pressure was monitored by either by Pirani gauges (Edwards PRL10K) and Penning gauges (Edwards CP25K), or gauges made up of a combination of Pirani and inverted magnetron gauges (Inficon MPG400).

3.3.1.2.1 Thermal evaporation

The first PVD technique we discuss is thermal evaporation. Here, a vacuum chamber is fitted with either resistive sources or Radak sources, or a combination of both. The chamber is first evacuated by a rough pump, either rotary vane or scroll, with either a turbo- or cryo-pump then generating a high vacuum. A current is run through the source of choice, causing it to heat up the material to be evaporated. A viscous cloud of material is generated above the boat or crucible, acting as a point source. From this cloud, particles are ejected, traversing the chamber and condensing on the substrate surface as well as the walls of the chamber.¹⁸ In this thesis, three separate thermal evaporation chambers are used. For the deposition of Au films an Edwards Auto 306 bell-jar evaporator is used. In all cases, deposition rates and thicknesses were controlled *via* the use of Au coated quartz crystal microbalances (QCBs) and Inficon monitors or controllers and software.

3.3.1.2.2 Electron beam evaporation

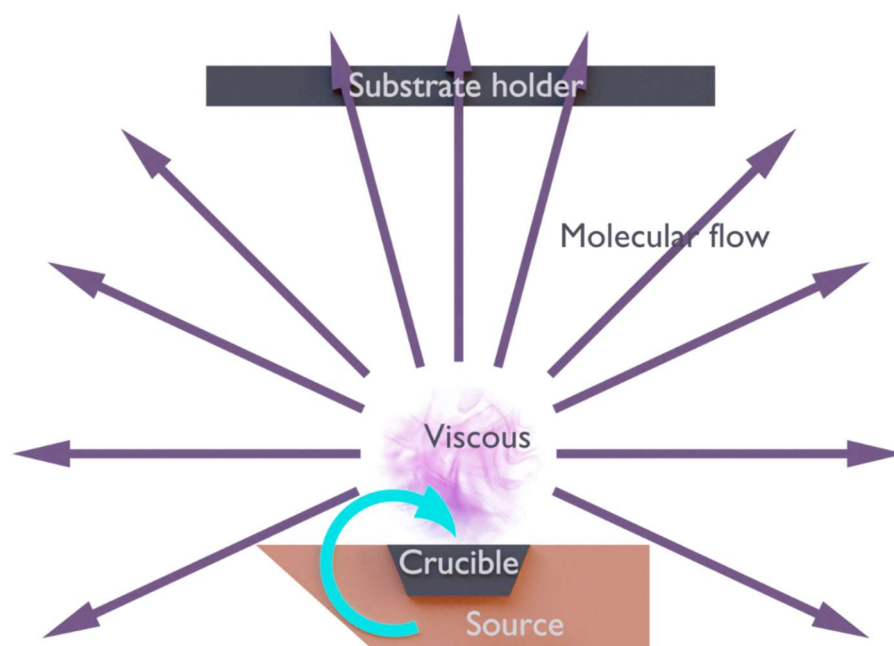


Figure 3.6: Schematic diagram of an ebeam evaporation source, the light blue arrow depicts the electron beam path through 270 ° whereupon it impinges on the target material. A viscous region is then formed directly above the crucible, acting as a virtual point source, the evaporant then enters the molecular flow region whereupon it is deposited onto the substrate, walls and even the source. Adapted from reference [18].

Electron beam (ebeam) evaporation is another example of a PVD technique. Here, an Angstrom Engineering AMOD vacuum chamber is first evacuated *via* a scroll pump, prior to the engagement of a cryo-pump to achieve a high vacuum. A Telemark 274 electron beam source, fitted with 4 x 25 cc crucibles and powered by a Spellman EVA power supply was used for fabrication of thin films. At the heart of the source is an emitter, here a 12 V potential difference is applied over a filament to generate thermionic emission of electrons. These electrons are then subjected to an accelerating voltage of up to 10 kV, guided *via* a transverse magnetic field in a 270 ° arc towards a crucible within which the material of interest is located (see **Figure 3.6**). This arrangement means that the emitter itself cannot contaminate the thin films, and also means that the emitter assembly is not coated by the source material during depositions. The ebeam can be swept across the crucible in a variety of patterns, governed by computer controlled XY coils which manipulate the magnetic field the beam travels through. The kinetic energy of the beam is transferred into the material, causing it to either melt and then evaporate, or sublimate.¹⁸ Deposition rates were controlled *via* Inficon controller and software *via* Au coated QCBs. It is important to note that ebeam evaporation can generate

brehmsstrahlung radiation, which can cause damage to substrates.¹⁹ For some experiments in this thesis additional metal foil masking was required to eliminate such damage. The major advantage of ebeam evaporation over thermal evaporation is the ability to reduce contamination from boats or crucibles, and to evaporate materials with much higher melting points. The increased purity stems from the fact that only a small amount of the charge material melts or sublimes, this has the effect of making the charge material itself analogous to a crucible.¹⁸

3.3.1.2.3 *Magnetron sputtering*

Two radio frequency (RF) magnetron sputterers were used for the work in this thesis. First, an AJA ATC 2200 system where the sputter targets were at the base of the chamber with the substrates rotating above, and secondly an AJA Orion 8 HV where the sputter targets were at the roof of the chamber with the substrates rotating below. Sputtering is a technique whereby a high vacuum is first generated, here *via* a combination of rotary vane and turbomolecular pumps. Next, a plasma is formed by admitting a mass flow of a gas, typically and in this case Ar. A potential difference, of an order of kilovolts, is applied between the sputter target (acting as the cathode) and an anode, which could be the substrates themselves, or a plate upon which they are situated. This causes electrons to pass through the vacuum, colliding with the atoms of Ar thus ionising them and forming a plasma, as depicted in **Figure 3.7**. The Ar^+ ions are then attracted to the target cathode, colliding with it and ejecting atoms of the target material which subsequently travel through the vacuum towards the substrate.¹⁸

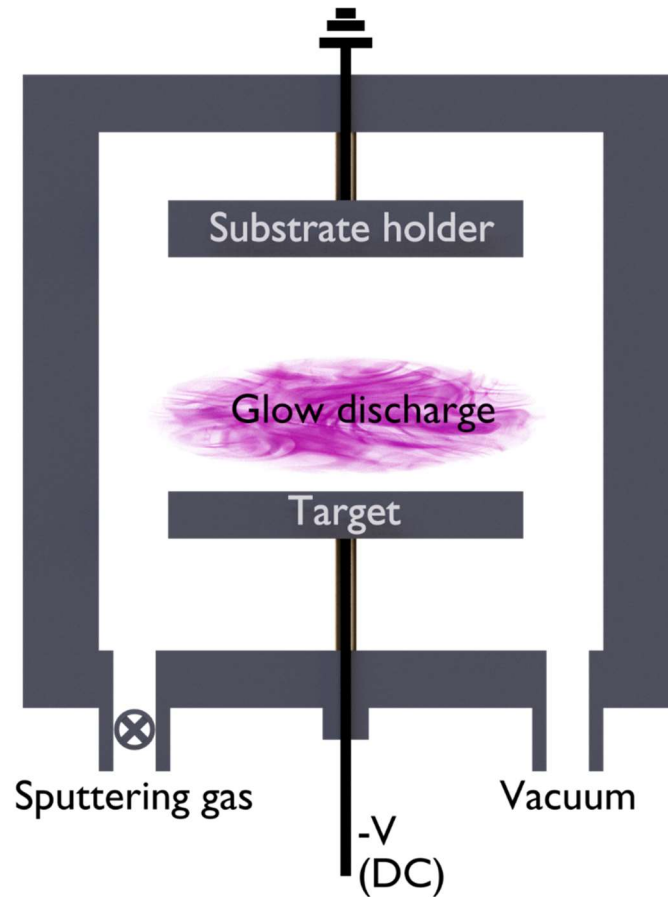


Figure 3.7: Schematic diagram of a DC sputter coater, here ions in the glow discharge collide with the target material and are ejected towards the substrate. Adapted from reference [18].

Magnetron sputtering uses strong magnetic fields to confine electrons, and thus concentrate the plasma close to the target, increasing ion flux and bombardment. If the target is highly conductive, DC sputtering is facile, however for low conductivity targets the necessary voltage becomes unattainable. The solution to this is to use RF alternating current, which reverses the electric field momentarily. In this scenario, a current can flow through a low conductivity dielectric due to the reduction in impedance which a capacitor undergoes at high frequency. At Mhz frequencies this allows for almost any material to be sputtered. Provided the timing of the AC signal is carefully controlled, it is possible to sustain a plasma in this regime, as electrons being passed back and forth between the plasma sheaths can pick up energy when encountering a growing sheath. The final challenge of AC sputtering is how to ensure that Ar^+ ions preferentially strike the target. Fortunately, due to the relative disparity in electron and ion mobility, where electrons are considerably more mobile, the target self-biases itself. In the first half of the AC cycle, a large electron current can flow, but in the second half of the AC cycle a smaller ion current flows, creating a net excess electron flow. This however is

impossible as charges cannot be passed through the capacitor, and therefore the target biases itself negatively such that no current flows.¹⁸

In this thesis magnetron sputtering was used solely for the deposition of ITO films as both bottom and top contacts. As it is necessary to control the Ar flow rate, a balance between the mass flow controller admitting gas into the chamber must be found with the gate valve leading to the turbomolecular pump. As such, the aperture to the turbomolecular pump can be controlled in size, so a steady flow of Ar is admitted equal to that being removed. Due to the relatively high Ar pressure in the chamber, target atoms on their journey to the substrate undergo a large number of collisions. For this reason, the level of directionality in comparison to thermal or ebeam evaporation is much lower.¹⁸ While this leads to improved step coverage, it also means that the sputtered material can leach underneath physical deposition masks. Therefore, it was necessary to space top electrode fingers quite far apart, dramatically reducing the number of devices that could be made per experiment.

3.3.2 *Fabrication processes*

3.3.2.1 *Fabrication of CFRP substrates*

To fabricate CFRP substrates, on the first day rolls of prepreg XC130, either unidirectional or 90 ° woven, and XA120 laminate were removed from freezer storage and allowed to warm to room temperature over 1 hour. 20 x 20 cm squares were cut from both prepreg and laminate and set aside, before the rolls were returned to freezer storage. Ultra flat glass panels were then cleaned using acetone and a razor blade with 6 strokes applied across every part of the panel. The glass panel was then soaked in acetone and wiped clean; this process was repeated 6 times. At this point, Marbocote release agent was applied to the glass panel and smeared all over it. The release agent was then dried off and buffed. This process was repeated 6 times. The XA120 laminate layer was then placed onto the prepared glass mould, and squeegeed in each cardinal direction onto the glass to remove any air pockets and ensure intimate contact with the mould. A ply of prepreg was then placed onto the laminate, and again squeegeed in each cardinal direction. A further two plies were adhered to the laminate/prepreg in the same manner to give a total of 3 plies of CFRP and 1 ply of laminate. Typically, two such stacks could fit onto the glass panel. Onto these stacks, a perforated plastic release film was placed, then a breather fabric was placed onto this. The breather fabric was then used to chart a path to a clear part of the glass panel, and vacuum grommets were placed here side by side, as demonstrated in **Figure 3.8**. A vacuum bag layer was then placed over the entire assembly,

and sealed to the glass panel using butyl polymer tacky tape. The grommets were then sealed by affixing their outer parts to them. Vacuum hoses were then connected to the grommets, and the whole assembly was evacuated to a pressure of 27 inHg. If this pressure was not attained, the entire vacuum bag and sealant assembly would be reapplied. If the pressure was successfully attained, the entire assembly was placed into an autoclave.

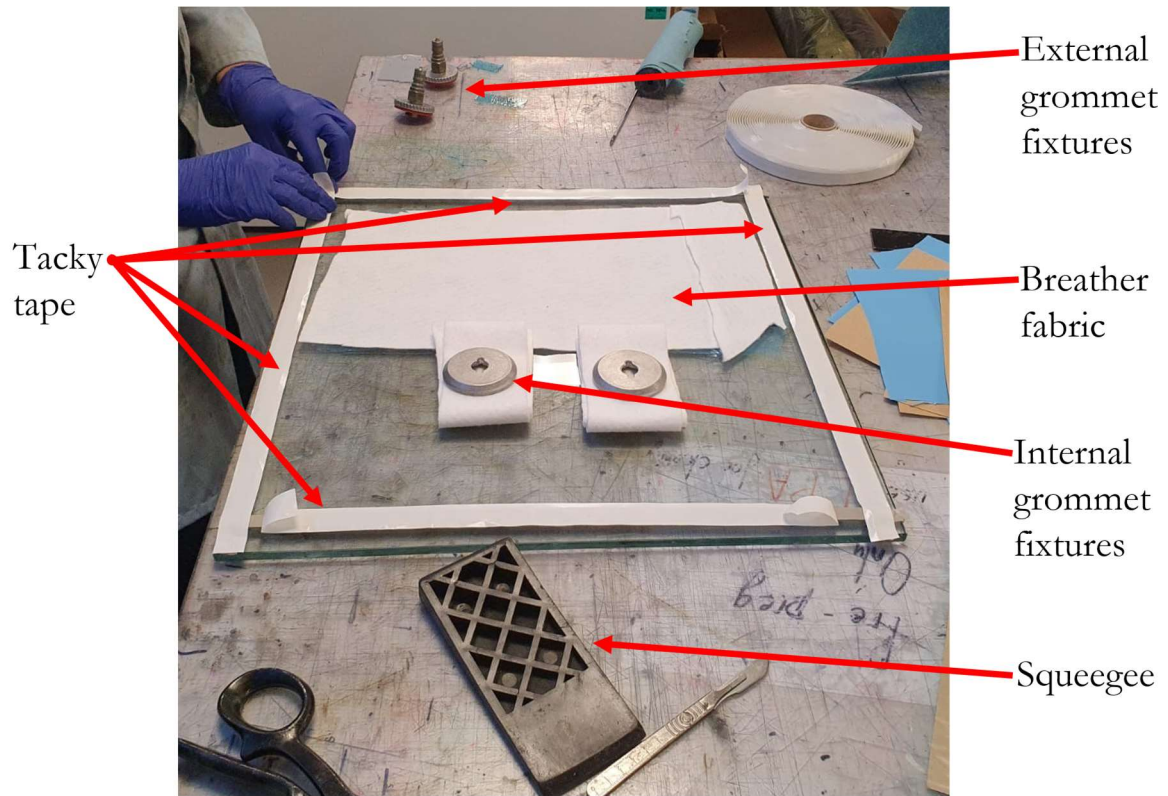


Figure 3.8: CFRP layup in process. Here, a smooth glass substrate has been used as a mould for an epoxy laminate and prepreg layer stack. In this image the laminate and CFRP layers are obscured by the breather fabric. Between the prepreg and the breather fabric is an obscured release layer. The breather fabric is used to create a pathway towards internal grommet fixtures. The entire assembly is surrounded by butyl polymer tacky tape. At this point, the backing tape will be removed from the tacky tape, and a sheet of vacuum bag material will be adhered to the assembly, before the outer grommet fixtures are attached.

For curved substrates, optical grade plano concave lenses were adhered to a glass panel, and a ramp was built around each lens using resin. These lenses were cleaned in the same manner as the glass panels used for flat substrates, and release agent applied in the same manner also. 5 x 5 cm pieces of laminate and prepreg were used to create the same stack on each lens, with the operator's thumb replacing the squeegee. Here, the benefits of a lifetime playing Nintendo are made apparent. Release film and breather fabric were then applied to the back of each

stack, and a path charted to a clear part of the panel using breather fabric. The rest of the vacuum bag sealing process was identical to that for flat substrates.

The autoclave was then run overnight at a pressure of 6 bar (4 bar) for flat (curved) substrates, and a temperature of 100 °C for 4 hours with a ramp rate of 2 °C/min. After this time, the autoclave was brought back to ambient at ramp rates of 0.2 bar/min and 2 °C/min.

Upon successful fabrication of panels, a waterjet cutter, or CNC cutter was used to create 15 x 20 mm substrates. For curved samples a pair of heavy duty composite scissors were used to cut the extra material off, with the edges of the curved samples then sanded smooth.

CFRP substrates were then cleaned by being rubbed with detergent (Hellmanex III, Helma) and rinsed off under running tap water. For unidirectional CFRP substrates, it was then necessary to apply a commercially available primer aerosol, sprayed at a 45 degree angle from a distance of 10 – 20 cm. Onto this primer, a layer of SiO₂ was deposited *via* ebeam evaporation. These substrates were then sent for ITO coating by our collaborators at the University of Loughborough. For woven CFRP substrates, the additional layers were not required, so substrates were sent for ITO coating immediately post cleaning.

3.3.2.2 *Substrate cleaning*

Removal of contaminants is of utmost importance for the fabrication of high quality devices. Such contaminants not only act to impede charge transfer processes, but can also act to cause dewetting effects. This is especially important when thin films are formed *via* spray coating, as there are no shear or meniscus forces to help spread solutions. Improperly cleaned substrates thus demonstrate significantly more pinholes than diligently cleaned ones.

The typical cleaning processes for standard glass/ITO and glass/quartz substrates was as follows. First, if substrates were Zn/HCl etched, the excess Zn/HCl was removed by a combination of rubbing with Hellmanex III and rinsing under running tap water. This step was skipped for prepatterned glass/ITO substrates or glass/quartz substrates. Substrates were then loaded into racks, and submerged in a beaker of 1 % solution of Hellmanex III in freshly boiled deionised (DI) water. This beaker was then placed in an ultrasonic bath and sonicated for 20 minutes to remove organic materials, oils and grease. The substrates were then transferred into a beaker of boiling DI water and agitated to remove as much detergent as possible. The substrates were then removed from this beaker, and the DI water was discarded. The beaker was then charged with another round of boiling DI water, into which the substrates

were then submerged. The beaker was then placed back into the ultrasonic bath where it was sonicated for a further 20 minutes to remove all residual detergent. After this, the substrates were removed and rinsed in acetone, before being submerged in a beaker of acetone and sonicated for a further 20 minutes. Finally, the substrates were removed and rinsed in isopropyl alcohol (IPA), before being submerged in a beaker of IPA and sonicated for a further 20 minutes.

3.4 *Characterisation techniques*

3.4.1 *Device characterisation*

3.4.1.1 *Current-voltage (JV) testing*

Devices were tested immediately after fabrication, with further measurements typically recorded over the next few days as certain perovskite compositions can improve in efficiency over the short term. *JV* measurements were taken under a simulated solar spectrum (AM 1.5G) generated by a Newport 92251A-1000 solar simulator equipped with a Xe arc lamp and the incident intensity at the device calibrated to 1000 W m^{-2} by an NREL-certified Newport Si reference diode. For some measurements in Chapter 6, instead an LED based Ossila solar simulator was used, reflected through a Ag mirror, with the incident radiation calibrated to 800 W m^{-2} by a Newport Si reference diode.

Glass based devices were mounted in Ossila test boards. These boards have spring loaded metal contacts and associated switches. Each device pixel was tested individually, requiring the user to select them using the appropriate switches. Typically, a dispersion of Ag particles in butyl acetate was used to improve electrical contact to the switches. This test board was connected *via* BNC to a Keithley 237 source measurement unit (SMU). Between the incident light and the device, an illumination mask was placed to accurately define illumination area. For 6-pixel devices this area was 2.506 mm^2 and for 8-pixel devices this area was 2.365 mm^2 .

Glass curved devices were tested using the same Newport solar simulator and Keithley SMU, however here the incident light was reflected through 45° using a mirror (Thorlabs) with the devices mounted in a lens holder (Thorlabs). A pair of semiconductor probes were used to make electrical contact to the devices, assisted by the use of Ag paste. Here, a cardboard illumination mask was used to define illumination area, with a measured aperture area of 7.73 mm^2 .

Flat CFRP based devices were mounted in Ossila test boards, however here the device substrate was in contact with the spring loaded pins, as the top transparent electrode necessarily needed to be facing the incident light source. Therefore, electrical connection to these devices was also made using a semiconductor probe station, assisted with Ag conductive paste. Here, an illumination mask with a measured aperture area of 2.385 mm^2 was used to accurately define illumination area. Curved CFRP devices were simply positioned on the breadboard, and contacted using the semiconductor probe station and Ag paste. For these devices, a cardboard illumination mask was fabricated with a measured aperture area of 8.814 mm^2 .

For some CFRP devices tested in Chapter 6 no test board or illumination mask was used. Instead, Ag paste was used to improve electrical connection to Cu tape, which was held securely using Kapton tape. To the Cu tape, crocodile clips were connected, and subsequently connected *via* BNC to an Ossila SMU. Here both pixels were “on” with each cell having roughly an area of 14 mm^2 based on the overlap between the top and bottom ITO electrodes. As such, data gleaned from these experiments report only either the stabilised current output, or normalised PCEs.

JV measurements were typically made by sweeping the voltage bias from -0.2 V through to 1.2 V at a rate of 0.1 V s^{-1} and then back from 1.2 V through to -0.2 V to generate both forward and reverse JV traces. From the JV data, a maximum power point voltage can be determined. This was then used to bias a device under illumination to record its stabilised current density and PCE over a period of time between 1 – 2 minutes. This was typically measured for champion devices to give both an idea of device operating stability, and a truer idea of the device PCE as it somewhat mitigates for the effect of hysteresis between the forward and reverse JV scans.

3.4.1.2 *External quantum efficiency (EQE)*

EQE measurements were taken using an Oriel QuantX-300 (Newport) measurement system. Here, a 100 W Xe arc lamp (Oriel 6252) was used to generate incident radiation. This white light was chopped at a frequency of 25 Hz with a virtual lock-in amplifier prior to being passed through a filter and a monochromator (Oriel CS130B). The now monochrome light was then directed through a beam splitter sending some light to a monitor diode and the rest to the device under test. The monitor diode was calibrated using a calibrated Si/Ge reference

detector prior to testing PV devices, with a Si reference cell used to verify this calibration. In all cases the spot size was focused down to 1.1 x 1.2 mm.

Glass devices were mounted in Ossila test boards, connected *via* BNC to the EQE system. Flat CFRP devices were also mounted in an Ossila test board, with these turned upside down to expose the top ITO electrode to the incident light. EQE measurements were recorded across a spectral range of 325 – 905 nm (EQE uncertainty in this range was $\pm 3\%$).

3.4.2 Thin film characterisation

3.4.2.1 Optical spectroscopy

3.4.2.1.1 Absorption

Absorption measurements were carried out *via* two set ups. First, an Horiba Fluoromax spectrofluorometer was used to collect absorption across a wavelength range of 350 – 1100 nm. Secondly, a bespoke set up using an Ocean Optics DH-2000 BAL Deuterium-Tungsten Halogen white light source, and an Ocean Optics Flame miniature spectrometer.

3.4.2.1.2 Steady state photoluminescence (PL)

PL was collected using a bespoke set up in reflection mode using a 405 nm blue excitation laser, focused onto the sample, with PL emission then collected through a 405 nm filter and an Ocean Optics Flame miniature spectrometer.

3.4.2.1.3 Angular dependant reflectivity

An Ocean Optics DH-2000-BAL Deuterium–Tungsten Halogen source delivered white light *via* optical fibre to one arm of a motorised goniometer. This light was focused onto the sample and an optical fibre on the other arm collected reflectivity spectra from 10° to 70° with 1° angular resolution. Here, the reflected light was coupled to an Andor Shamrock SR-303i-A triple-grating CCD spectrometer for spectral analysis. Absolute reflectance was calculated by calibration of angle resolved intensity spectra against the known reflectance of a Ag standard.

3.4.2.2 Surface profilometry and microscopy

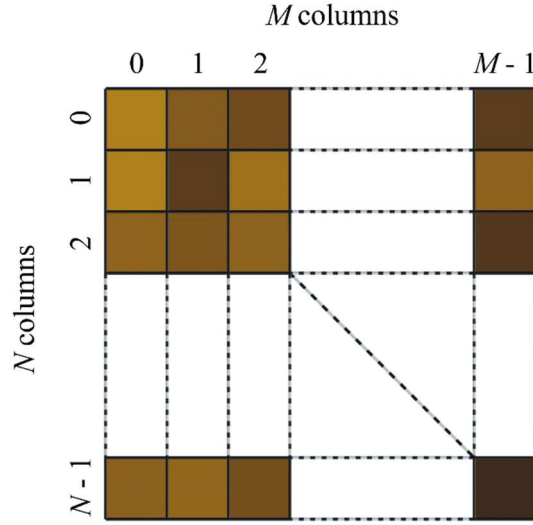


Figure 3.9: Representation of a surface characterised by a height (z) function in x,y (represented by the lightness of the brown boxes), yielding a matrix z_{ij} from which a height distribution can be calculated.

Throughout this thesis there are numerous surface profilometry measurements taken across 3 dimensions so as to create topological maps. These measurements yield data from which roughness values may be calculated. Typically, the data quoted are root mean squared (RMS) roughness (S_q) values, and these are calculated according to the **Equation 3.1**.

$$S_q = \left[\frac{1}{MN} \sum_{i=0}^{N-1} \sum_{j=0}^{M-1} z_{i,j}^2 \right]^{\frac{1}{2}} \quad \text{(Equation 3.1)}$$

Per **Figure 3.9** the surface can be visualised as a 2D grid, where discrete points are sampled to return a value for $z_{(x,y)}$. We then find a matrix of $z_{i,j}$ where $i = 0, 1, \dots, M-1$ and $j = 0, 1, \dots, N-1$. With this in mind, we can see in Equation 3.1, M and N are the total number of points in x and y , while $z_{i,j}$ is the measured height at pixel i,j . We can then determine the distribution of heights $\rho(z)$, the second order moment of which is S_q .

However, it is important to note that there are various limitations of both this formula, and the measurement methodology used to collect the raw data, which can yield results that are not physically accurate. Indeed, in some of the experimental chapters it could be considered that the results of such calculations demonstrate degrees of roughness (or perhaps more accurately, smoothness) that are entirely unrealistic. For this reason, in later chapters the presented data also include other measurements, such as maximum peak heights and minimum pit depths.

Limitations of calculations for S_q include that the result consists of a single value, which gives the interpreter no information regarding the shape of features e.g. jagged versus wavy surfaces can demonstrate the same value of S_q . Equally, variations in spatial topography can also result in identical values of S_q , which is to say that a largely flat surface with a small moiety of spikes might yield a value the same as a surface characterised by an even spread of smooth waves. Another limitation of the calculation is that of symmetry blindness. Here, the deviations being squared removes information regarding the direction of the deviations such that a surface characterised by pits or valleys can demonstrate identical values of S_q to a surface characterised by spikes or ridges. It is therefore worthwhile to include both skewness (S_{sk}), and kurtosis (S_{ku}) values to give the interpreter information regarding symmetry, and sharpness of the surface respectively and are the third and fourth order moments of $\rho(z)$. Furthermore, as deviations are squared the results of the calculation are skewed towards outliers, making it essential to ensure that scratches and artifacts are excluded or avoided entirely. Finally, S_q measurements are heavily reliant on the sampling length of the measurement system.

The measurement methodology also has a significant impact on S_q values. In particular, for surface profilometry techniques the tip or stylus geometry (e.g. physical radius, shape, damage) impacts the degree to which deep crevices or micro-cracks can be accurately imaged. It is also possible that the surface being measured is deformed by the stylus during the measurement. Already discussed are the cutoff limits of the measurement, which have disproportional impact on the final S_q value. Clearly, both lateral and vertical resolution also limit the accuracy of any measurement and therefore the final value for S_q .

3.4.2.2.1 *Stylus profilometry*

A Bruker DektakXT was used for measuring thin film thicknesses and creating large area topographical maps. The DektakXT works by applying a fixed force through a stylus onto the surface of interest. For all measurements conducted in this thesis, the force applied was 3 mg, through a diamond tipped stylus with a tip diameter of 12.5 μm . First, the sample is positioned under the stylus tip using an XY stage. The stage itself is then used to translate sample underneath the tip so as to draw a straight line in the Y direction. The deflection of the stylus is measured using a linear variable differential transformer to create an electrical signal which can be transformed into a height displacement measurement.

Vertical resolution was controlled by setting the maximum range, and horizontal resolution by altering the duration of the measurement for a given line scan length. For map scans, repeated

line measurements were made, with the sample stage moving a fixed distance in X prior to each scan, thus building up a series of line scans producing a topographical map. Here, the resolution in X is simply the chosen fixed distance.

For measurements of thin film thicknesses, films were gently scratched with a razor blade and the depth of the valley formed was measured to extract the thickness. Typically, this would be repeated between 3 and 9 times to give an average thickness. For map scans, a relevant area was selected, with data processed in Gwyddion along with resulting statistical quantities (e.g. RMS roughness).

3.4.2.2.2 *Atomic force microscopy (AFM)*

A few different atomic force microscopes were used in this thesis, with these detailed in the experimental methods sections of the relevant chapters. Here, we will simply discuss the operating principles of AFM, to avoid repetition.

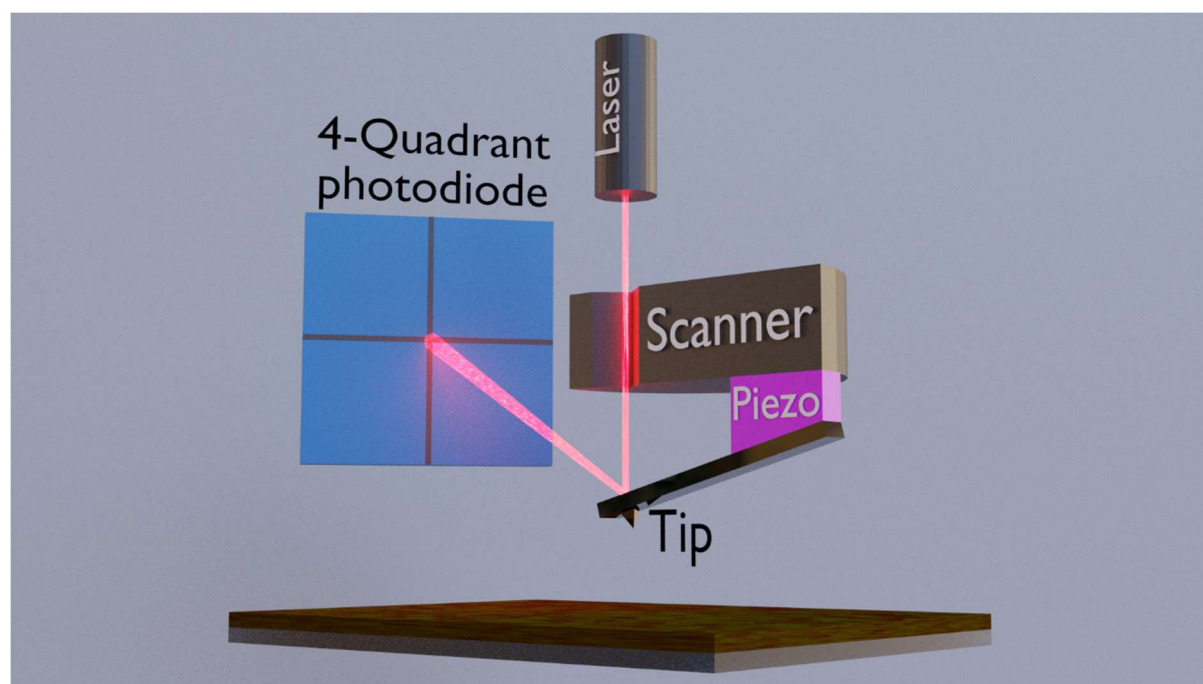


Figure 3.10: Schematic diagram of an AFM using a laser/PSPD deflection/amplitude measurement mechanism.

AFM is capable of carrying out far higher resolution map scans compared to the surface profilometry afforded by the Dektak described above. This method is also capable of resolving atoms themselves, making it one of the most powerful microscopy methods extant. This is primarily down to two reasons, a) the AFM's cantilever tip can be so sharp as to be of an order

of atoms at its point, and b) because a laser shined onto the back of the tip and reflected onto a four-quadrant photodiode, or position sensitive photodetector (PSPD), can record the deflection of the cantilever with exceptional accuracy (see **Figure 3.10**). The cantilever acts as a spring, with a fixed spring constant. This combined with the deflection of the cantilever means a restoring force can be calculated, which is simply the reverse of the force acting upon the tip.²⁰ Note, other mechanisms for detection of displacement are also extant.

There are both attractive and repulsive interatomic forces which dominate at different distances between two given atoms. Here, we can treat the interaction of the tip and the surface of interest at a given point as being comprised of both collective tip-surface interactions and atom-atom interactions. As the tip is moved closer to the surface, initially collective tip-surface attractive forces (e.g. van der Waals) begin to dominate, and the cantilever is deflected closer to the surface. However, as the tip is brought even closer, atomic-atomic repulsive forces between the foremost atoms in the tip and the surface atoms immediately surrounding them cause the cantilever to deflect away from the surface.²⁰

AFMs typically operate in two distinct modes. The first is *contact* mode, whereby the tip is in contact with the surface of interest, and a fixed force is applied to the cantilever such that the tip-surface interaction is in the repulsive regime. As the tip is scanned, and approaches features in the surface, the forces acting on the tip change and the resulting deflection is picked up by the PSPD. A feedback loop uses the deflection measured by the PSPD to change the z-height of the sample (thus keeping the applied force constant), and this data can be used to recreate a z-height image. Due to the force applied, the sample surface can be damaged, and the tip itself undergoes significant wear from lateral forces.²⁰ Contact mode was not used in this thesis.

The second mode is *dynamic* mode. As implied by the name, here the tip oscillates vertically above the surface of interest. The tip can make intermittent contact with the surface, so called tapping mode (here the operating regime is between the repulsive and non-interactive, travelling through the attractive), or can slightly interact with attractive forces (i.e. between the attractive and non-interactive regimes) without making contact, so called non-contact mode. Dynamic modes can be either amplitude (AM-AFM), frequency (FM-AFM), or even phase modulated. FM-AFM is typically used under ultra-high vacuum conditions, and not relevant to this thesis. In AM-AFM the driven cantilever is oscillated close to its natural resonance frequency. As the tip approaches the surface, attractive forces begin to deflect the cantilever, typically reducing its resonance frequency. This results in a change in the amplitude measured at the driven frequency as measured by the PSPD. If the cantilever was driven at a slightly

higher frequency than the resonant frequency, then the amplitude would decrease in this instance. As the tip is backed off, the amplitude change reverses at the driven frequency. Somewhere between these points, a set reference amplitude can be fixed to govern a feedback loop. This loop alters the z-height based on whether the amplitude is higher or lower than the set point amplitude, thus keeping the tip at a fixed height.²⁰

When AFM measurements are conducted under ambient conditions, both the tip and the surface of interest are coated in a thin layer of water. Indeed, at 30 %RH, not dissimilar to an air-conditioned lab, this layer of water is around 0.8 nm thick.²¹ Due to this, when the tip is close enough to measure forces between the tip and the surface, a meniscus layer is formed, creating a capillary force which binds the tip to the surface. Therefore, use of non-contact mode under ambient conditions simply images the water and any other contaminants on the surface, and provides a false image. It is possible to oscillate the tip with the meniscus layer intact, but this requires exceptionally stiff cantilevers and is difficult to perform. As such, non-contact mode is mostly used under ultra-high vacuum. Typically, due to the inherent limitations of lasers and photodiodes under high vacuum conditions, FM-AFM is used as this technique directly measures cantilever frequency without using such devices.²⁰

In ambient conditions, tapping mode is often used instead, as here the tip is oscillated at a much higher amplitude, travelling through the meniscus layer, striking the surface layer and then withdrawing with enough force that it easily breaks the attractive capillary force of the meniscus layer. As the tip makes contact with the surface a true image of the sample can be achieved despite the contaminant layer. However, as the tip only contacts the surface momentarily, lateral forces are minimised and neither the surface or tip are damaged. As such, all measurements in this thesis were conducted in tapping mode.²⁰

All AFM images were processed using Gwyddion, which was also used to extract statistical quantities.

3.4.2.3 *Microscopy*

3.4.2.3.1 *Optical microscopy*

Optical microscopes were first invented in the 1600s, allowing for the observation of sub-mm to around 1 μm length scales. Not dissimilar to a telescope in function, simply pointed down rather than up, they allowed for the observation of biological cells and bacteria. In this thesis, optical microscopy was used to observe larger scale film morphology and for the precise

determination of illumination masks. In the latter instance, individual images were captured using a Carl Zeiss optical microscope and digitally recorded. Such images were stitched together using software such as ImageJ, and digitally processed to accurately determine aperture areas.

3.4.2.3.2 *Scanning electron microscopy (SEM)*

SEM is a technique first conceptualised in the early 1930s by Knoll, and demonstrated in the late 1930s by von Ardenne. It would take another 3 decades before the first commercially available SEM was released onto the market by the Cambridge Scientific Instrument Company in 1965. Here, the diffraction limit of visible light could be overcome by using electrons instead to image objects. The SEMs used in this thesis were an FEI Inspect F and an FEI Nova Nano-SEM 450.²²

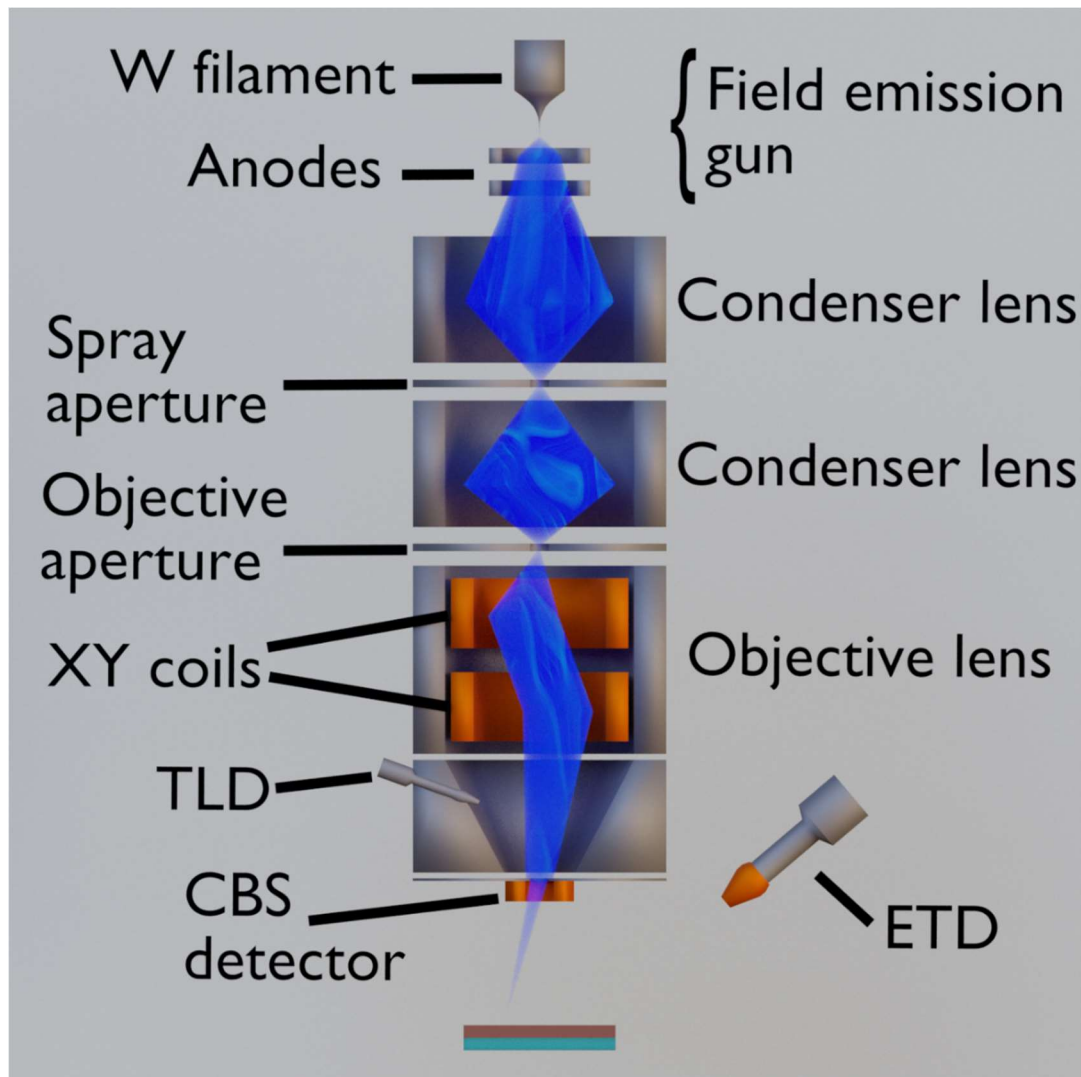


Figure 3.11: Schematic diagram of a typical SEM used in this thesis, adapted from reference [22].

In both SEMs electrons are first generated under vacuum by a field emission gun (FEG). In these cases, the FEG is of the Schottky type, whereby a combination of thermionic emission, and the generation of an electric field results in an electron beam. The emitter is made of a finely sharpened tungsten filament, coated in zirconia. An initial anode is used to generate electron emission with the filament biased relative to this anode at negative 3 – 5 kV. A second anode is used to fully accelerate the beam. This beam then travels through two electromagnetic condenser lenses, before entering an electromagnetic objective lens. The focus of the objective lens is controlled *via* the current entering the coil. Within this lens are scanning coils, which serve to precisely control the destination of the focused beam, allowing it to raster across the imaging area.²² These stages are depicted in **Figure 3.11** for clarity.

The electron beam next interacts with the sample, creating an interaction volume which takes a shape similar to that of an onion. The greater the accelerating voltage, the larger the size of this volume, affecting resolution in techniques such as energy dispersive X-ray spectroscopy or cathodoluminescence.²²

From the very top of the interaction volume, secondary electrons (SEs) are emitted from the sample. Here, the incident electron beam inelastically knocks valence electrons out of the sample, with these emitted in all directions. Due to the inelastic generation of SEs, they have very low kinetic energies, and cannot travel far through the sample. This makes SE imaging highly surface sensitive. Detection of SEs is highly topologically sensitive for this reason, as SEs emitted from the edge of a ridge have a comparatively greater exposed angle from which SEs can escape, rather than being reabsorbed.²²

Back-scattered electrons (BSEs) result from elastic collisions of the incident beam with the nuclei of atoms in the sample. Because of this, BSE images can give insight into the spacial distribution of heavier elements, as the likelihood of elastic scattering increases with Z number. BSEs can travel much deeper in the interaction volume because they retain most of their original kinetic energy, and undergo repeated elastic collisions. For this reason, the lateral resolution is compromised, but they can offer insights from deeper within the sample.²²

SEs are typically collected by an Everhart-Thornley detector (ETD). This detector is usually positioned off to one side of the vacuum chamber at an angle with respect to the incident beam. A slightly positively biased Faraday cage (up to +300 V), positioned across the mouth of the detector, attracts low energy SEs towards the detector. Once arriving at the detector electrons are drawn towards and collide with a highly positively biased (+ 12 kV) scintillator.

This then emits photons which are guided to a photomultiplier tube (PMT). Importantly, the Faraday cage prevents the highly charged scintillator from deflecting the beam. BSEs carry too much kinetic energy to be attracted by the Faraday cage, so only those already somewhat incident on the detector are imaged. To collect only these BSEs, the Faraday cage can also be negatively biased to repel SEs.²²

The majority of the BSEs are collected by a concentric backscatter (CBS) detector. The CBS detector is made up of a series of solid state detectors arranged as concentric rings. It is positioned at the end of the pole piece and does not pick up low energy electrons, thus filtering out SEs.²²

The Nova Nano-SEM 450 is also capable of a high resolution “Immersion” mode. This technique is especially useful for imaging samples easily beam damaged, such as perovskites, as it allows for much lower accelerating voltages and beam currents. This is afforded because the electromagnetic lens used to focus the beam is now also used to include the sample itself within the magnetic field. As such, almost 100% of SEs emitted are guided straight back by suction electrodes towards the pole piece and into the objective lens where a through lens detector (TLD) is able to collect them. This greatly increases the signal despite the lower beam energy, reducing the size of the beam spot and interaction volume, resulting in far superior resolution.²² The TLD itself is similar to the ETD in that it also uses a scintillator, although specific details are closely guarded by the manufacturers.

Samples for imaging were always prepared onto ITO coated substrates, to ensure high conductivity and to minimise charging of the sample. As perovskites are conductive, it was unnecessary to coat the films with a conductive layer, however Ag loaded paste was used to contact the perovskite film and ITO edges to an Al stub which was adhered to the rear of the sample either by Ag paste or latterly with carbon tape. The samples would usually be prepared the day before imaging to ensure all solvent had evaporated from the Ag paste.

3.4.2.4 *X-Ray Diffraction*

XRD was developed on ideas first expounded by Max von Laue, who found that a beam of X-rays shone at a copper sulphate crystal underwent diffraction, simultaneously demonstrating the wave nature of X-rays and the periodicity of crystalline solids. Von Laue demonstrated that it was possible to calculate the wavelength of the incident X-rays if one already knew the interatomic distances between atoms in the crystal. It follows on from this that if one knows

the wavelength of the incident radiation it should be possible to determine the interatomic spacings within a crystal.²³

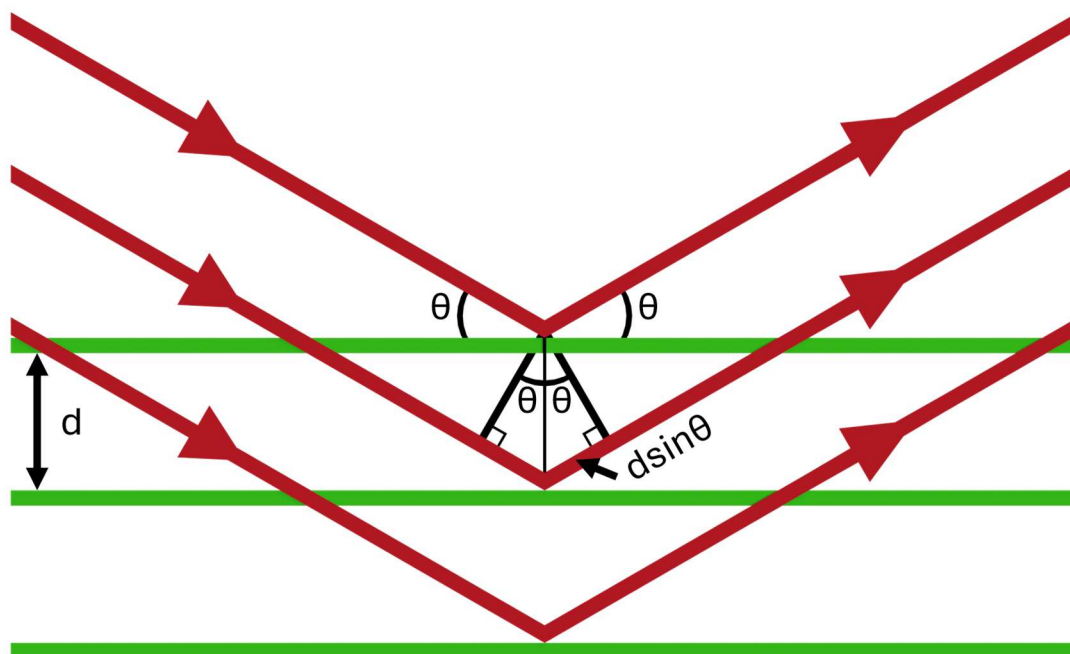


Figure 3.12: Atomic planes (green) spaced by distance (d) cause constructive interference when $2d\sin\theta = n\lambda$.

We have the Bragg condition for constructive interference or scattering (**Equation 3.2**). Here, we can consider parallel sheets of atoms, separated by a distance d , and a source of coherent X-rays directed towards it at an angle θ . One X-ray is elastically scattered by the upper plane, and another by the lower plane. For these scattered beams to constructively interfere, the additional path length travelled by the second X-ray must be equal to $n\lambda$.

$$2d\sin\theta = n\lambda \quad \text{Equation 3.2}$$

For this to be the case, the relationship between θ and d must be $2d\sin\theta$, as demonstrated by **Figure 3.12**. Therefore, providing $2d\sin\theta = n\lambda$, the Bragg condition is satisfied.²³ Bragg constructed a tool by which X-rays with known λ could be directed at a crystal at varying angles and was able to elucidate the crystal structures of various simple crystals.²⁴

In this thesis, all X-ray diffraction (XRD) measurements were carried out using a Malvern Panalytical X'pert³ Powder diffractometer. This is a goniometer based diffractometer, and can be used in either grazing incidence, or Bragg-Brentano geometry. X-rays were generated using a Cu line focused X-ray tube. Here, a tungsten filament was used to generate an electron cloud *via* thermionic emission. These electrons were then accelerated at 45 kV towards a Cu target,

affixed to a water cooled Cu anode, with a beam current of 40 mA. Upon arrival at the Cu target the high velocity electrons collide with the target and emit *bremsstrahlung* radiation (continuous X-rays) as well as characteristic X-rays.²³

Characteristic X-rays are emitted when a target atom is ionised *via* the ejection of a core shell electron. Outer shell electrons then fall into the core shell radiatively, emitting as X-rays of known wavelengths characteristic to these transitions. Typically, $K\alpha_1$, $K\alpha_2$ and $K\beta$ transitions occur, each with a characteristic X-ray wavelength. In the case of Cu, the $K\alpha_1$ and $K\alpha_2$ emission wavelengths are very close to each other, whereas the $K\beta$ peak is usually of a noticeably higher energy. To ensure a single wavelength X-ray beam suitable for XRD measurements the continuous, $K\alpha_2$ and $K\beta$ X-rays ideally need to be filtered. While a monochromator can be used for this, for our purposes it was adequate to simply use a Ni β -filter, filtering out most X-rays of energies somewhere above the $K\alpha_1$ peak.²³



Figure 3.13: A perovskite sample mounted in a bulk sample holder, prepared for XRD measurement. The non-elastic putty is visible through the perovskite film. Here, the sample is positioned at an exact height, and perfectly horizontal, within the holder using a clean microscope slide and the rim of the sample holder.

The incident beam was passed through a series of divergence, Soller and anti-scatter slits, chosen by the operator. The reflected beam similarly passed through a set of slits en route to the detector.

Samples were mounted onto so called bulk sample holders, within which a small amount of high plasticity putty was placed (see **Figure 3.13**). The glass side of the sample was positioned onto the putty, and a clean microscope slide was used to perfectly level the sample within the holder.

3.4.2.5 *X-ray Photoelectron Spectroscopy*

Photoelectron spectroscopy is a technique which fundamentally relies upon the photoelectric effect. Incident photons liberate electrons from a sample of interest, yielding various forms of information depending on the energy of said photons. In X-ray photoelectron spectroscopy (XPS) X-rays are used to probe the sample under a high vacuum. These X-rays are of an energy high enough to eject core-shell electrons, the ejected photoelectrons have a kinetic energy which can then be used to work out their binding energy. The binding energy affords information about the chemical environment which atoms find themselves in and therefore can be used to discern changes in chemical environment when processed differently. Ejected electrons are collected through various electromagnetic lenses used for area analysis and energy adjustment before entering a hemispherical energy analyser. Here, two concentric hemispherical domes with a voltage applied across them are used to separate electrons as a function of their kinetic energy. The photoelectrons then arrive onto a multi-channel electron multiplier plate to record their kinetic energy. XPS is a highly surface sensitive technique, with typically just 10 nm into the film being probed. For through film analyses, Ar⁺ sputtering can be used to sequentially etch layers away between measurements.²⁵

In this thesis, a Kratos AXIS Supra X-ray photoelectron spectrometer was used. This system used an Al target to generate X-rays using an X-ray tube not dissimilar to that described above in the XRD section. Samples were held in place using Cu alloy bars to ensure electrical connection.

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Chapter 4

Nonplanar Spray-Coated Perovskite Solar Cells

4.1 *Publication Foreword*

With the successful demonstration of high efficiency, fully spray-coated triple cation n-i-p perovskite solar cells (PSCs) by our group in 2020, the opportunity for development of rigid, curved PSCs presented itself. Here, we were able to take advantage of the droplet based deposition mechanism afforded by ultrasonic spray coating to coat nonplanar substrates which otherwise cannot be performed *via* meniscus based techniques. Despite this, several challenges remained to be overcome, not least substrate roughness, heat stability and efficacious nucleation of the perovskite film along with more pragmatic concerns including adequate masking for both back contact deposition and *JV* testing under illumination.

Sections 4.2, 4.3, and 4.4 comprise author contributions, the publication main body, and the associated supporting information respectively. Here, we report the results of an investigation into the suitability of our processes for coating substrates held at a series of angles. Unfortunately, it became apparent that our vacuum processing post perovskite deposition step was not suited to curved substrates. Instead, we introduced the use of an air-knife for post-deposition processing. We report on the limitations of this technique at higher inclination angles and the causes for these limitations before demonstrating the successful fabrication of curved, rigid, PSCs.

In the first instance, we sought to fabricate our devices on low cost, laboratory grade watch glasses, however it was soon apparent that such surfaces were much too rough, resulting in devices shorting. We then moved to optical lenses made of CR39, however we were thwarted this time by a coefficient of thermal expansion mismatch between the polymer and the ITO electrode resulting in cracks leading to the formation of ridges shorting the devices once again. Finally, by switching to optical grade lenses made of borosilicate glass we were able to successfully create curved devices.

4.2 *Author Contributions*

T.T., O.S.G., and J.E.B. fabricated and tested devices. T.T., O.S.G., J.E.B. and E.J.C. contributed to the design of the device testing set up. T.T. conducted SEM imaging and XRD, PL and SCLC measurements. E.J.C. conducted transmission measurements and contributed 3D schematic figures to the manuscript. M.E.O.K and T.I.A. conducted cross-sectional SEM measurements. T.J.R. contributed to the design of experiments. P.J.M.I, M.T., L.C.I-O. and J.M.W. developed and

executed the deposition process of ITO onto curved substrates at CREST. D.B.H conducted XPS measurements and XPS data analysis. D.G.L. contributed to the conception and design of experiments, analysis of data and writing of the manuscript in collaboration with T.T., O.S.G., J.E.B. All authors reviewed the written manuscript.

4.3 *Publication Main Body*

Non-planar Spray-Coated Perovskite Solar Cells

Timothy Thornber,[†] Onkar S. Game,^{†#} Elena J. Cassella,[†] Mary E. O’Kane,[†] James E. Bishop,[†] Thomas J. Routledge,[†] Tarek I. Alana^{zi},^{1†} Mustafa Togay,[‡] Patrick J. M. Isherwood,[‡] Luis C. Infante-Ortega,[‡] Deborah B. Hammond,^{*} John M. Walls,[‡] and David G. Lidzey^{*†}

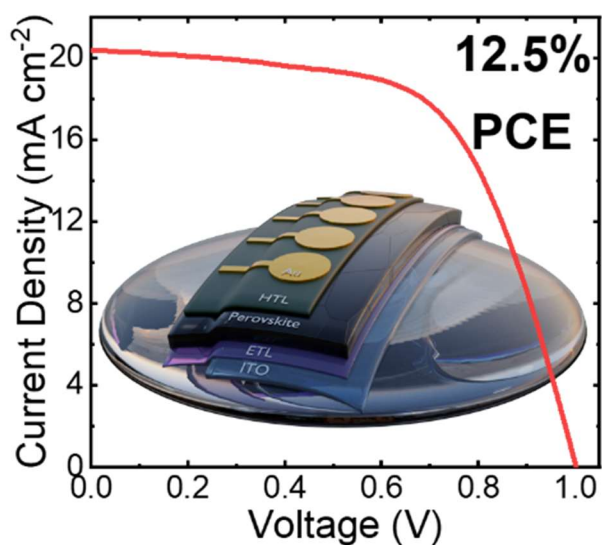
[†]Department of Physics & Astronomy, University of Sheffield, Hicks Building, Hounsfield Road, Sheffield, S3 7RH, United Kingdom

¹Department of Physics, College of Science, Northern Border University, Arar, 73222, Kingdom of Saudi Arabia

[‡]CREST, Wolfson School of Mechanical, Electrical and Manufacturing Engineering, Loughborough University, Loughborough, Leicestershire, LE11 3TU, United Kingdom

^{*}Department of Chemistry, University of Sheffield, Dainton Building, Brook Hill, Sheffield, S3 7HF, United Kingdom

Keywords: perovskite solar cells, curved solar cells, ultrasonic spray coating, integrated photovoltaics, air-knife, scalable fabrication



4.3.1 Abstract

Spray coating is an industrially mature technique used to deposit thin-films and combines high throughput with the ability to coat non-planar surfaces. Here, we explore the use of ultrasonic spray coating to fabricate perovskite solar cells (PSCs) over rigid, non-planar surfaces without problems caused by solution dewetting and subsequent ‘run-off’.

Encouragingly, we find that PSCs can be

spray-coated using our processes onto glass substrates held at angles of inclination up to 45° away from the horizontal, with such devices having comparable power conversion efficiencies (up to 18.3%) to those spray-cast onto horizontal substrates. Having established that our process can be used to create PSCs on surfaces that are not horizontal, we fabricate devices over a convex glass substrate, with devices having maximum power conversion efficiencies of 12.5%. To our best knowledge, this study represents the first demonstration of a rigid, curved perovskite solar cell. The integration of perovskite photovoltaics onto curved surfaces will likely find direct applications in the aerospace and automotive sectors.

4.3.2 Introduction

Since the first reports of perovskite solar cells (PSCs) in 2009,¹ much research has been dedicated to increasing their efficiency, enhancing their operational stability and investigating methods by which they can be manufactured at high volume. Perovskites exhibit a number of very desirable properties that make them excellent materials for solar cell applications, including high optical absorption coefficients,² high defect tolerance,³ long charge carrier diffusion lengths,⁴ low exciton binding energies,⁵ and high charge-carrier mobility leading to low non-radiative recombination rates.⁶ The past 13 years have witnessed improvements in PSC power conversion efficiency (PCE) from 3.8%¹ to a certified 25.7%⁷ in 2022, with the low energy-input solution processing techniques used in their fabrication suggesting that this technology is likely to have a short energy payback time.⁸

In order to fabricate PSCs at volume, a number of roll-to-roll applicable techniques have been explored that exploit the ability of perovskites to be deposited from solution, with such techniques including slot-die,⁹ gravure,¹⁰ blade-coating,¹¹ inkjet-coating,^{12,13} and spray coating.¹⁴ Of these

techniques, spray coating is unique in the fact that the solution delivery nozzle does not need to be positioned close to the surface on which the film is to be deposited. This in principle allows spray-based techniques to be used to rapidly coat non-planar, non-horizontal substrates¹⁵ as is – for example – used to apply surface coatings in the automotive industry. Indeed, ultrasonic spray coating has previously been used to fabricate colloidal quantum dot solar cells on rigid hemispherical surfaces, indicating that this is not an unreasonable target.¹⁶

The fabrication of perovskite layers *via* ultrasonic spray coating typically proceeds *via* a series of steps. Firstly, a perovskite precursor ink is ‘atomised’ into a very fine droplet mist using an ultrasonic spray tip, with a shaping gas then used to direct the droplets towards the substrate. On arrival at the surface, the droplets coalesce to form a wet film, which – following evaporation of the casting solvent – creates a semi-dry film.¹⁷ To produce high quality perovskite films, it is critical to control the growth dynamics of the perovskite crystals.¹⁸ This step can be facilitated using a number of techniques to induce crystal nucleation, including (i) use of an anti-solvent to forcibly eject any remaining carrier solvent,¹⁹ (ii) air-blading using a pressurised gas to rapidly remove the casting solvent,²⁰ and (iii) vacuum assisted solvent removal.²¹ Following this step, films are then annealed to create a homogeneous polycrystalline layer.

Spray coating has now been used to create PSCs demonstrating PCEs of over 20%.²² We note however, that most research and development using spray coating to create PSCs has focused on the deposition of the perovskite layer alone, with the hole and electron transport layers typically being deposited by spin coating. It is clear however that spin coating is unsuited to high-throughput manufacturing and cannot be used to coat non-planar surfaces. We have previously addressed the challenges of PSC manufacture by spray coating and have developed protocols to deposit all solution processed layers in a standard PSC stack *via* spray coating. In our typical process, indium tin oxide (ITO)-coated glass substrates are sequentially spray-coated with a dilute, aqueous colloidal SnO₂ solution, a ‘triple cation’ perovskite²³ (treated by post deposition vacuum processing to initiate perovskite crystal nucleation), followed by a spiro-OMeTAD film to create *n-i-p* architecture devices. Using this ‘fully-sprayed’ process, we have been able to demonstrate PSCs with champion PCEs of over 19%.²⁴

In this study, we explore the spray coating of formamidinium-caesium lead iodide (CsFAPbI₃) perovskite solar cells onto non-planar and curved surfaces. Our objective is to determine whether PSC solutions that are spray-coated onto a non-horizontal substrate adhere to the surface, or simply de-wet and ‘run-off’ causing substantial thickness variations across the substrate. We explore this by spray coating PSC devices onto substrates held at various angles of inclination (up

to 60°) and show that our process is remarkably robust. Indeed, we find that by simply changing the relative spray-head velocity to ensure a film of approximately constant volume is deposited, it is possible to create PSCs having high efficiency and uniformity on surfaces held at angles of up to 45° away from the horizontal. We then use this understanding to spray-cast PSCs onto plano-convex glass substrates, realising devices having a stabilised PCE of up to 11.7%. We believe that this study will prompt research into the seamless integration of PSCs into a variety of environments in which non-planar surfaces are found, including the aerospace²⁵ and automotive²⁶ industries, and the built environment.²⁷

4.3.3 Results and Discussion

We have fabricated planar *n-i-p* PSC devices by spray coating, with devices having the following architecture: glass/ITO/nanoparticle (np)-SnO₂/Cs_{0.17}FA_{0.83}PbI_{3-x}Cl_x/spiro-OMeTAD/Au. The CsFAPbI₃ perovskite system used here has emerged as a promising material for solar cell application due to its improved thermal stability compared to perovskites that incorporate the relatively volatile cation methylammonium (MA).^{28–30} Additionally, this system demonstrates compatibility with gas-jet processing to induce nucleation of perovskite crystallites, greatly increasing its suitability towards upscaling.³¹ In previous work we have used a brief exposure to a coarse vacuum to initiate nucleation (a so-called VASP process).³² Here, the use of an air-knife reduces the complexity of the deposition process as it does not require the use of a time-consuming vacuum-transfer step. We have previously described the use of a gas-jet in the fabrication of spray-cast MAPbI₃ perovskite devices³³ and report the full optimisation of this process when applied to CsFAPbI₃ based devices in ref [34].

In our experiments we deposited both np-SnO₂ and spiro-OMeTAD charge transport layers in low humidity air using a Prism Ultra-coat 300 (Ultrasonic Systems Inc.) ultrasonic spray coater. To fabricate devices, an electron transport layer (np-SnO₂) was first deposited by spray coating a dilute aqueous nanoparticle solution onto 15 mm x 20 mm 8-pixel prepatterned ITO/glass substrates. A CsFAPbI₃ perovskite precursor solution was then spray-coated from DMF and NMP, where the amount of NMP added was equimolar with respect to lead iodide.³¹ We emphasize that we did not add any rheological modifiers to any of the solutions deposited which may have had detrimental effects on device performance. Spray coating was performed using a Sonotek Exactacoat ultrasonic spray coater housed in a nitrogen-filled glovebox. Here the use of a glovebox eliminated the deleterious effects of moisture and oxygen on the crystallisation dynamics of the perovskite. Shortly after the deposition of the perovskite, the semi-wet films were exposed to a nitrogen gas-jet supplied by an air blade (20 psi) to induce crystal nucleation.²⁰ The resultant films were then

annealed at 70° C for 5 minutes, followed by a second anneal at 150° C for 10 minutes to create a dense polycrystalline film. A doped spiro-OMeTAD hole transport layer was then spray-cast from a dilute solution utilising a 1:1 mixture of chlorobenzene and chloroform. In all cases, the individual layers were deposited using a ‘single pass’ technique in which the spray head moved across the substrate at a fixed velocity, fluid flow rate and head height. To help control film drying dynamics and to enhance solution wetting (*via* control of solution surface tension),³⁵ substrates were usually held at a slightly elevated temperature¹⁴ (see Experimental Methods for full experimental details).

Following deposition of the spray-coated layers, 90 nm thick gold contacts were deposited *via* thermal evaporation through a shadow-mask. Device pixels were characterised by recording JV curves under illumination using light from an AM1.5 solar simulator, with each pixel covered by an illumination mask having an aperture of 2.5 mm².

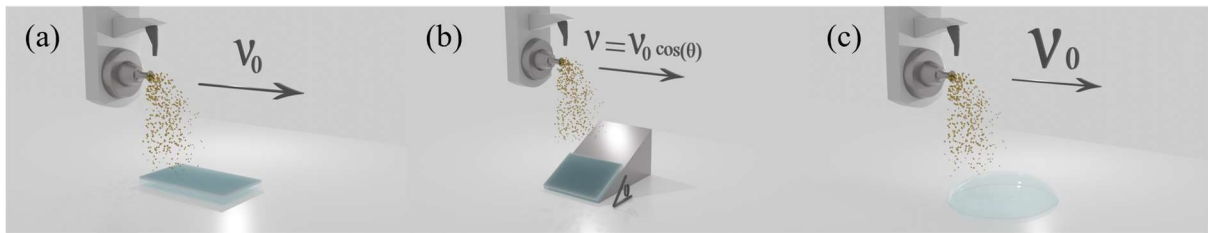


Figure 1: Schematic representation of the experimental set up. Part (a) depicts the standard geometry for spray coating a horizontal substrate, part (b) shows spray coating an inclined substrate, and part (c) shows spray coating onto a curved substrate. In parts (a) and (c), the spray-head speed is v_0 , while in part (b) it is reduced to $v_0 \cos(\theta)$, where θ is the substrate inclination angle as shown. An air-knife used to induce perovskite nucleation is not shown in this figure but can be seen in the schematic shown in Figure S1.

To explore whether spray coating could be successfully used to coat PSCs onto non-planar surfaces, devices were fabricated on flat substrates held at a series of different inclinations (15°, 30°, 45° and 60°) away from the horizontal (see Figure 1(b)). In these experiments, devices were fabricated onto commercially available pre-patterned 8-pixel glass/ITO substrates. These substrates had a nominal sheet resistance of 20 Ω /sq and an optical transmission of 90% at 430 nm (see Figure S2). To control the surface temperature of the inclined substrates, they were mounted on thermally conductive stainless steel ‘wedges’ that were placed onto a temperature-controlled hotplate, with substrate temperature measured using an IR laser-thermometer. These were then compared to control devices that were fabricated from substrates placed flat on a hotplate (see Figure 1(a)). Here, our objective was to determine whether spray coating onto inclined substrates caused solution run-off, resulting in the creation of thin, non-uniform films.

For each angle of inclination, a constant fluid flow rate and head height was maintained. However, as the angle of inclination (θ) increased, the spray-head velocity (v_o) was reduced by a factor of $\cos(\theta)$ in order to maintain an approximately constant mass-transfer of spray-fluid per unit area to the substrate. In all cases, all solution processed layers in the devices were deposited at the same inclination angle with the spray-head velocity adjusted as described above. Here, due to the small size of the substrate, we ignore the relatively small change in the separation-distance between the nozzle and different parts of the surface as the spray-head head passed over the inclined substrate.

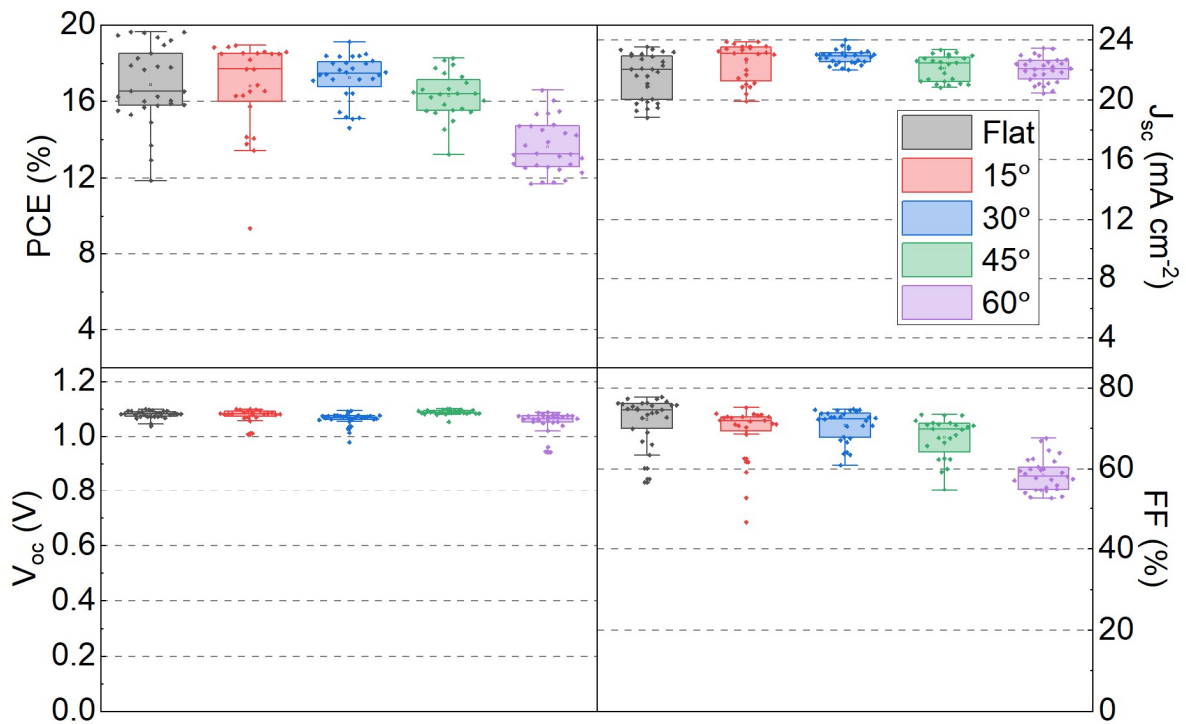


Figure 2: Box-plot summary for key reverse sweep device metrics recorded as a function of inclination angle.

Table 1: Reverse sweep performance metrics as a function of inclination angle

Angle [°]	0	15	30	45	60
PCE [%]	19.6	19.0	19.1	18.3	16.6
	(16.9 ± 2.1)	(16.8 ± 2.4)	(17.3 ± 1.2)	(16.3 ± 1.2)	(13.6 ± 1.4)
J_{sc} [mA cm⁻²]	23.5	23.9	24.0	23.4	23.5
	(21.6 ± 1.5)	(22.5 ± 1.2)	(22.9 ± 0.5)	(22.1 ± 0.9)	(22.0 ± 0.8)
V_{oc} [V]	1.10	1.10	1.09	1.10	1.09
	(1.08 ± 0.01)	(1.08 ± 0.02)	(1.06 ± 0.02)	(1.09 ± 0.01)	(1.05 ± 0.04)
FF [%]	78	75.2	74.8	73.4	67.7
	(72 ± 6)	(69 ± 7)	(71 ± 4)	(68 ± 5)	(59 ± 4)
Dead cells	3/32	0/24	4/32	0/24	3/32

Data pertaining to champion devices are presented in bold, with mean averages and standard deviations presented in parentheses.

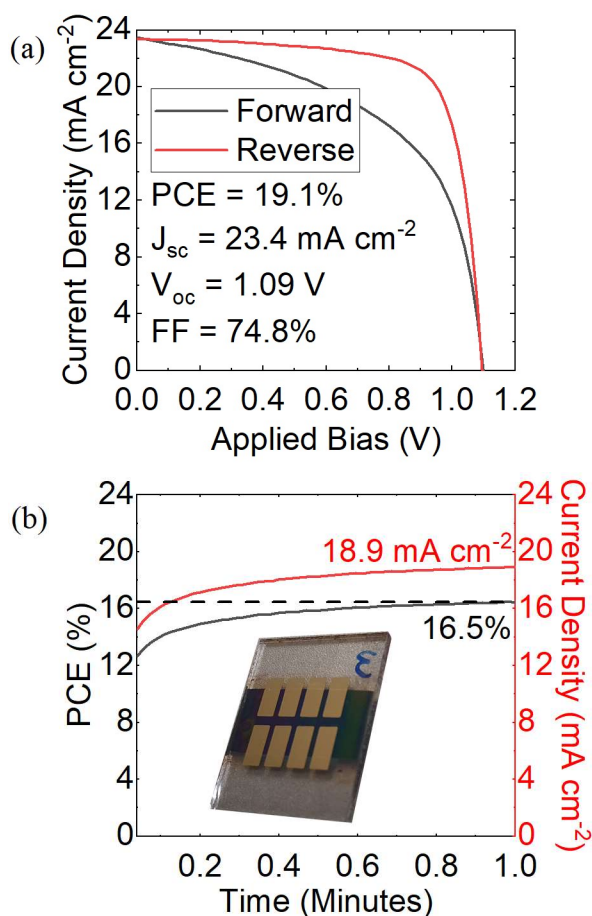


Figure 3: Part (a) shows the current-voltage characteristics of a champion device fabricated at an inclination angle of 30° (metrics derived from reverse sweep), with its stabilised power output (SPO) at a voltage close to the maximum power point recorded over 1 minute shown in part (b). The inset in part (b) is an image of a typical series of device pixels deposited on a $15\text{ mm} \times 20\text{ mm}$ substrate.

Figure 2 summarises the performance metrics of spray-cast devices as a function of deposition angle. Figure 3(a) plots the JV characteristics of a ‘champion’ device deposited onto a substrate inclined at 30° . Here, the device had a PCE of 19.1% and a stabilised power output (SPO) of 16.5% (see Figure 3(b)). For completeness, Table 1 tabulates the average reverse scan performance metrics for each deposition angle, as well as the frequency at which non-functional (“dead”) pixels were observed at each deposition condition. It is clear that these devices suffer from a relatively significant degree of hysteresis that reduces their SPO. This hysteresis has been previously reported in CsFAPbI₃ perovskites,²⁹ and can be mitigated by the introduction of both bulk³⁶ and interfacial passivation.³⁷ We note however that we have not employed either passivation strategy in this study. Future work will explore the use of interfacial passivation agents such as i-BABr, which we have recently shown can be spray-cast on the surface of a perovskite to substantially reduce

hysteresis through the formation of a surface 2D perovskite layer,³⁴ as well as the incorporation of bulk passivating agents such as KPF₆.³¹

As can be seen, we observe no statistically significant change in J_{sc} or V_{oc} as a function of angle up to 60°, however at angles above 45° we observe a reduction in device fill factor (FF). To explore the origin of the reduction in FF, we used X-ray diffraction (XRD) measurements to study the structure of perovskite films deposited at the different inclination angles (see Figure 4). Figure 5 shows complementary scanning electron microscopy (SEM) images recorded from the surface of the same set of films. As can be seen in Figure 4 we observe no significant change in peak positions between XRD diffractograms of films prepared at the different inclination angles, suggesting that in all cases the same perovskite material is formed. This observation is consistent with the fact that devices made from the films all have similar values of J_{sc} and V_{oc} . Significantly, we find that the structure of the films deposited at angles up to 45° are very similar (see Figure 5(a) to (d)), with a dense, polycrystalline grain-structure observed. However, the film deposited at an angle of 60° (see Figure 5(e)) is characterised by a series of submicron pinholes. We suspect that when such films are incorporated into devices, these pinholes act as shunt sites and reduce device FF; a conclusion in accord with our device studies. We believe that the formation of pinholes results from the fact that at high inclination angle, the gas-jet from the air knife no-longer flows across the surface in a laminar fashion. Rather the relative velocity of gas flow across the surface is likely reduced with the flow becoming turbulent (see Figure S1). We suspect that this effect occurs as the relative orientation of the air knife was kept fixed in our experiments, while the angle of the substrates with respect to the horizontal was changed. This reduced, turbulent gas flow at high inclination angle likely results in inhomogeneous solvent evaporation, with any trapped solvent within the film generating submicron pores in the perovskite film upon annealing. Nevertheless, we conclude that the air-knife quench process used here can be successfully applied to process perovskite film deposition over surfaces having inclination angles up to 45°, with improved gas-jet management protocols likely being able to process films over more steeply inclined surfaces.

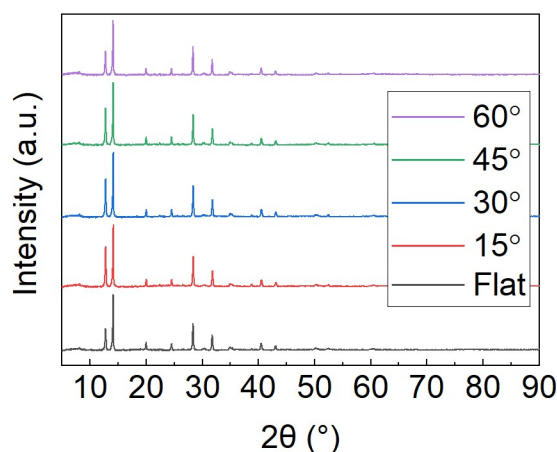


Figure 4: XRD diffractograms as a function of deposition angle.

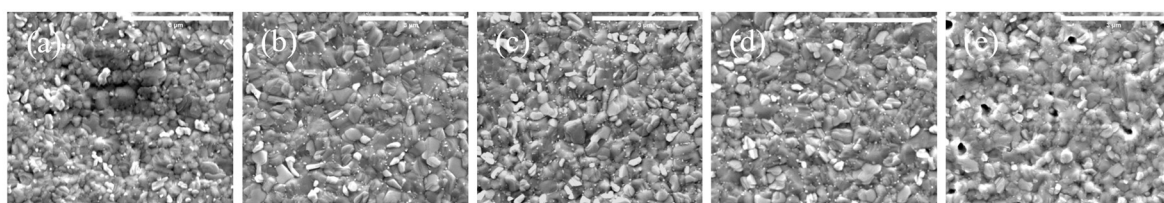


Figure 5: SEM images for perovskite films deposited at increasing angles of inclination. Parts (a-e) represent perovskite films deposited on surfaces held flat and at 15°, 30°, 45° and 60° away from the horizontal respectively. Note the presence of submicron pores in part (e), 3 μ m scale bar inset.

The results presented in Figure 2 indicate that the relatively low viscosity solutions from which devices are processed do not undergo “run-off”, especially at high deposition angles. Interestingly, we observed that the np-SnO₂ solution exhibited a limited degree of flow down the substrate even at low angles of inclination, however this did not appear to be reflected in reduced device performance. We suspect that as the SnO₂ nanoparticles adhere sufficiently strongly to the ITO surface, a small amount of flow does not matter, and that sufficient material remains present to act as an efficient electron extraction / hole blocking layer. In contrast, we did not observe any flow of the perovskite precursor solution or the spiro-OMeTAD solution across the surface at any deposition angle.

To investigate whether the electronic properties of the electron-transfer interface are affected by the angle at which the SnO₂/perovskite were deposited, we recorded steady state photoluminescence (PL) (see Figure S3) on SnO₂/perovskite bilayers deposited at different angles. Here, we noted a small increase in the steady-state PL emission intensity as the deposition angle was increased from flat to 15°, with intensity remaining approximately constant thereafter. We suspect that this may result from a reduction in the relative concentration of K⁺ ions that remain

on the surface due to run off; an effect that is likely to reduce the degree to which the SnO₂ layer was passivated.³⁸ We have also performed space-charge limited current measurements on electron only devices fabricated as a function of deposition angle. Here, it appears that the trap density is largely unaffected at deposition at angles up to 45° (see Figure S4). XPS measurements taken at the SnO₂/perovskite interface indicated no change in chemical environment between bilayers deposited on substrates held either flat, or at 60° (see Figure S5). We have also recorded cross-sectional SEM images of devices fabricated at a deposition angle of 0° and 60°, with our measurements suggesting a high degree of film homogeneity at all angles (up to 60°) explored (see Figure S6).

We have therefore established that devices can be successfully deposited onto surfaces that are not held horizontally. This key result suggests that it should be possible to deposit devices over surfaces that are curved. To test this idea, we have explored using our process to fabricate PSCs over the surfaces of plano-convex glass lenses that have a relatively high radius of curvature (64.4 mm), with their surface having an angle of inclination up to 20°. This radius of curvature is smaller than that which would be encountered on the wing of a solar powered unmanned aerial vehicle³⁹ (see Figure S7) or the roof of an automobile, and thus such substrates should provide a reasonable test of the applicability of spray-cast PSCs for mobile power applications.

To fabricate PSCs onto the lenses, they were first coated by a 120 nm layer of ITO *via* magnetron sputtering in a room-temperature process, with the ITO (and all devices) deposited onto the convex side of the lens. Here, the sputtered ITO had an optical transmission of 77.4% at 532 nm (see Figure S2), and a sheet resistance of 25 Ω/sq, with these values being highly uniform (to within 2%) across the entire curved surface. The ITO was then etched to give two patterned lines which were located slightly away from the centre of the lens. This patterning was achieved using pieces of adhesive Kapton tape that were stuck to the ITO surface to define the area to be protected, with the remaining ITO etched using a standard Zn / HCl wash (see Methods for more details). Following this, a np-SnO₂ layer was deposited using the techniques described above, with the lens located on a hotplate during film deposition. The perovskite layer was then deposited using a similar process used to fabricate films over a flat substrate, however due to the relatively large size of the lens it was necessary to increase air-knife velocity and to make repeated passes of the air-knife over the lens surface. The device was then completed by the deposition of the spiro-OMeTAD layer using techniques described above, followed by the deposition of a gold anode-contact. Here, the gold film was patterned using a conformal silicone-resin evaporation shadow-mask that provided an intimate covering of the lens surface (see Figure S8 for image). To test

devices, they were illuminated using a solar simulator through an aperture-mask held next to the planar side of the lens substrate (see Figure S9) with contact made to devices using a probe-station.

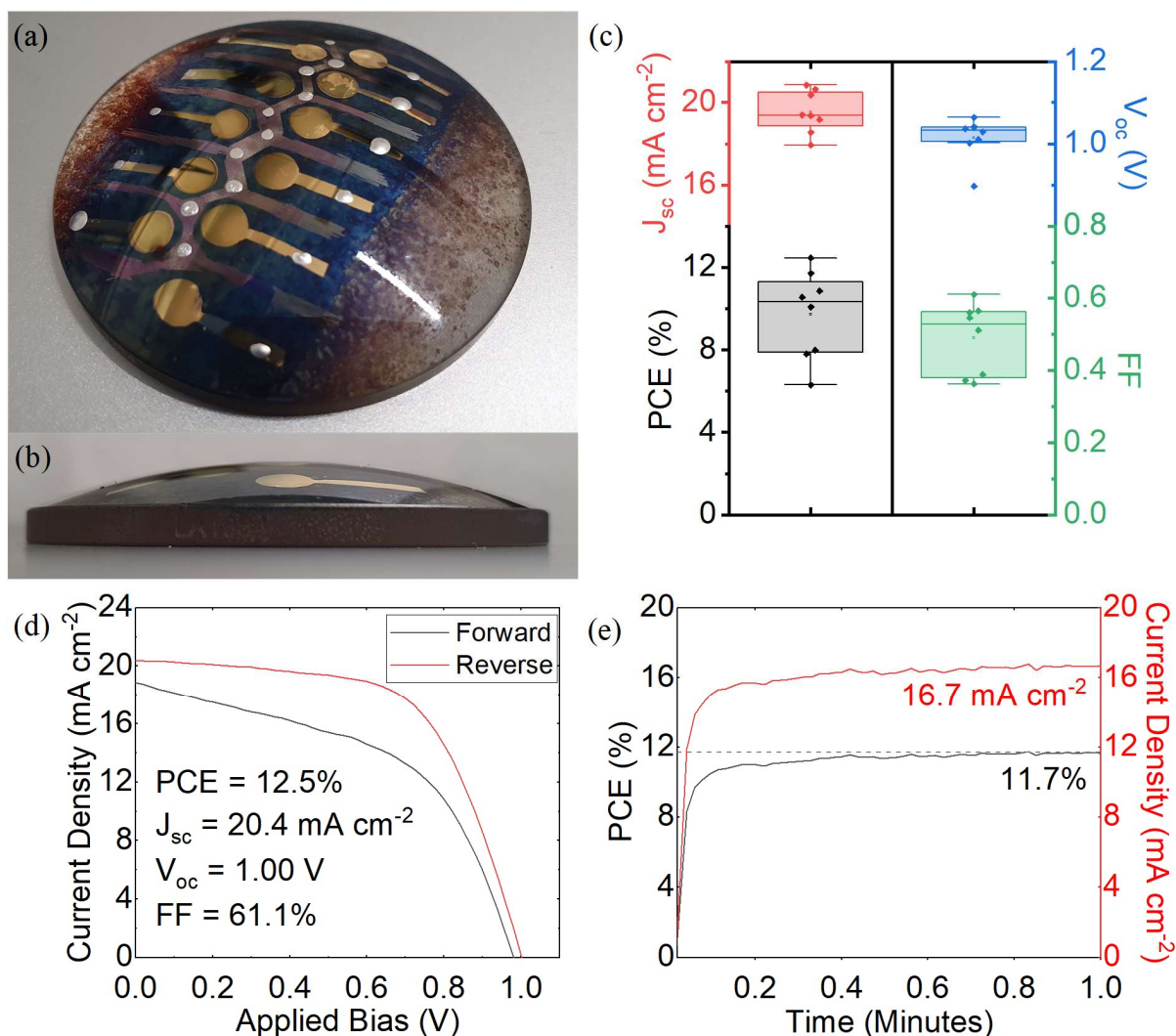


Figure 6: Part (a) shows an image of a fully-sprayed perovskite solar cell on a curved rigid substrate, (b) shows the same device in profile to illustrate curvature, (c) box plot summary of key performance metrics, (d) represents JV data for the best performing cell (metrics derived from reverse sweep), (e) details results of a stabilised measurement carried out near the maximum power point for 60 seconds.

Figure 6(a) shows an image of a series of 11 devices fabricated onto the surface of the curved lens. Here, the grey material that is visible on the surface of the gold contacts is a silver loaded paste that was used to improve the electrical connection to the anode and cathode contacts. The JV curve of a champion device is shown in Figure 6(d); here we determine a PCE of 12.5%, J_{sc} of 20.4 mA cm^{-2} , a V_{oc} of 1.00 V and a FF of 61.1%. The stabilised PCE of this device held close to its maximum power point is shown in Figure 6(e) and had an efficiency of 11.7%. To assess the uniformity of the perovskite and spiro-OMeTAD depositions across the surface of the curved

device, we have determined the relative thickness of the SnO_2 /perovskite and SnO_2 /perovskite/spiroOMeTAD layers using a surface profilometer, as a function of distance from the centre of the lens. Such measurements indicate that the thickness of such solution processed layers is relatively uniform across the entire substrate (see Figure S10).

We believe these results clearly demonstrate the feasibility of spray coating high efficiency PSC devices over curved surfaces. It is clear however that a practical utilisation of this technology would rely on devices in which light enters through a transparent top contact;⁴⁰ such a development would allow perovskite PV to be directly integrated onto the surface of an automobile or onto an aeroplane wing. We note that the efficiency of the devices presented here was partly limited by hysteresis effects that can be suppressed through the use of both bulk⁴¹ and interfacial passivation techniques.³⁴ We also expect further enhancements in device efficiency through the use of surfactants to improve surface coverage of the perovskite layer⁴¹ and through optimization of the processes used to spray-cast the charge transport layers.^{42,43} We note that spray coating can be used to rapidly coat large areas at high-speed, potentially allowing PSCs to be fabricated over relatively large-area substrates.²⁴ We expect the combination of spray-coating with device modularisation techniques (e.g. *via* laser patterning)⁴⁴ to allow spray coated modules to be fabricated over very large areas. Such an approach should be capable of generating mobile power with a higher degree of specific power (power to weight) compared to current generations of laminated solar cell technologies.⁴⁵

4.3.4 Conclusion

We have demonstrated that we can fabricate fully spray-coated PSCs having the structure glass/ITO/np- SnO_2 / $\text{Cs}_{0.17}\text{FA}_{0.83}\text{PbI}_{3-x}\text{Cl}_x$ (CsFAPbI₃) /spiro-OMeTAD/Au, with high efficiency (up to 19.1%) realised even when the device substrates were held at an angle up to 30° away from the normal. The deposition of spray-cast films appears relatively tolerant to the fact that such films are not held horizontally; indeed, we observed very little flow of spray-cast CsFAPbI₃ perovskite precursor and spiro-OMeTAD solutions across a surface, even when it was held at an angle of up to 60° away from the normal. We build upon this finding and fabricate PSCs over the surface of a convex glass lens. Here, we have developed techniques to pattern both the ITO and metallic charge extraction contacts over highly curved surfaces. Using this process, we fabricate devices onto the surface of a convex lens having a maximum power conversion efficiency of 12.5%. We expect that the processes developed here will have direct application in the development of mobile solar power for automotive and aerospace applications. Looking further ahead, we also expect this process to

be capable of the deposition of perovskite⁴⁶ and organic light emitting diodes⁴⁷ on non-planar substrates, creating new opportunities for the development of integrated lighting and displays.

4.3.5 Experimental Methods

Materials: Perovskite precursor salts, PbI₂ (TCI), PbCl₂ (Sigma), FAI (Ossila), and CsI (Sigma) were weighed into a vial, with the following mass of material added to each ml of DMF: PbI₂ (645.4 mg), PbCl₂ (38.9 mg), FAI (119.8 mg), and CsI (61.8 mg). These salts were dissolved in DMF before the addition of 135.0 μ L of NMP (equimolar with respect to PbI₂). The resultant perovskite precursor solution had the composition Cs_{0.17}FA_{0.83}PbI_{3-x}Cl_x and had a concentration of 1.4 m (prior to addition of NMP).

Device Fabrication: Small area devices were fabricated on 15 x 20 mm ITO substrates (20 Ω /sq, Ossila Ltd), with substrates prepatterned into 8 individual pixels. Curved devices were fabricated on uncoated optical grade borosilicate glass plano-convex lenses (Thorlabs, LA1384). Lenses were sequentially cleaned in Hellmanex, deionised water and IPA in an ultrasonic bath. Substrates were then exposed to UV ozone for 20 minutes. Finally, they were coated with ITO *via* magnetron sputtering before being etched with zinc powder and 4 m HCl solution into a stripe for device fabrication.

Table 2: Summary of head velocities for use on inclined substrates

Angle [°]	Head velocity [mm s ⁻¹]		
	SnO ₂	Perovskite	Spiro-OMeTAD
Flat	180	80	150
15	174	77	145
30	156	69	130
45	127	57	106
60	90	40	75

To deposit the electron-transporting layer (ETL), a commercially supplied np-SnO₂ solution (15% wt aqueous colloidal solution) was diluted in deionised water at a ratio of 1:70. Spray deposition was conducted using a Prism Ultra-coat 300 ultrasonic spray coater in air. The spray head was moved across the substrate at a velocity of 180 mm s⁻¹ (V_0) and was maintained at a height of 30 mm above the bench-top. When spray coating substrates inclined at an angle θ , the head velocity was reduced to a value V , where $V = V_0 \cos(\theta)$ (see Table 2). The same parameters were used to coat both flat surfaces and curved substrates. All substrates were held at 30 °C during deposition, with fluid flow rate controlled by a nitrogen feed into the fluid reservoir at a pressure of 10 mbar.

After deposition of the np-SnO₂ layer, the films were allowed to dry for 45 s before being annealed for 30 minutes at 150 °C and subsequently exposed to UV ozone for 20 minutes.

The SnO₂ coated substrates were then moved into a nitrogen-filled glovebox for perovskite layer deposition. This was performed using a Sonotek Exactacoat ultrasonic spray coater equipped with an “Impact” head. Substrates were held at 30 °C throughout the deposition process. This was achieved using a single pass at a head height of 100 mm with a head velocity of 80 mm s⁻¹. The head velocity was reduced (see Table 2) when spray coating inclined surfaces. The perovskite precursor solution was delivered at a flow rate of 1 mL min⁻¹ through a tip driven at 2 W, using a N₂ shaping gas at a pressure of 3 psi. After a delay of 20 s, substrates were then exposed to a nitrogen air-knife (20 psi) moving at 3 mm s⁻¹. The film was then annealed for 5 min at 70 °C before being removed from the glovebox and further annealed for 10 minutes at 150 °C under ~40-50% relative humidity. The same parameters were used to coat both flat surfaces and curved substrates, except the air-knife traversed the substrate at 10 mm s⁻¹ over the curved substrates and completed a total of 4 passes across the substrate.

For deposition of the hole-transporting layer (HTL), a solution of 2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD) at a concentration of 86.6 mg mL⁻¹ in chlorobenzene was prepared. This solution was doped with 4-tert-butyl-pyridine (TBP Sigma), lithium bis(trifluoromethanesulfonyl) imide (LiTFSI Sigma) and tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine) cobalt(II) di[hexafluorophosphate] (FK209 Co(II) PF₆ Dyesol). Here, 34 µL of TBP, 20 µL of LiTFSI (500 mg mL⁻¹ in acetonitrile) and 11 µL of FK209 (300 mg mL⁻¹ in acetonitrile) were added per 1 mL of spiro-OMeTAD solution. This solution was then filtered and diluted to 14 mg mL⁻¹ in a 1:1 chlorobenzene and chloroform solvent system. Deposition was carried out in air using a Prism Ultra-coat 300 ultrasonic spray coater. The spray-head traversed the substrate at a rate of 150 mm s⁻¹ at a head height of 60 mm. The head height and velocity used are summarised in Table 2. During deposition, substrates were held at 30 °C with fluid flow rate controlled by a nitrogen feed into the fluid reservoir held at a pressure of 20 mbar. Curved and flat surfaces were coated using the same deposition parameters.

Following deposition of solution processed layers, dry films were allowed to oxidise overnight in dry air before 90 nm gold back contacts were thermally evaporated in an Edwards bell jar evaporator at a pressure of $\approx 10^{-6}$ mbar through a metal evaporation mask to yield individual cells. For the curved devices, evaporation was performed through a conformal mask made of room temperature vulcanising silicone resin (Easy Composites, AS40). This mask was fabricated by mixing of 6 mL of resin and hardener, which was then poured over an identical, uncoated, lens

which was then allowed to cure for 24 hours. The silicone mask was then peeled off the lens and a series of 5 mm diameter holes were cut (see Figure S8)

Device Characterisation: A Newport Solar Simulator calibrated using a silicon reference cell (Newport) at 1000 W m^{-2} , operating at AM 1.5 illumination was used to test devices. Illumination masks with areas of 2.5 mm^2 were used to test planar devices. For curved devices an illumination mask was fabricated with a measured aperture area of 7.73 mm^2 (see Figure S9). JV characteristics of each device were recorded using a Keithley 237 source measurement unit. Planar devices were scanned at a rate of 0.4 Vs^{-1} from -0.0 V to 1.2 V and back to -0.0 V , while curved devices were scanned at the same rate from -0.1 V to 1.2 V and back to -0.1 V . The maximum power point voltage was determined from the JV sweeps, with stabilised measurements recorded while holding the device near this voltage for 60 seconds and measuring the photocurrent.

X-ray Diffractometry: Samples for XRD were prepared in the same way as those used in device fabrication. Measurements were performed using a Panalytical X'pert³ diffractometer equipped with a Cu line focus X-ray tube operating at a voltage of 45 kV and a current of 40 mA. Data was collected *via* a 1D-detector in Bragg-Brentano geometry.

Scanning Electron Microscopy: Samples for SEM were prepared in the same way as those used in device fabrication. Imaging was performed using an FEI Inspect F field emission gun SEM at a working distance of 10 – 12 mm operating at an acceleration voltage of 5kV. Cross-sectional SEM imaging was performed using an FEI Nova Nano-SEM 450 field emission gun SEM at a working distance of 4.6 - 4.7 mm operating at acceleration voltage of 1 kV.

Steady-state Photoluminescence: Samples for PL measurements were fabricated in the same way as those used in device fabrication. Samples were excited using a 405 nm continuous wave blue laser with PL emission collected *via* an optical fibre connected to an Ocean Insight Flame spectrometer.

Space-charge Limited Current: Samples for SCLC measurements were fabricated in the same way as those used in device fabrication, except that the hole-extracting contact was replaced by a PCBM/Ag which was used to extract electrons. Dark JV curves were then measured using a Keithley 237 source measurement unit.

X-ray Photoelectron Spectroscopy: Samples for XPS were prepared in the same manner as those used in device fabrication. XPS measurements were conducted at the Sheffield Surface Analysis Laboratory. Data was collected using a Kratos AXIS Supra X-ray photoelectron spectrometer

under ultrahigh vacuum conditions using a monochromatic Al source (1486.6 eV). Samples were fixed in place using Cu alloy bars to ensure electrical connection between the sample surface and the sample stage. Samples were etched using an argon cluster source (Ar_{1000}^+) at 10 keV with an ion beam current of 27 nA. High resolution spectra were then collected over a 60 s sweep for I 3d, O 1s, Sn 3d and In 3d transitions. For Pb 4f, it was necessary to collect spectra using two sweeps.

Notes

D.G.L. is co-founder and a director of the company Ossila Ltd which retails materials and equipment used in thin-film device development, including perovskite photovoltaics.

ACKNOWLEDGMENTS

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4.4 Supporting information

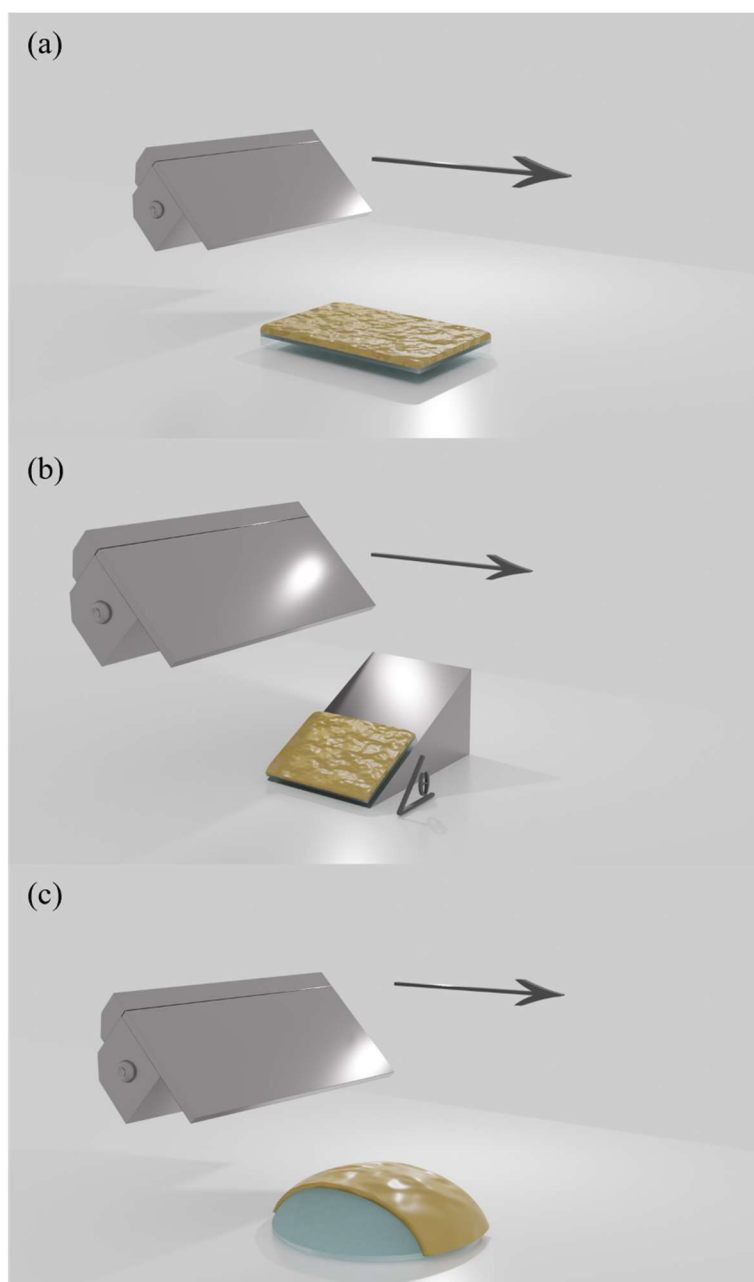


Figure S1: Schematic representation of the experimental set up showing the orientation of the air blade and its direction across the substrate. Parts (a-c) represent configurations for deposition onto a flat, angled and curved surface respectively.

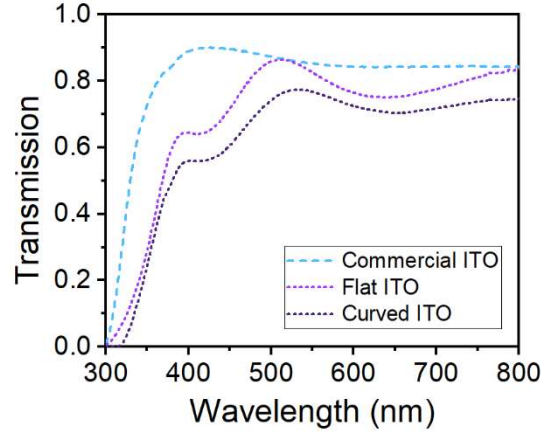


Figure S2: ITO transmission spectrum for a) commercially available ITO substrates ($20 \Omega/\text{sq}$) used for angle dependant depositions, b) flat substrate with ITO deposited ($23.7 \Omega/\text{sq}$) via the same process as that for curved substrates, c) curved substrate with ITO deposited ($25.0 \Omega/\text{sq}$) via magnetron sputtering.

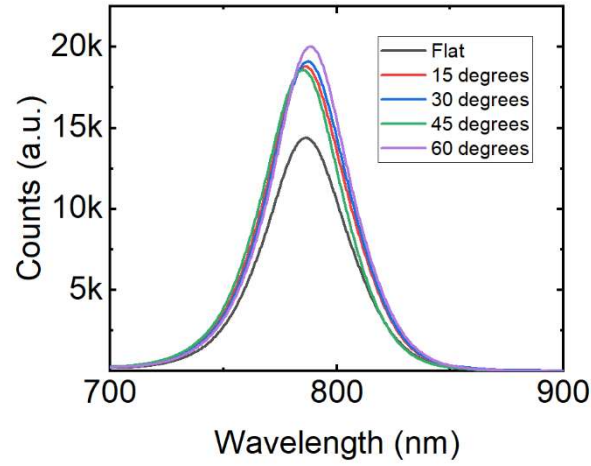


Figure S3: Steady-state photoluminescence of SnO_2 /perovskite bilayers held at 0° , 15° , 30° , 45° and 60° during film deposition. We note that there is a slight increase in photoluminescence intensity when the films are deposited at higher angles.

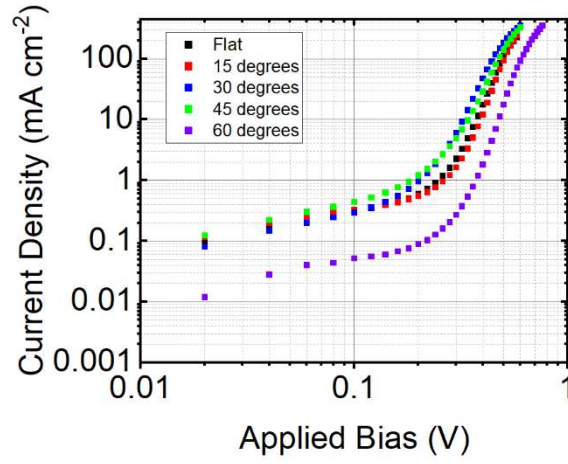


Figure S4: Space-charge limited current measurements of electron only devices (ITO/ SnO_2 /perovskite/PCBM/Ag) where SnO_2 /perovskite layers were deposited at 0° , 15° , 30° , 45° and 60° . We note there is no significant change in the dark JV curve up to 45° . We have extracted trap densities of 1.61×10^{17} , 1.74×10^{17} , 1.35×10^{17} , 1.59×10^{17} and $1.97 \times 10^{17} \text{ cm}^{-2}$ for bilayers deposited at 0° , 15° , 30° , 45° and 60° respectively.

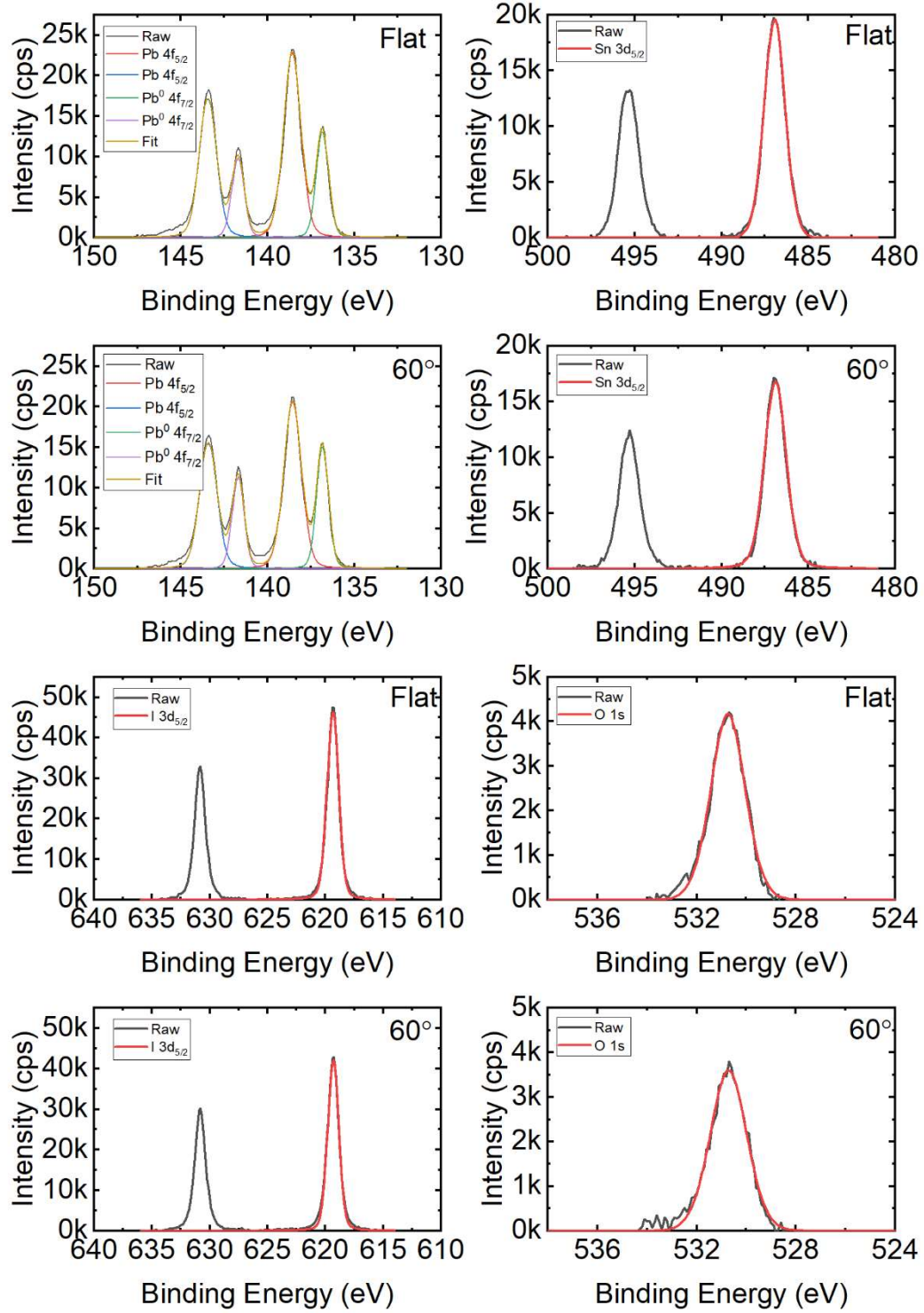


Figure S5: X-ray photoelectron spectra of SnO_2 /perovskite interface where SnO_2 /perovskite layers were deposited at 0 and 60°. We note that there is no significant change in chemical environments at different angles of inclination.

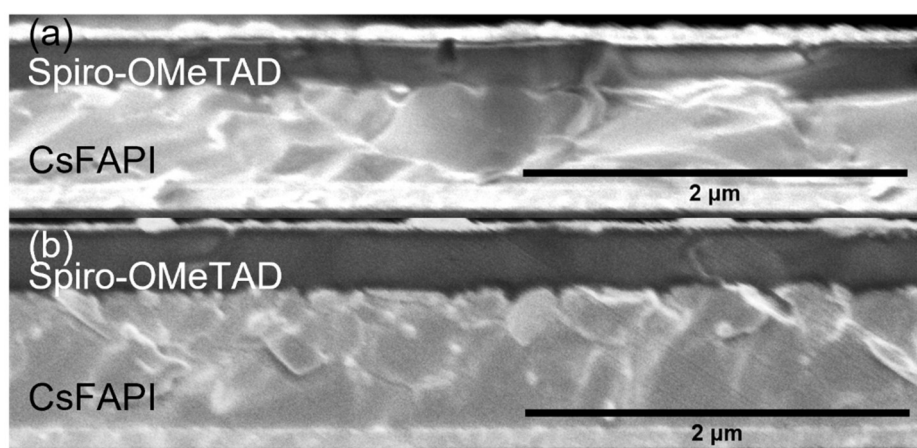


Figure S6: Cross-sectional SEM images of flat devices deposited at a) 0° and b) 60°. A similar degree of film uniformity is observed in both images.

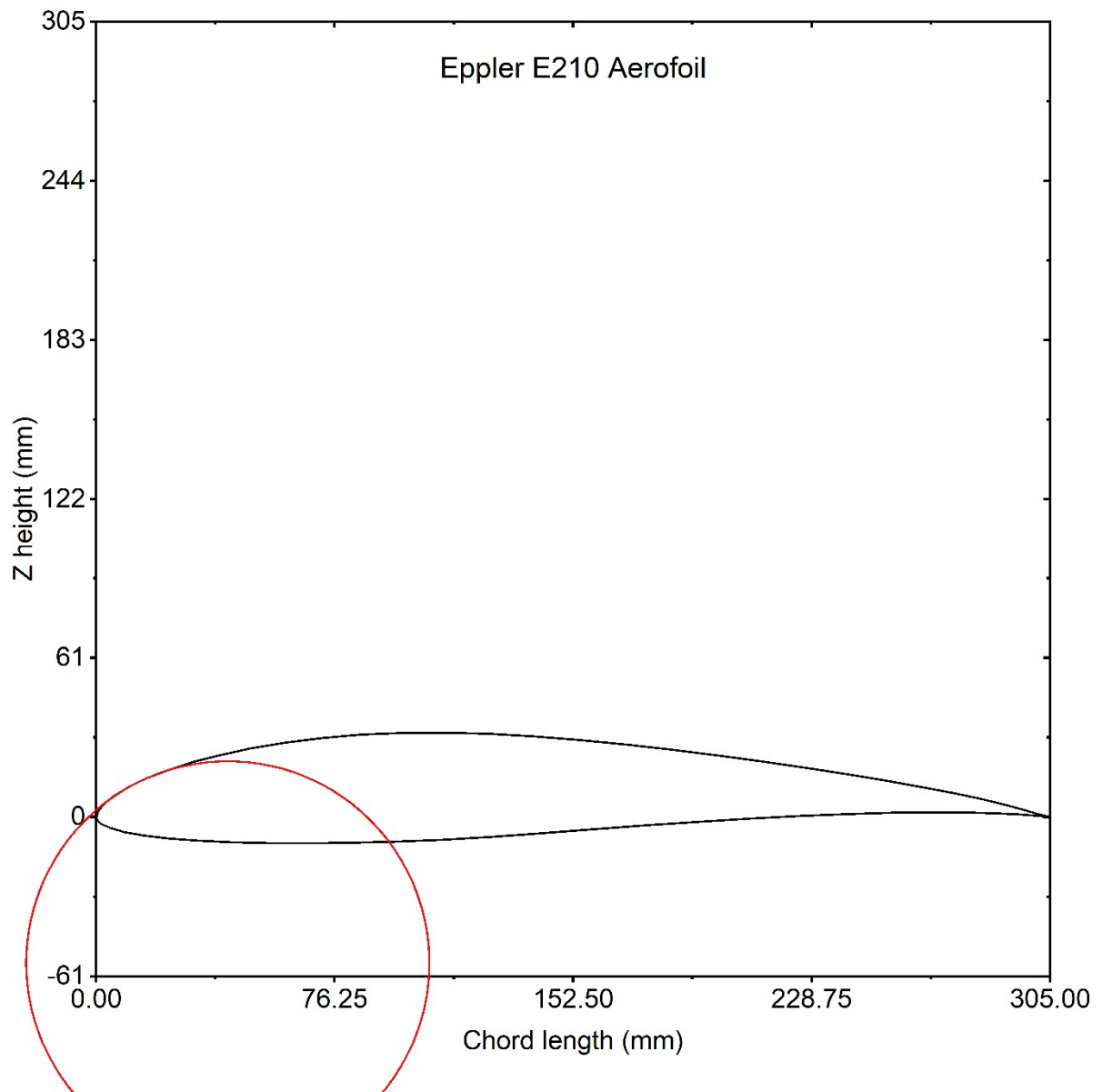


Figure S7: Scale depiction of an Eppler E210 aerofoil with a chord length of 305 mm,¹ superimposed with a perfect circle of curvature radius 64.4 mm.⁴⁸



Figure S8: Conformal silicone mask used to pattern gold back contacts; this image was taken post deposition.

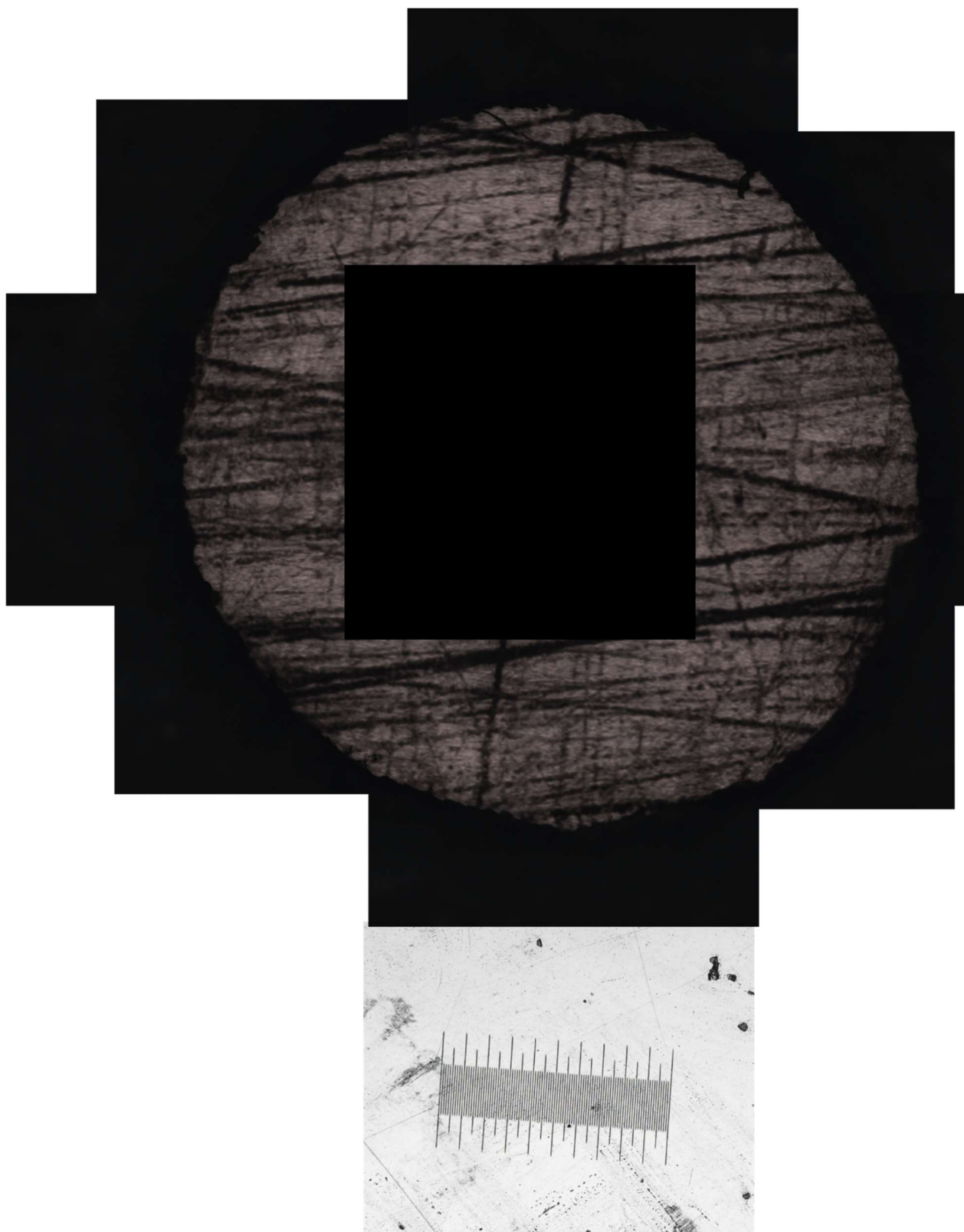


Figure S9: Optical microscope composite image of illumination mask aperture for use in testing of curved devices. Images were processed and aperture area measured using ImageJ. The aperture area was calculated to be 7.73 mm^2 .

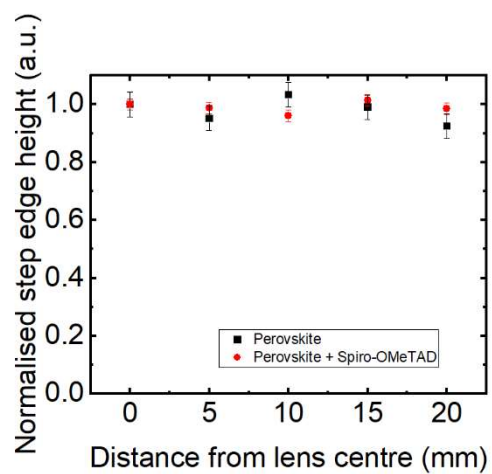


Figure S10: Normalised thickness measurements across curved substrates of SnO_2 /perovskite, and SnO_2 /perovskite/spiro-OMeTAD stacks as a function of distance from the lens centre. Measurements were taken using a Bruker Dektak XT profilometer.

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Chapter 5

Direct Integration of Perovskite Solar Cells with Carbon Fiber Substrates

5.1 *Publication Foreword*

Having established that the fabrication of perovskite solar cells onto curved substrates was feasible, it became necessary to ensure that fabrication onto carbon fibre-reinforced polymer substrates was also feasible. To this end, we elected to simplify matters by restricting ourselves to flat substrates and spin coating of the solution processed layers. The first issues which needed to be addressed were those of substrate conductivity and roughness. This was overcome by the inclusion of a planarization layer, a layer of epoxy which was placed in between the carbon fibre prepreg sheets and the glass mould. It was then found that the moulds themselves were not flat enough, necessitating the purchase of new moulds specifically for PV applications. The curing of the panels also needed to be optimised to ensure that the scrim present in the planarization layer did not protrude through the resin. To further reduce roughness, unidirectional carbon fibre prepreg was used.

Various transparent coating oxides were deposited onto the carbon fibre based substrates, however as the substrates were cured in an autoclave they harboured very low surface energies as any dangling bonds which may have been present had been driven to react. This resulted in poor adhesion of the TCOs to the substrates, a significant problem when using Kapton tape to mask regions when acid etching. To mitigate against this, a commercially available aerosol based plastic primer was used to improve adhesion. This approach was quite effective, however the next hurdle to overcome was that at fairly low temperatures the TCO would crack due to coefficient of thermal expansion mismatch with the substrate. It was subsequently found that deposition of SiO₂ *via* ebeam onto the primer surface created a wrinkled interlayer which prevented cracking. It was then possible to fabricate devices *via* normal fabrication processes.

I was not involved with the identification of the crack prevention layers, having joined the project at least 2 years after it had commenced. My specific contributions to this research included fabricating samples for testing and characterisation. As the lead author departed from the group quite abruptly, I was tasked with completing the dataset and writing the majority of the manuscript. I was also responsible for curating data, and creating all the figures. I was also responsible for addressing reviewer responses, and directed further research into the role and mechanism by which the crack prevention layers operated, with a great deal of assistance from Dr Nic Mullin.

5.2 *Author Contributions*

O.S.G and T.T. fabricated and characterised PV devices on CFRP substrates. O.S.G., T.T. and E.J.C. wrote the initial drafts of the manuscript. F.C-M. fabricated CFRP substrates and performed electromechanical testing. L.C.I-O, M.T. and R.C.G. fabricated TCO films onto substrates and samples. R.C.K. performed AFM measurements. R.H.G. performed angular reflectivity measurements. N.M. carried out HT-AFM and CTE measurements. P.J.M.I., J.M.W., J.P.A.F. and D.G.L. conceptualised, funded and supervised the research. All authors contributed to editing of the manuscript.

5.3 *Publication Main Body*

Direct Integration of Perovskite Solar Cells with Carbon Fibre Substrates

*Onkar S. Game, Timothy Thorner, Fernando Cepero-Mejías, Luis C. Infante-Ortega, Mustafa Togay, Elena J. Cassella, Rachel C. Kilbride, Robert H. Gordon, Nic Mullin, Rachael C. Greenhalgh, Patrick J. M. Isherwood, J. Michael Walls, J. Patrick A. Fairclough and David G. Lidzey**

*Corresponding author, E-mail d.g.lidzey@sheffield.ac.uk

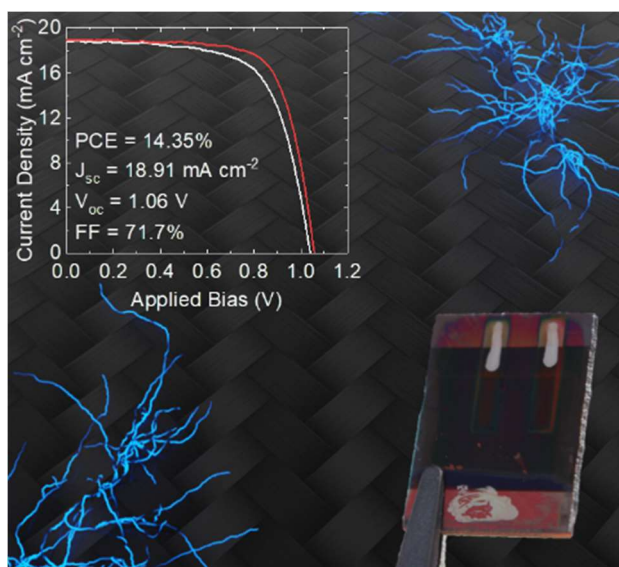
Department of Physics & Astronomy, University of Sheffield, Hicks Building, Hounsfield Road, Sheffield, S3 7RH, U.K.

Department of Mechanical Engineering, University of Sheffield, Sir Frederick Mappin Building, Mappin Street, Sheffield, S1 3JD, U.K.

CREST, Wolfson School of Mechanical, Electrical and Manufacturing Engineering, Loughborough University, Loughborough, Leicestershire, LE11 3TU, U.K.

[#]Department of Physics, Indian Institute of Technology Indore, Khandwa Road, Simrol, Indore-453552, India

Department of Chemistry, University of Sheffield, Dainton Building, Brook Hill, Sheffield, S3 7HF, United Kingdom



5.3.1 Abstract

Integrating photovoltaic devices onto the surface of carbon fibre-reinforced polymer substrates should create materials with high mechanical strength that are also able to generate electrical power. Such devices are anticipated to find ready applications as structural, energy-harvesting systems in both the automotive and aeronautical sectors. Here, we demonstrate the fabrication of triple-

cation perovskite *n-i-p* solar cells onto the surface of planarised carbon fibre-reinforced polymer substrates, with devices utilising a transparent top ITO contact. These devices also contain a 'wrinkled' SiO_2 interlayer placed between the device and substrate which alleviates thermally-induced cracking of the bottom ITO layer. Our devices were found to have a stabilised power conversion efficiency of 14.5 % and a specific power (power per weight) of 21.4 W g^{-1} (without encapsulation), making them highly suitable for mobile power applications.

5.3.2 Introduction

Organic-inorganic hybrid perovskite materials have generated substantial interest within the photovoltaic (PV) research community, with the record power conversion efficiency (PCE) of single-junction devices (25.7 %) now approaching that of top-performing silicon solar cells.¹ The outstanding optoelectronic properties, high lab-scale efficiencies, and facile, low-cost solution processability make perovskite PV an ideal system for integration with novel substrate materials that have thermal processing limitations.² This allows perovskite solar cells (PSCs) to be deposited onto flexible polymer substrates, with other work demonstrating devices that are transparent or have high performance under diffuse or low light conditions.^{3,4} These advantages may allow PSCs to operate in niche applications where crystalline silicon is poorly suited. Indeed, PSCs have been integrated with a variety of materials, including transparent polymers – namely poly(ethylene terephthalate)⁵ (PET) and poly(ethylene naphthalate)³ (PEN), metal foils such as titanium^{6,7} and copper⁸, titanium⁹ and steel¹⁰, metal wires^{11,12} and fibres^{13,14}; and even paper^{15,16}. For the reader interested particularly in fibre based PSCs, we direct them to a recent review by the Peng group in

2022.¹⁷ This opens a broad range of possible applications ranging from portable or wearable consumer electronics to power sources for the 'internet of things'.^{18–20}

One particular emerging application of PSC-based technologies is in decentralised solar power generation, where high power-per-weight (or specific power) is critical. This is most important in the automotive and aerospace industries, building-integrated PV and military applications. Previous work by Kaltenbrunner *et al.* demonstrated that the specific power of PSCs outperforms that of all other PV materials whilst rivalling those of other power generation technologies.²¹ Here, ultra-lightweight, 3 μm thick PSCs were fabricated on a PET foil, with devices having a PCE of 12% and a specific power of up to 23 W g^{-1} . Such devices were shown to be capable of powering a direct-current motor for a model aeroplane when connected to an 8 x 8 PSC array. Kang *et al.* have also created flexible PSCs having a specific power of 29.4 W g^{-1} with devices being light enough to rest on the surface of soap bubbles.²² More recently, Wu *et al.* have demonstrated ultrathin PSCs fabricated on parylene substrates using a flip-over transfer technique, with devices demonstrated to have a PCE of up to 20.2% with a record specific power of 30.3 W g^{-1} .²³

The application of PSCs for portable power applications therefore represents an extremely attractive prospect, with one possible application route being the lamination of flexible PSC devices onto curved surfaces such as the envelope of a dirigible, the fuselage of an aircraft or the monocoque of an automobile.²¹ We believe, however, that this approach has some drawbacks. In particular, the weight of the substrate and associated adhesives is expected to reduce the specific power of the resultant device, with the potential delamination of the device from the surface of interest representing a possible failure mechanism. Furthermore, while it is possible to 'wrap' a two-dimensional flexible PV device over a surface that curves in one direction (e.g. a cylinder), it is not possible to wrap a flexible device over a complex surface that curves in two directions (e.g. a sphere); a limitation that restricts the surfaces over which such an approach can be applied.²⁴ Indeed, PSC devices fabricated on flexible substrates can also have a limited bend-radius²⁵; a feature that could limit the curvature of the surface on which they can be fixed. Finally, we note that the performance metrics of flexible PSCs currently lag behind those of rigid cells with such devices prone to mechanical fracture due to repeated flexing.²⁶

An alternate approach to utilising PSCs for mobile power applications that we explore here involves directly coating such devices onto a surface of choice. Here, a key material of interest for mobile power applications are carbon fibre-reinforced polymer (CFRP) composites. These materials are widely used in the automotive (e.g. high-performance race cars) and aerospace (e.g. aircraft fuselages) industries as they combine high strength and elastic modulus compared to metallic materials or other structural polymers.^{27,28} Here, the combination of PSCs with CFRP

composites creates materials having a unique balance of high power-per-weight and high strength-per-weight, realising a class of structural materials that also act as a power source. Critically, the ability to process PSCs from solution using techniques such as spray coating allows them to be deposited over curved surfaces.²⁹ PSC devices on CFRP composites could be readily employed in unmanned aerial vehicles (UAVs) and high-altitude pseudo-satellites (HAPSs), where there are stringent weight limitations and finite fixed wingspans.³⁰ Indeed, it has been demonstrated that by integrating solar cells over curved surfaces, devices can be realised having a power output exceeding that of planar cells occupying an equivalent area.^{31,32} We note, however, that the CFRP composites often have a high level of surface roughness that is much greater than the polished glass surfaces on which PSCs are most often deposited, and planarising such surfaces is expected to be a key challenge.

In this paper, we directly fabricate *n-i-p* architecture 'triple-cation' (TC) based PSCs (ITO/SnO₂/TC-perovskite/spiro-OMeTAD/Au (0.8 nm)/ITO) in substrate configuration onto epoxy-planarised CFRP composite substrates, with devices *illuminated through a transparent* top indium tin oxide (ITO) contact. A key challenge we address is the preparation of the CFRP surface. We show that the roughness of such a surface can be substantially reduced to a root mean squared (RMS) roughness of 29 nm by using a commercial epoxy-based mesh material. However, the differing thermal expansion coefficients of the ITO charge-extracting layer and the CFRP substrate leads to severe cracking during the thermal annealing necessary to process the TC-perovskite. We show that this problem can be overcome *via* the use of an intermediate 'wrinkled' SiO₂ film placed between the ITO and the CFRP surface, which prevents cracking of the ITO during annealing. Using this approach, we realise devices having PCEs up to 14.4% and stabilised PCEs of 14.5%. The use of Au (0.8 nm)/ITO as a transparent top contact results in devices having promising stability, with control (glass-substrate) PSCs having dark-storage lifetimes in excess of 1 month.

5.3.3 Results

5.3.3.1 Preparation of the CFRP Substrate

Samples were fabricated from unidirectional XC130 'pre-preg' (Easy Composites Ltd, Stoke on Trent, UK). This material is typical of materials used in the automotive and aerospace industries and was selected due to its high carbon fibre-content and strength after curing. XC130 is composed of unidirectional carbon fibre pre-impregnated with a bisphenol-A-based epoxy resin. A cleaned, scratch free, smooth glass substrate was prepared with a release film and three XC130 20 × 20 cm sheets. A breather fabric was then placed on top of the CFRP pre-preg sheets and the assembly

placed inside an air-tight bag before a vacuum was applied. The pre-preg-glass assembly was then placed inside an autoclave which was pressurised to 6 bar and heated at a rate of $2\text{ }^{\circ}\text{C min}^{-1}$ to $100\text{ }^{\circ}\text{C}$. The assembly was then held at $100\text{ }^{\circ}\text{C}$ for 4 hours to cure. Pressure and temperature were then slowly reduced at 0.2 bar min^{-1} and $2\text{ }^{\circ}\text{C min}^{-1}$ to return the assembly to atmospheric conditions. The resultant sample had a thickness of 0.9 mm and an areal mass of 1050 g m^{-2} . To prepare samples for device fabrication, the $20 \times 20\text{ cm}$ sheets were waterjet cut (ProtoMax) into $19 \times 15\text{ mm}$ sections.

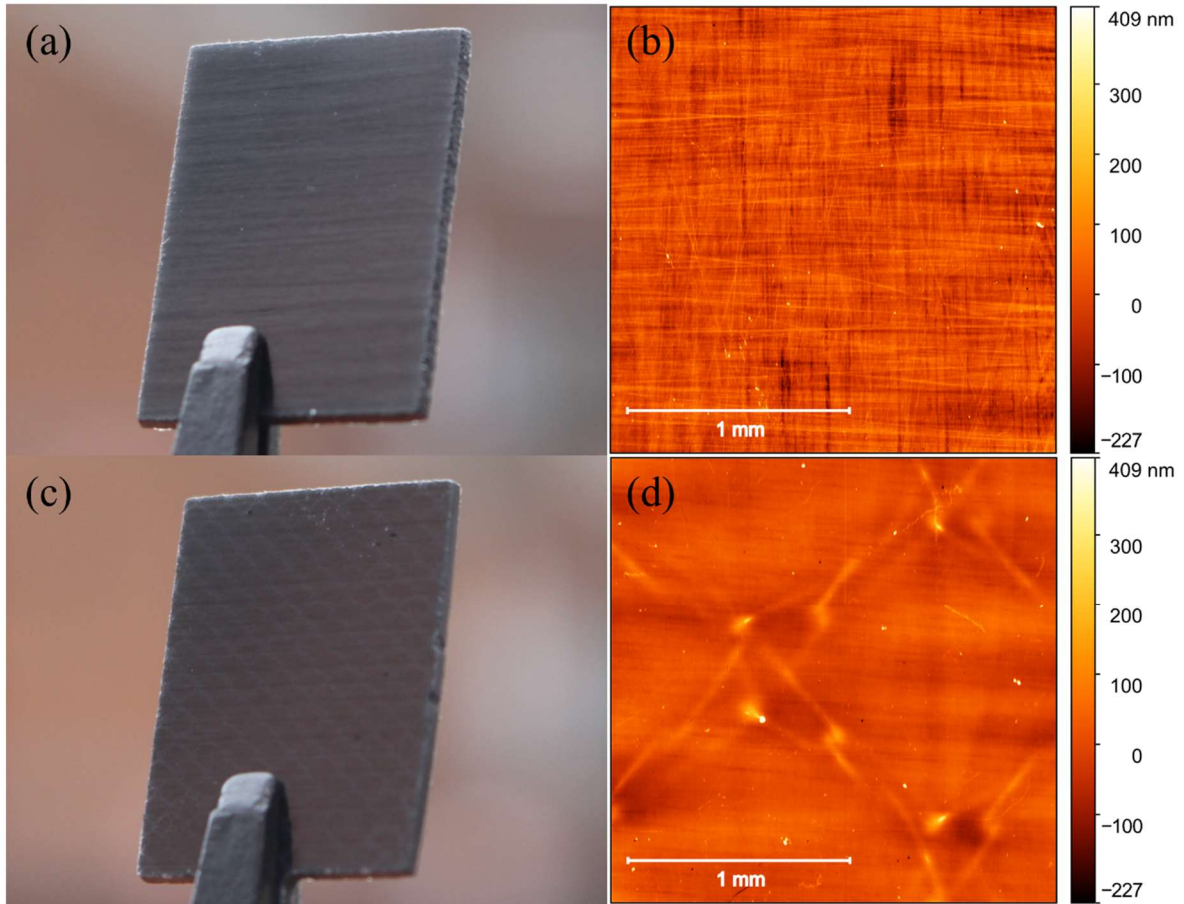


Figure 1: Photographs of (a) unplanarised, and (c) planarised CFRP composite substrates. Corresponding surface topography maps of (b) unplanarised and (d) planarised CFRP composite substrates.

Figure 1(a) shows an image of a CFRP substrate, with Figure 1(b) showing a surface topograph of its surface recorded using a Dektak surface profilometer system. It was found, as expected, that such surfaces were relatively rough with an RMS roughness of 35 nm over a $2 \times 2\text{ mm}$ area, and peak height features of up to $1.2\text{ }\mu\text{m}$, values likely problematic for the direct integration of PSC devices. Here, a series of carbon fibres can be seen that are close to the surface and are not entirely encapsulated by the epoxy matrix. Such carbon fibres render the CFRP electrically conductive, with a resistance of $20\text{ }\Omega$ typically measured between points 1 cm apart on the surface. While such conductivity could be potentially helpful for future applications, it was found to generate electrical

pathways that resulted in short-circuited devices. To overcome such issues, the surface was coated by a planarisation layer that both reduced the roughness of the CFRP and rendered its surface electrically insulating.

The planarisation layer was based on an XA120 epoxy-resin adhesive film (Easy Composites) which is generally utilised to bond honeycomb aluminium, Nomex[®] or foam structures to composite parts. This material was placed on the surface of the CFRP next to the glass mould surface. XA120 was used due to its excellent adhesion to the XC130 CFRP and its ability to reduce surface roughness substantially. Figure 1(c) shows an image of a CFRP substrate with an XA120 epoxy laminate that was obtained by cutting individual substrates *via* a waterjet cutter, with a surface topograph of the same surface shown in Figure 1(d). The planarisation layer was found to reduce the RMS surface roughness to 29 nm over 2×2 mm, with maximum peak heights being around 400 nm. This compares with a typical RMS roughness of 13 nm for a quartz-coated glass substrate over a similar length scale. A honeycomb motif having a height of around 350 nm can be seen in the topography map. This structure originates from the supporting mesh within the epoxy planarisation layer. As the core-mesh structure has a low aspect ratio, we found that subsequent coatings formed a completely conformal layer over the surface which made them suitable substrates for device fabrication.

5.3.3.2 *Deposition of the ITO Bottom Contact*

PSC device fabrication proceeded with an ITO bottom contact deposition onto the planarised CFRP. To ensure an effective, strong bond was formed between the ITO and the CFRP, the surface was first treated using a commercially available primer layer (Plasticcoat Plastic Primer) which was spray-cast onto the CFRP surface. ITO was then deposited onto the primed planarisation layer *via* RF sputtering at a deposition power of 155 W from a 4" diameter ITO target in a vacuum chamber through which argon gas flowed at 7 SCCM. In all cases, ITO films were not heated during or after their deposition. The bottom ITO films deposited on the CFRP substrate had a typical thickness of 200 nm and sheet resistance of $20 \Omega/\square$. The transmission of a typical ITO film deposited on glass is shown in **Figure 2(a)**, where the film has an optical transmission of around 86.1% at 480 nm. While it is not possible to directly measure the optical transmission of ITO films deposited onto CFRP substrates (*as they are completely opaque*), we have characterised their optical properties by measuring their angular-dependant optical reflectivity. Typical reflectivity data for ITO films deposited by sputtering on both glass and CFRP substrates is shown in Figure S1. Here, we find that the optical-reflectivity of the ITO deposited on each type

of substrate is very similar, with any differences likely resulting from the morphology of the underlying CFRP/ITO interface.

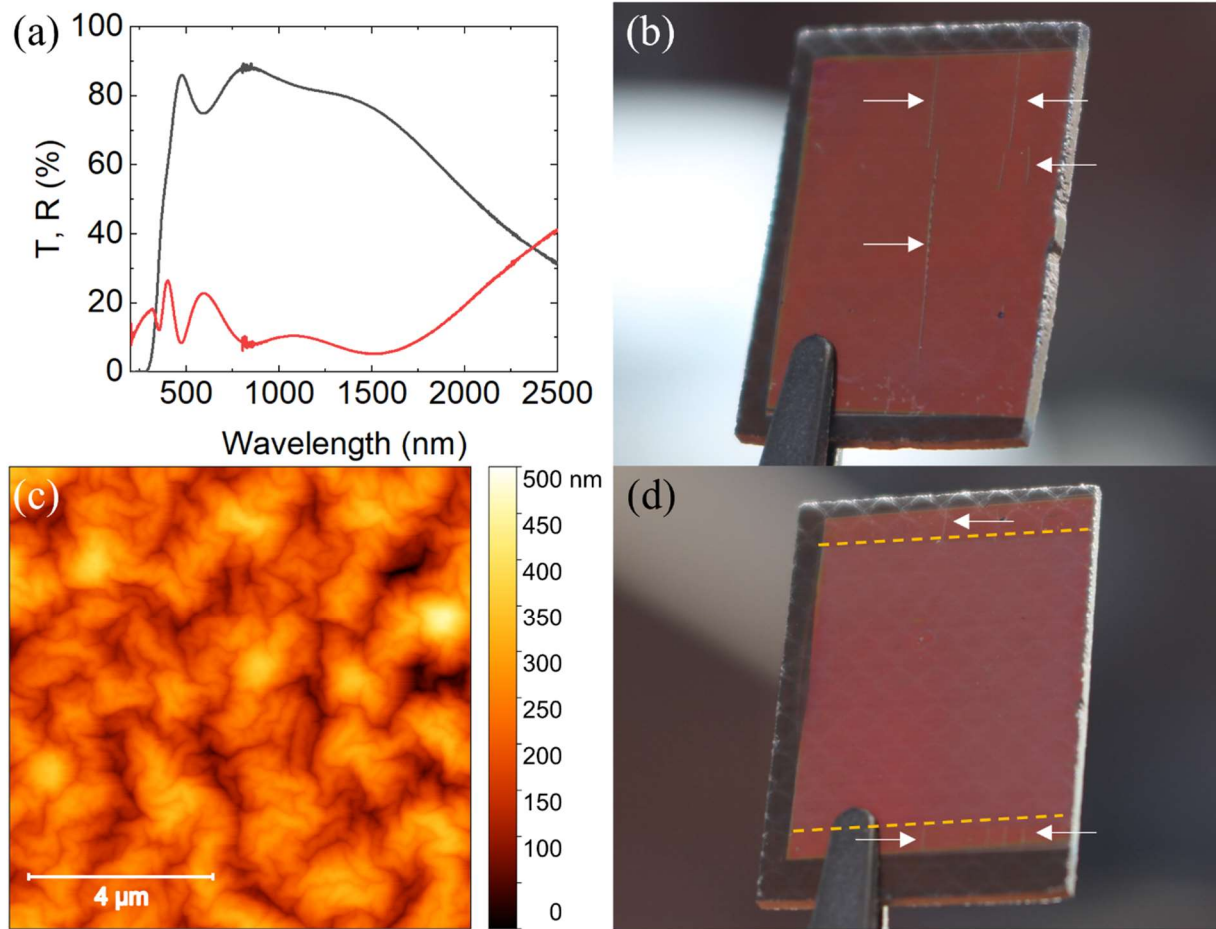


Figure 2: Part (a) shows the optical transmission (T) (black) and reflectance (R) (red) for the bottom ITO electrode when fabricated on glass. Part (b) shows a photograph of an ITO-coated CFRP-planarised substrate heated to 100 °C in the absence of the crack-preventing SiO₂ layer. Here, cracks (marked by white arrows) in the ITO layer can be clearly seen. Part (c) shows an AFM image of the surface of a CFRP-planarised substrate upon which SiO₂ has been deposited via e-beam evaporation. Part (d) is a photograph of an ITO coated CFRP-planarised substrate incorporating the crack-prevention layer, with the whole structure subsequently heated to 100 °C. Note that cracks are visible near the edges of the ITO, but these are completely arrested at the SiO₂ boundary (marked by yellow dotted lines).

Atomic force microscopy (AFM) measurements (see Figure S2) indicated that the ITO deposited onto the CFRP/primer surface was relatively smooth, having an RMS roughness of 15 nm over a length scale of 10 x 10 μm. Despite this promising finding, we found that such multilayer structures were highly unstable when thermally annealed at the temperatures typically used to process materials used in perovskite solar cells. Indeed, significant surface cracking became evident after an ITO covered CFRP substrate had been heated to 100 °C and then cooled to

room temperature (see Figure 2(b)). This resulted in the failure of all devices fabricated onto such CFRP surfaces, as the cracks generated electrical short circuits between the ITO and the PSC top contact. We suspect that the cracking of the ITO resulted from the fact that the coefficient of thermal expansion (CTE) of ITO is an order of magnitude lower than that measured (see Table S1) for our planarised CFRP (being $7.2 \times 10^{-6} \text{ K}^{-1}$ and $7.9 \times 10^{-5} \text{ K}^{-1}$ respectively).³³ As a result of this mismatch, the difference in expansion between the substrate and ITO during thermal annealing resulted in the generation and long-range propagation of cracks in the ITO. Such cracks apparently do not 'heal' when the substrate is cooled; we suspect that internal tensile stress in the ITO film causes the edges of the cracks to curl away from the surface.

To alleviate this issue, we have incorporated a 'crack-prevention' layer between the ITO contact and the planarised CFRP. This approach was inspired by previous work in which ITO was deposited by DC sputtering onto an optically curable epoxy which underwent 'wrinkling' and increased both the optical reflectance and flexibility of the ITO film.³⁴ We note that similar wrinkled poly(vinylidene fluoride-hexafluoropropylene) substrates have previously been shown to improve the ductility of a brittle poly(selenophene-alt-3,6-dithiophene-2-yl-2,5-bis-(2-octyldodecyl)-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione) thin film *via* a stress-reduction mechanism.³⁵ In our experiments, the crack-prevention layer was based on a 150 nm thick layer of SiO₂ deposited *via* e-beam evaporation onto the primed CFRP substrate. As seen in the AFM image shown in Figure 2(c), this layer has a densely wrinkled structure, with such wrinkles having lateral dimensions of up to 2.5 μm with a height of up to 450 nm. The wrinkled structure is created by the combination of thermal radiation that is generated by the e-beam source as it heats the SiO₂ target and the kinetic energy of the evaporated material. We suspect that this process provides sufficient energy to cause localised heating of the primer layer and planarisation epoxy to cause it to partially soften and expand during the SiO₂ deposition. On cooling, these layers contract, causing the dense, non-compressible SiO₂ layer to adopt a highly crenulated structure, as has been demonstrated by depositing metallic films using an e-beam on poly(dimethylsiloxane) (PDMS)³⁶. An ITO layer was then deposited onto the wrinkled SiO₂ layer *via* RF sputtering, forming a near conformal coating. Our experiments demonstrate that such 'wrinkled' structures do not form when ITO is directly deposited on the surface of the planarised CFRP as the sputtering process does not appear to generate sufficient heat to soften the surface layer (see Figure S2). AFM measurements (see Figure S3) indicate the surface roughness of the wrinkled ITO is rougher than that of ITO deposited on a polished glass surface (RMS roughness being 27 and 12 nm, respectively, over a scan area of 5 x 5 μm). We believe that such wrinkles are not sufficient to cause device failure –

indeed, similar structures have been used to enhance light management in thin-film optical devices by - for example - preventing optical waveguiding in organic light emitting diodes and improving light outcoupling.³⁷ Importantly the ITO layer is strongly bonded to the wrinkled SiO₂; this has been confirmed by sticking and then removing an adhesive tape to the surface, performing a so-called 'peel test'. Here it was found that the removal of the adhesive tape did not remove or delaminate the ITO layer, indicating that it is strongly attached to the SiO₂ surface.

We have found that such a wrinkled structure effectively 'protects' the ITO during subsequent thermal annealing and cooling processes. Figure 2(d) shows an image of a SiO₂-ITO layer on planarised CFRP which has been thermally annealed at 100 °C before being allowed to cool. Here it can be seen that the ITO remains uncracked, making it a suitable substrate for PSC device deposition. Indeed, we find that if a surface is partially coated using such a 'protective' silica layer, then cracks form in the ITO in the unprotected regions upon heating and cooling, however such cracks do not propagate into the protected region (see Figure S4).

To explore the crack prevention mechanism, we firstly recorded the CTE of the surface of CFRP substrates both with and without the SiO₂ layer (see Supporting Information for exact methodology, Table S1 and Table S2 for raw data, Figure S5 and Figure S6 for experimental set up). Here, measurements were made along and across the unidirectional carbon fibre axis, as any expansion could reasonably be assumed to be anisotropic. We found that the CTE for samples without the SiO₂ interlayer measured along and across the fibre axis were $<1.0 \times 10^{-6} \text{ K}^{-1}$ and $7.9 \times 10^{-5} \text{ K}^{-1}$, respectively. On addition of the SiO₂ layer, the CTE of the surface layer was largely unchanged, indicating that the wrinkled layer does not modify the degree to which the surface layer expands when heated. Notably, however, the significant anisotropy measured in the CTE explains our observation that cracks in the ITO only develop parallel to the fibre axis, as can be seen in Figure 2(b). We have also characterised the surface structure of CFRP substrates with and without the wrinkled-SiO₂ and ITO layers as a function of temperature up to 150 °C. Here, we identify only fairly small changes in the roughness of the wrinkled surface as a function of temperature (see Figure S7 and S8). We conclude therefore that such wrinkled layers most likely prevent cracking by (1) creating a roughened surface to which ITO bonds very securely and (2) by preventing the long-range propagation of cracks.

For completeness, we have also investigated the degree to which the wrinkled layer confers additional mechanical protection to the ITO. Here, we carried out 4-point bend tests on ITO-covered CFRP-planarised substrates (having dimensions 100 x 25 mm) either with or without a wrinkled SiO₂ protection layer. Details of the experimental set up are shown in Figure S9 and Figure S10. During these bending tests, the ITO resistance was measured as a function of roll

displacement. Here, we found that ITO resistance remained constant until the centre rolls were displaced by around 3.5 mm. This level of bend corresponded to an apex displacement of about 4.6 mm, and a strain of 0.45 %, as calculated *via* FEA. Beyond this point, the samples without the SiO₂ layer underwent a dramatic increase in resistance as a function of deflection. However, the samples incorporating the SiO₂ layer underwent a more modest, linear increase in resistance (see Figure S11). We suspect that the crack-prevention layer reduces damage to the ITO at any given strain due to improved adhesion as a result of higher surface roughness that provides a good key for the ITO. We note that during these tests, the force required to achieve a strain of 0.45% was calculated to be in excess of 100 N; this force is well beyond that which soda-lime glass substrates of the same thickness would undergo complete failure.^{38,39}

5.3.3.3 Device Fabrication and Testing

We have used the structures described above as the substrates for PSC devices. A typical device stack is shown schematically in **Figure 3(a)**. Devices were fabricated on planarised CFRP substrates together with control devices on standard ITO/glass substrates. In all cases, devices utilised an electron extraction layer based on a colloidal SnO₂ nanoparticle dispersion that was spin-cast onto the ITO and then thermally annealed at 100 °C for 30 minutes before being treated *via* exposure to a UV-generated ozone source for 20 minutes. Following this, a spin-cast TC-perovskite was deposited onto the SnO₂ layer from a DMF/DMSO solution and then quenched during the spin-coating cycle using a chlorobenzene anti-solvent to initiate nucleation of the perovskite grains. Following a thermal anneal at 100 °C for 20 minutes, a perovskite film was formed, having an optical band-gap of 1.61 eV, or 770 nm (see Figure S12). Following this, a hole-extraction layer of doped spiro-OMeTAD was spin-cast onto the perovskite surface. Full experimental details of materials and processing techniques can be found in previous publications and Supporting Information.^{40,41}

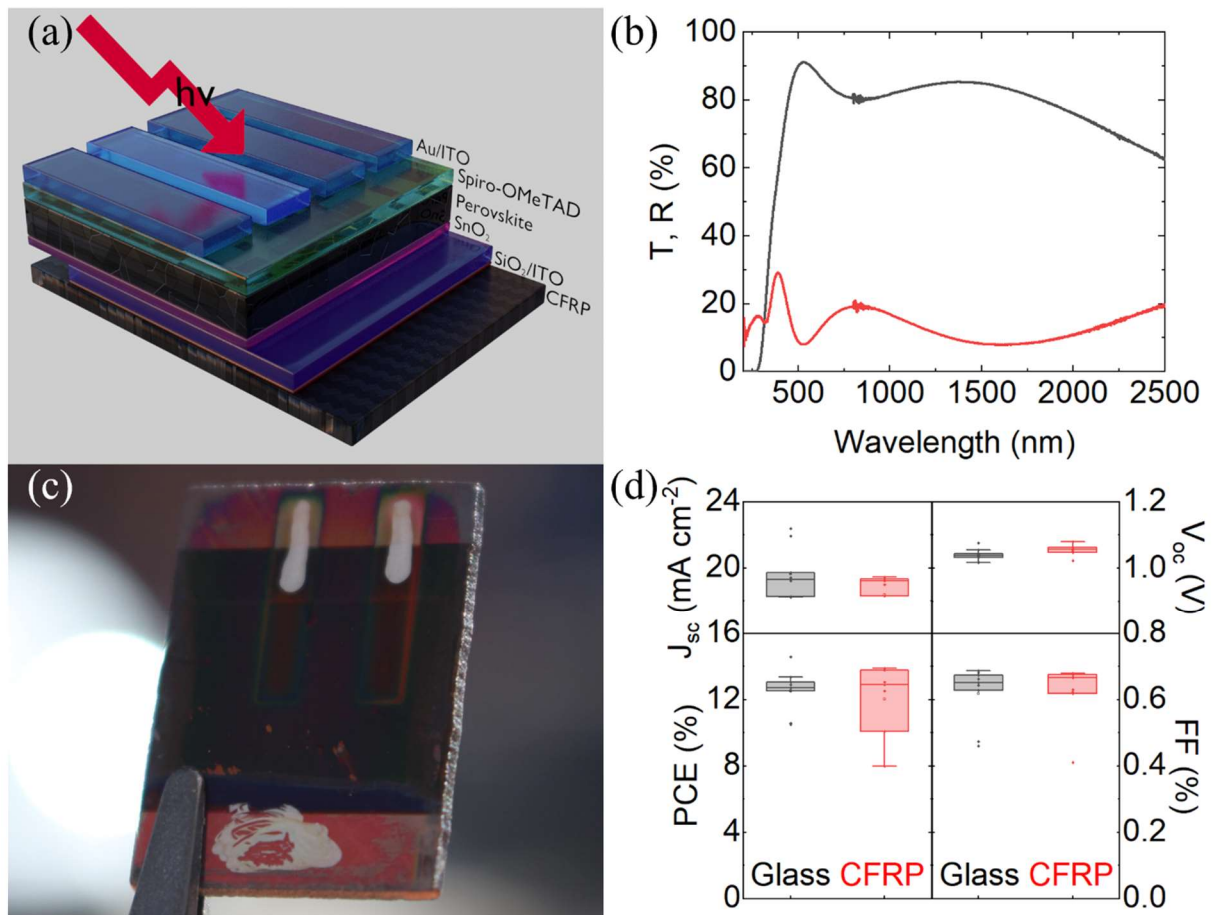


Figure 3: Part (a) is a schematic of our typical device structure, with an arrow to indicate direction of illumination. Part (b) shows the optical transmission (T) (black) and reflectance (R) (red) of the top ITO electrode when deposited on glass. Part (c) is a photograph of PSC devices on CFRP composite. Note that the light-grey material visible on each device pixel and the bus bar is silver loaded paste which was used to improve electrical contact to the device. Part (d) shows a box-plot summary of key device performance metrics derived from reverse JV sweeps of control devices fabricated on glass together with those on CFRP.

Importantly, as the CFRP substrate is *completely opaque*, it was necessary to design the device such that *light could enter the device through a transparent top contact*. This was achieved by sputter coating a film of ITO onto the top spiro-OMeTAD. This was done *via* a two-step deposition process⁴² in which a 30 nm thick ITO 'buffer' layer was first sputtered at 40 W, followed by the deposition at 200 W of a thicker (80 nm) 'bulk' layer. The use of a buffer layer deposited at a lower magnetron power was found to reduce damage to the spiro-OMeTAD hole-transport layer due to reduced exposure to the magnetron plasma. The two-step deposition process used 10 SCCM of argon for both stages, creating a film with a sheet resistance of 42 $\Omega/\square$ and an optical transmission of 91.2% at 529 nm (see Figure 3(b)). The ITO contact was deposited through a shadow mask, creating a series of pixels, each having an active area of 6 mm². To further protect the spiro-OMeTAD hole

transport layer, we found that it was necessary to insert a thin (0.8 nm) gold film (deposited by thermal evaporation) between the ITO and the spiro-OMeTAD hole transport layer. Without this layer, we found that the device JV curves typically had an 's-shape', indicating an inefficient extraction of carriers (see Figure S13). Here, we suspect that the plasma utilised during the ITO sputter deposition partially degraded the surface of the spiro-OMeTAD and reduced its ability to conduct charge, with the thin gold layer both acting as a protection layer by attenuating the passage of ionising species into the spiro-OMeTAD and also enhancing charge extraction from the spiro-OMeTAD into the ITO. Finally, to improve device efficiency, an anti-reflection layer consisting of 100 nm of LiF was deposited onto the ITO surface *via* thermal evaporation.

Figure 3(c) shows an image of a fully fabricated device on a CFRP substrate. Electrical contact was made to each device using a semiconductor probe station, with efficiency measurements performed through an aperture mask (area 2.385 mm²) placed onto the surface of the substrate (see Figure S14). Figure 3(d) shows box plots of the key device metrics (PCE, J_{sc} , V_{oc} and FF), with data recorded from 8 independent devices containing 16 pixels in total. Here, it can be seen that we record a mean average device PCE of 12.0% with a typical device yield of around 40%. We attribute the relatively low device yield to the fact that the ITO/CFRP surface is rougher than commercially-available ITO coated glass substrates. Such roughness can result in device failure through the generation of electrical short-circuits. We believe that further optimisation of the CFRP fabrication and planarisation processes will lead to surfaces having reduced roughness and thus improved device yield.

Figure 3(d) also shows device performance metrics for a series of control devices fabricated onto an ITO/glass substrate. Here, the device stack is identical to that shown in Figure 3(a) except for the CFRP substrate (i.e. incorporating a transparent ITO top contact). For the sake of fair comparison, control devices were illuminated through the top ITO contact using an aperture mask in a similar way to that used to study devices on the opaque CFRP substrates. Here, we find that the mean average device efficiency was around 12.5%, with the performance of the control devices closely matching that of the devices fabricated on CFRP. We attribute the relatively low PCE of the control devices on a glass substrate to the fact that they are illuminated through the top of the device, with light passing through ITO, gold (0.8 nm) and spiro-OMeTAD layers before reaching the active perovskite layer. This results in significant parasitic absorption by the UV/blue absorbing spiro-OMeTAD layer (band gap of 2.70 – 2.98 eV^{43,44}). This is in contrast to a typical *n-i-p* stack which is illuminated through its substrate. In such devices, it is only necessary for light to pass through a thin (30 nm), wide band gap (3.6 – 4.2 eV⁴⁰) SnO₂ layer before absorption by the perovskite, with the SnO₂ layer resulting in negligible optical losses. To confirm that our glass

control devices were fully optimised, we first recorded JV curves in which devices were instead illuminated through the glass substrate. Here, we determined PCE values of up to 16.2%; a result that confirms the effect of parasitic absorption within the spiro-OMeTAD (see Figure S15). We then fabricated identical control devices in which the top Au (0.8 nm)/ITO layer was replaced by a conventional thick (80 nm) Au electrode. Devices were then illuminated through the bottom ITO/SnO₂ contact. Figure S15 plots typical JV curves, where it can be seen that best performing devices had a PCE of 20.2%; a value commensurate with this $n-i-p$ device architecture. We therefore conclude that the efficiency of devices fabricated on CFRP substrates results from optical absorption in the spiro-OMeTAD layer and the lack of a back-reflector to recycle light not absorbed in the perovskite on its first optical pass, together with a relatively higher sheet resistance of the ITO top contact in comparison with that of a thick gold electrode.

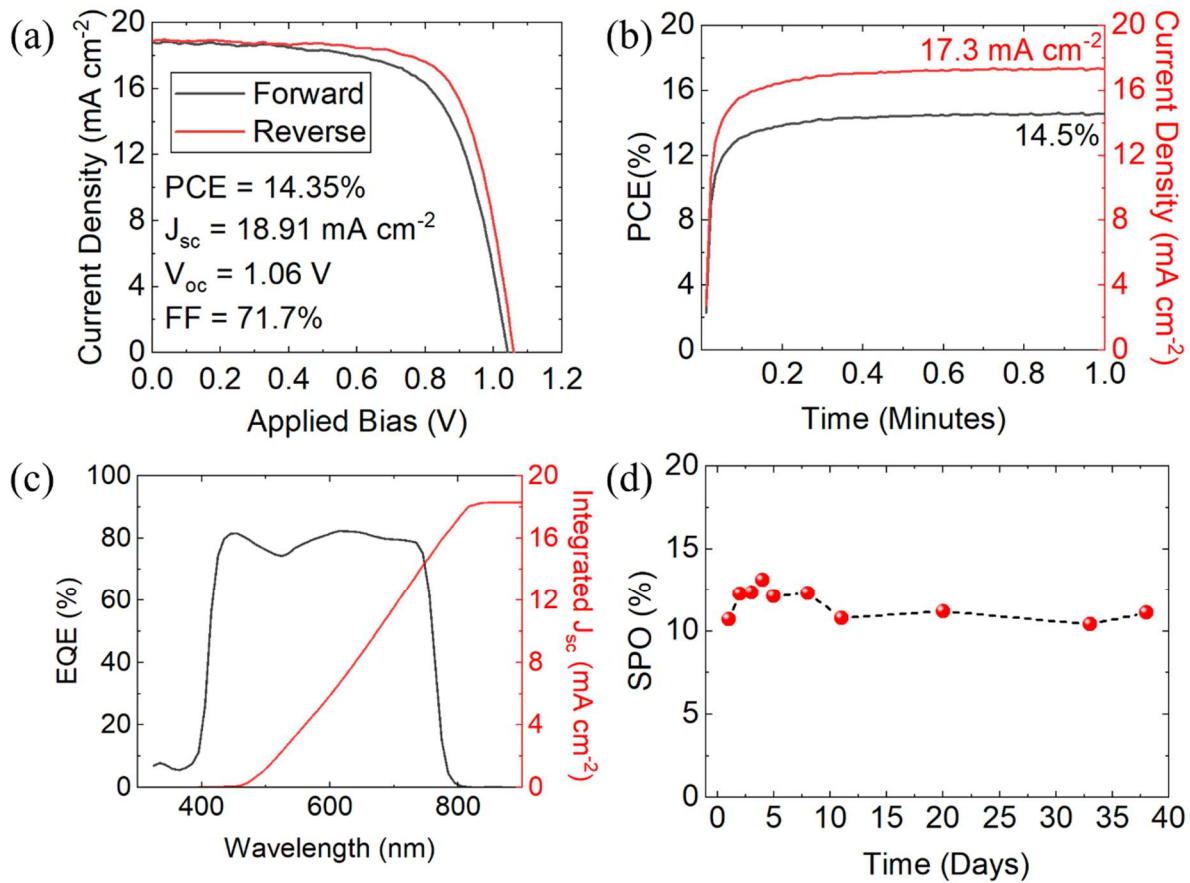


Figure 4: Part (a) represents JV data for the champion CFRP-based device, with metrics derived from the reverse sweep, (b) details the stabilised power output of the same device held at close to the maximum power point voltage for 60 s, (c) shows an EQE spectrum of a typical CFRP-based device, (d) shows the stabilised power output of glass control devices as a function of storage time in air.

For completeness, **Figure 4(a)** plots a JV curve under AM1.5 irradiation of the champion CFRP device. Here, the device had a J_{sc} of 18.91 mA cm^{-2} , a V_{oc} of 1.06 V, a FF of 71.7 % and a PCE

of 14.35 %. A stabilised power output of 14.5 % was recorded for this device when held under illumination near the maximum power point voltage, as shown in Figure 4(b). Figure 4(c) shows a typical EQE spectrum of a device on a CFRP substrate. Here we extract an integrated J_{sc} value of 18.3 mA cm^{-2} ; a value in agreement with the short circuit current determined from the solar simulator measurements. Note that due to parasitic absorption by the spiro-OMeTAD HTL, we see a drop-off in the EQE response between 300 – 400 nm. The effect of the spiro-OMeTAD absorption is illustrated in Figure S16, where we plot an EQE measurement of a glass control device illuminated through the glass substrate. Here, a UV/blue EQE response is evident as the incident light no longer passes through a spiro-OMeTAD layer.

We have also made a preliminary assessment of the operational stability of the Au(0.8 nm)/ITO top electrodes using dark-storage tests, with unencapsulated devices fabricated on glass/ITO electrodes stored in 30% RH air as per ISOS-D-1 requirements.⁴⁵ Here, such devices were illuminated through the top electrode during testing, with such measurements providing some measure of the stability of this transparent contact. As shown in Figure 4(d), we find that devices retain 85% of their peak efficiency during a period of over 35 days. Here, we ascribe the promising stability to the TC perovskite formulation⁴⁶ together with the use of an ITO top contact. We note that other approaches to the development of semi-transparent top-contact electrodes based on ultra-thin metallic films typically suffer from reduced stability resulting from oxidation or reactions with I⁻ ions that diffuse out of the perovskite.⁴⁷⁻⁴⁹ Here, such reactions do not occur with transparent conductive oxide materials such as ITO, with our selection of materials, therefore, conferring a high degree of intrinsic stability to the device. Indeed, our preliminary findings also suggest that devices fabricated onto CFRP can show a promising level of dark-storage stability (see Figure S17). Future work will investigate the long-term stability of larger-scale, encapsulated CFRP-based PSCs.

5.3.4 Discussion

We have demonstrated the integration of PSC devices onto planarised carbon fibre substrates, with devices having a similar PCE to control devices fabricated on conventional glass substrates. Although we have used spin-coating to deposit the solution-processable device layers (np-SnO₂ electron-transport layer, TC perovskite precursor, and spiro-OMeTAD hole-transport layer), we note that such layers can be deposited *via* spray-coating, allowing devices to be created over complex, curved substrates.²⁹

Our devices are fabricated directly onto a surface which could have a significant second function – e.g. acting as the wing of an aircraft or the roof of a car. To estimate the specific power of our

devices, we simply consider the masses of the layers which we have deposited. In our calculation of the areal mass of each layer, we use its known thicknesses and reported density (see Supporting Information, Table S3, for exact methodology). Using this approach, we find the mass per unit area of our complete PSC devices to be around 6.78 g m^{-2} , indicating that their specific power is about 21.4 W g^{-1} . This value compares favourably with *a*-Si cells⁵⁰ that have a maximum reported specific power of 8.31 W g^{-1} but is, however smaller than the specific power of PSC devices fabricated onto ultrathin flexible PEN (29.4 W g^{-1})²² or ultrathin flexible parylene-C (30.3 W g^{-1}).²³ We note however that the fabrication of PSC devices onto ultra-thin substrates will also require an adhesive layer to attach them to a surface of interest, thereby reducing their effective specific power. Furthermore, as such devices are illuminated through the substrate, the application of adhesives might damage the semiconductor layers, necessitating the use of a back encapsulant layer, with this layer also reducing effective specific power. Finally, as noted above, wrapping of complex shapes *via* lamination is likely to introduce unwanted pleats into the PSC device.²⁴

We note that our estimate of specific power ignores the mass of any encapsulation material, with encapsulation being critical for 'real-world' applications. Typically, we encapsulate regular devices using a glass coverslip and a UV-cured epoxy; however, this would account for over 98% of the total device mass and would reduce device specific power to just 0.4 W g^{-1} . To enhance the specific power of our devices, it will clearly be necessary to develop ultra-low mass encapsulation layers, with such layers likely being deposited *via* a combination of vapour deposition and spray-coating, allowing them to also cover curved surfaces. If we assume the thickness of the encapsulation layers could be reduced to about $3 \text{ }\mu\text{m}$ (e.g. composed of an evaporated metal oxide), then we might expect a specific power of about 5.4 W g^{-1} . If devices were instead encapsulated using a $1 \text{ }\mu\text{m}$ thick solution-processed polymeric film (such as polyurethane),²¹ then we estimate a specific power of around 18.2 W g^{-1} should be possible. We note that our devices are designed to be rigid rather than flexible; therefore, any polymeric material used would not require a great deal of flexibility. This would allow the utilisation of materials having a higher crosslink density and thus superior oxygen and moisture barrier properties.⁵¹ Such devices would clearly represent an important step towards the development of practical power sources for mobile automotive and aerospace applications.

5.3.5 Conclusion

We have outlined an approach to the direct integration of PSCs with a planarised CFRP composite substrate. We show that the successful integration of devices onto the surface of the CFRP necessitates the planarisation of the substrate, together with the use of a crack-prevention layer

that is formed from a 'wrinkled' SiO₂ film that is formed onto the surface of the planarisation layer. This wrinkled structure is created by partially softening the surface of the primer and planarisation layer as a result of the thermal energy provided by the e-beam deposition process. This wrinkling likely enhances the bonding of the ITO electrode to the surface, and prevents the long-range propagation of cracks which would otherwise result in short-circuit devices. The PSC devices fabricated employ transparent bottom and top ITO contacts, which impart an enhanced degree of stability to the device. The devices fabricated had a stabilised PCE of 14.5 %; a value that compares favourably with control devices fabricated onto conventional ITO/glass substrates. The devices realised had a specific power (power per mass) of 21.4 W g⁻¹ (an estimate that ignores the mass of the CFRP substrate), with the practical application of this technology requiring the development of ultra-low mass encapsulation layers. The substrates utilised combine high strength and low mass, making them directly applicable as structural materials that can simultaneously generate electrical power. We expect further work (including device deposition by spray-coating, device scale-up, modularisation and encapsulation) to create systems having direct employment in mobile power applications, including UAVs, HAPSs, and electric vehicles.

5.3.6 Acknowledgements

O.S.G., T.T. and F.C-M. contributed equally to this work. This work was funded by the Engineering and Physical Sciences Research Council (EPSRC) grant EP/S009213/1 (The Integration of Photovoltaic Devices with Carbon-Fibre Composites). E.J.C. thanks the EPSRC for a PhD studentship from grant EP/L01551X/1 (Centre for Doctoral Training in New and Sustainable PV). R.H.G thanks the EPSRC for a PhD studentship from grant EP/T012455/1 (Molecular Photonic Breadboards). T.T. thanks the University of Sheffield for the provision of a PhD studentship.

5.3.7 Conflict of Interest

D.G.L. is a co-director of the company Ossila Ltd. which retails materials and equipment used in perovskite photovoltaic device research and development.

5.4 Supporting Information

5.4.1 Experimental methods

5.4.1.1 Device fabrication

Carbon fibre substrate preparation: Planarised carbon fibre substrates were prepared on top of a smooth glass substrate by stacking the following in sequence: a release film, a 20 x 20 cm planarization layer of XC120 epoxy laminate, three layers of 20 x 20 cm XC130 unidirectional prepreg sheets, and a breather fabric (all purchased from Easy Composites). This stack was then placed inside an air-tight bag and the air was evacuated, before placing inside an autoclave. The carbon fibre composite was subjected to a pressure of 6 bar while being heated to 100 °C at a rate of 2 °C/min. Once the temperature reached 100 °C it was held there for 4 hours, to ensure full curing of the composite. Following this, the pressure and temperature were reduced to ambient at a rate of 0.2 bar/min and 2 °C/min, respectively. A ProtoMax (OMAX) waterjet was used to cut substrates to a size of 19 x 15 mm, suitable for device fabrication.

Carbon fibre substrates were cleaned in Hellmanex (Hellma), deionised water and isopropyl alcohol (IPA) and dried using a nitrogen stream. Subsequently, a commercial aerosol plastic primer (Plasticoat Plastic Primer) was spray cast by hand onto the substrates, before they were loaded into an electron beam evaporation chamber housed in a nitrogen filled glove box. Here, a 150 nm layer of SiO₂ was evaporated onto the substrates at a rate of 2 Å/s. The silica coated substrates were then coated in a 200 nm thick layer of ITO *via* magnetron sputtering using an argon flow rate of 7 SCCM at a power of 155 W to complete the substrates.

Perovskite solar cell fabrication: To construct glass control devices, unpatterned ITO/glass (Ossila) substrates were first etched using zinc and 4M HCl. These were then sequentially cleaned *via* ultrasonication in Hellmanex, DI water and IPA before treatment under UV ozone for 20 mins. For carbon fibre devices, substrates were etched using zinc and 4M HCl prior to cleaning by hand with Hellmanex, DI water and IPA. All substrates were exposed to UV ozone treatment for 20 mins.

The electron transport layer was deposited in air from a 15 wt% aqueous solution of tin oxide nanoparticles, diluted at a ratio of 1:4 with deionised water. This solution was filtered and spin-coated at 3000 rpm for 30 s before heating at 100 °C for 30 mins and subsequent exposure to UV ozone treatment for 20 minutes. Subsequent solution-processing steps were performed in a nitrogen-filled glovebox.

A triple cation perovskite ($\text{Cs}_{0.05}\text{FA}_{0.81}\text{MA}_{0.14}\text{PbI}_{2.55}\text{Br}_{0.45}$) precursor solution was prepared using the following material quantities per 1 mL of solvent: FAI (167 mg - Ossila), MABr (19 mg – Ossila), CsI (16 mg – Thermofisher), PbI_2 (467 mg – TCI), PbBr_2 (68 mg – TCI). The solvent system used was a 4:1 mixture of DMF (Sigma) and DMSO (Sigma). Prior to deposition, the precursor solution was filtered through a 0.2 μm PTFE syringe filter. The precursor solution was statically spin-coated at 4000 rpm for 30 seconds. With 5 s remaining, the films were antisolvent dripped with 100 μL of anhydrous chlorobenzene to initiate perovskite nucleation. The resultant film was then annealed at 100 °C for 20 mins.

The hole transport layer was deposited from a solution of 2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD) at a concentration of 86.6 mg mL⁻¹ in anhydrous chlorobenzene. To every 1 mL of this solution was added 34 μL of 4-*tert*-butylpyridine (TBP - Sigma), 20 μL of lithium bis(trifluoromethanesulphonyl)imide in acetonitrile (500 mg mL⁻¹ – Merck) and 11 μL of Co(II) (trifluoromethanesulphonyl)imide in acetonitrile (300 mg mL⁻¹ – Sigma). This solution was filtered using a 0.2 μm PTFE syringe filter before being spin coated onto the annealed perovskite films at 4000 rpm for 30 s. The films were then allowed to oxidise overnight before a 0.8 nm thick buffer layer of gold was deposited *via* thermal evaporation using an Edwards 306 bell-jar evaporator.

The deposition of the top ITO electrode was performed *via* magnetron sputtering through a shadow mask with an argon flow rate of 10 SCCM. First, a buffer layer of 30 nm was sputtered at 40 W, before an 80 nm bulk layer was deposited at 200 W.

5.4.1.2 Device characterisation

Current-voltage measurements: A Newport 92251A-1000 solar simulator was used to generate AM 1.5G illumination, calibrated to 1000 W m⁻² using a Newport silicon reference cell. A matte black illumination mask with a measured aperture area of 2.385 mm² was used to accurately define the illumination area. A semiconductor probe station was used to provide an electrical connection between the illuminated devices and a Keithley 237 source measurement unit. Current-voltage measurements were recorded by sweeping the applied bias between 0 V and 1.2 V at a rate of 0.2 V s⁻¹ and recording the resultant current density. Stabilised power output measurements were conducted by holding the pixel of interest at the maximum power point voltage as determined by the current-voltage sweep and recording the current density over 1 min.

Surface profilometry: Topographical measurements were carried out using a Bruker DektakXT surface profilometer equipped with a 12.5 μm stylus operating with a stylus force of 3 mg. Topographical maps with a vertical resolution of 15 nm per point were created by recording 2000 individual line scans separated by a distance of 1 μm , each of which traversed a distance of 2 mm over 10 s, creating a linear resolution of 0.666 μm per point. Data was processed using Gwyddion 2.58 for image generation and calculation of statistical quantities.

External quantum efficiency: Measurements were recorded using a QuantX-300 Quantum Efficiency Measurement System. White light from a Xenon arc lamp was amplitude modulated through an optical chopper at 25 Hz, referenced to a virtual lock-in amplifier, prior to passing through an Oriel CS130B monochromator to filter out a narrow bandwidth of incident radiation. The input/exit slit width was set to 750 μm resulting in a bandwidth FWHM of 10 nm. Spectral response was measured from 325-905 nm with a wavelength step size of 10 nm.

Atomic force microscopy (AFM): AFM measurements were recorded using a Veeco Dimension 3100 scanning force microscope operating in tapping mode. The cantilever tip (Bruker TESPA-V2) resonated at a frequency of 320 kHz with a spring constant of 42 N m^{-1} . Data was processed using Gwyddion 2.58 for image generation and calculation of statistical quantities.⁵²

Coefficient of thermal expansion: Samples were marked with a dot at the approximate centre of each side using a fine marker pen. The sample was then placed on a JPK High Temperature Heating Stage (HTHS) using thermal coupling compound. The HTHS was mounted on the sample stage of a Dimension Icon AFM using one inch diameter, half inch and quarter inch tall stainless steel posts (Thorlabs) and silicone moulding rubber (ReproRubber, Flexbar) as a removable adhesive. The AFM itself was not used to image the sample. Instead, the motorised stage and viewing optics were used as a travelling microscope to measure the location of small features (see Figure S5 and Figure S6) on the sample surface immediately adjacent to the dots made with marker pen. The stage has a built in position encoder and a specified bidirectional repeatability of 3 μm . This allowed the (x,y) position of each feature to be recorded at 50°C, and then again at 150°C. Such measurements were then repeated 5 times. The separation between the features was calculated from the measured (x,y) positions at each temperature, and converted into a coefficient of thermal expansion assuming linear strain per unit temperature (see Table S1 and Table S2).

CFRP 50 °C												CFRP 150 °C											
		left point		right point		top point		bottom point		left point		right point		top point		bottom point							
	x	y	x	y	x	y	x	y	x	y	x	y	x	y	x	y							
1	89111	178622.3	81774.3	178004.3	86106.8	175476.5	85034.3	182379.3	89105.3	178626.3	81768.3	178019	86097.8	175458.8	85036.5	182424.5							
2	89110.8	178622.5	81773.8	178002.3	86109	175473.8	85034	182380	89106	178626.5	81769	178018	86094.8	175458	85034	182423							
3	89108.5	178621	81774.8	178003.5	86108.5	175476.3	85035	182380.5	89105.8	178626.8	81770	178018.8	86096.8	175459.5	85036	182423							
4	89108.5	178621	81776	178004	86107.3	175472.3	85033.8	182382	89103.3	178625.8	81768.8	178017.5	86096.5	175458.3	85033.3	182421.5							
5	89110.8	178623.5	81775	178003.3	86109	175475.5	85034.8	182381.3	89106.5	178627	81769	178019.3	86095.8	175459.5	85036	182422							
mean	89109.92	178622.06	81774.78	178003.48	86108.12	175474.88	85034.38	182380.62	89105.38	178626.48	81769.02	178018.52	86096.34	175458.82	85035.16	182422.80							
sd	1.30	1.07	0.83	0.77	1.01	1.79	0.51	1.06	1.24	0.47	0.62	0.75	1.12	0.68	1.42	1.15							
xl-xr		yl-yr		xt-xb		yt-yb		length lr		length lb		length lr		length tb									
7335.14		618.58		1073.74		-6905.74		7336.36		607.96		1061.18		-6963.98		7044.37							
Change 50 – 150		1.22		-10.62		-12.56		-58.24		0.33		55.65		4.50E-07		7.96E-05							
CTE																							

High-temperature atomic force microscopy: All imaging was carried out using a NanoWizard 3 Ultra AFM (JPK Instruments, now JPK BioAFM (Bruker)) with a $30 \times 30 \times 6.5 \mu\text{m}^3$ scanner and equipped with a sample heating stage (HTHS, JPK Instruments). Good thermal contact between the sample and the HTHS was ensured by using a thin layer of thermal coupling compound (HTSP, Electrolube) between the back side of the sample and the hot plate of the HTHS. In all cases, the sample was oriented such that the fibre axis was approximately along the fast scan axis. All imaging was performed in AC mode using PPP-NCL cantilevers (Nanosensors) (nominal resonant frequency: 190 kHz, nominal stiffness : 48 N/m). These cantilevers do not have a reflective metal coating on the upper surface, so minimal deflection drift was caused by sample heating. To ensure consistent imaging parameters, the deflection sensitivity was calibrated for each cantilever immediately before each temperature cycle, using the non-contact method implemented in the JPK SPM Desktop software, which uses the nominal plan view dimensions of the cantilever and a thermal noise spectrum captured far from the surface at room temperature. The cantilever was tuned to an amplitude of 25 nm at a distance of approximately $3 \mu\text{m}$ above the surface immediately before each scan to account for the effects of squeeze film damping and shifts in the amplitude and resonant frequency due to heating. For the majority of scans an amplitude setpoint of approximately 75% was used, though in a few cases it was necessary to reduce this to 65-70% to ensure good tracking of the surface.

Scans were taken at room temperature (typically 25-28°C at the sample location, measured from the sensor in the HTHS), and at 10°C intervals from 60 – 150°C. The AFM tip was retracted 50 μm from the surface while the sample temperature was adjusted and allowed to fully stabilise before re-engaging. Features on the surface were used to identify the area of interest, and the scanner was manually offset at each temperature to compensate for thermal drift in the XY position and ensure that approximately the same area was imaged over the full range of temperatures. All scans were $10 \times 10 \mu\text{m}^2$, with 512×512 pixels and captured at a line rate of 1 Hz. The feedback gains were optimised during scanning.

AFM data processing: All data processing was performed in Gwyddion 2.58.⁵² Raw height data from the Height (measured) channel were processed by first mean plane levelling, with rows then aligned *via* median of differences. The RMS roughness of the flattened images was calculated using the Statistical Quantities Tool.

Mechanical testing: For mechanical testing of ITO coated substrates, fabrication proceeded in the same manner as those for devices, except that the substrates were cut to 100 x 25 mm. These substrates were either coated in primer or primer/SiO₂ before ITO deposition. A 30 mm strip of ITO was then sputter coated in the middle of the substrate. The substrates were mounted in a 5 kN Tinius Olsen H5K-S Tensile & Compression machine, configured to a four-point bend test geometry. The bottom span was 70 mm while the top span was 30 mm. Horizon software was used to control crosshead movement and record load cell output. The top rolls were moved at a rate of 2 mm/min through a distance of 15 mm. Resistance was measured using a BK Precision 2841 resistance meter, connected to the ITO either side of the apex *via* aluminium wires and copper tape to ensure good electrical contact. A LabVIEW program was used to record the measured resistance throughout the bend test. Figure S8 and S9 shows further details of the four-point bend test set up.

Specific power calculation methodology: Specific power is a measure of power per unit mass and is calculated by dividing the areal power (at an incident solar power of 1000 W m⁻²) by the areal mass, or mass per unit area. Here, we calculate the areal mass of our devices and disregard the mass of the CFRP substrate. This is done using the known thickness of each layer and their reported densities as shown in Table S3. Our value of specific power calculated is based on our measured device stabilised power output of 14.5 %.

Material	Density (kg/m ³) ⁵³⁻⁵⁷	Thickness (m)	Areal mass (g/m ²)	Specific power (W/g)
primer	1500	8 x10 ⁻⁷	1.20	
SiO₂	2648	1.5 x10 ⁻⁷	0.40	
ITO	6800	2 x10 ⁻⁷	1.36	
SnO₂	6900	3 x10 ⁻⁸	0.21	
Perovskite	4000	6.5 x10 ⁻⁷	2.60	
Spiro-OMeTAD	1020	2 x10 ⁻⁷	0.20	
ITO	6800	1.2 x10 ⁻⁷	0.82	
		Total	6.78	21.37

Table S3: Details of densities, known thicknesses and areal masses for each layer, along with device total areal mass and final specific power value. Note, we have used a conservative estimate for the thermoplastic primer density.

5.4.2 Supporting Information Figures

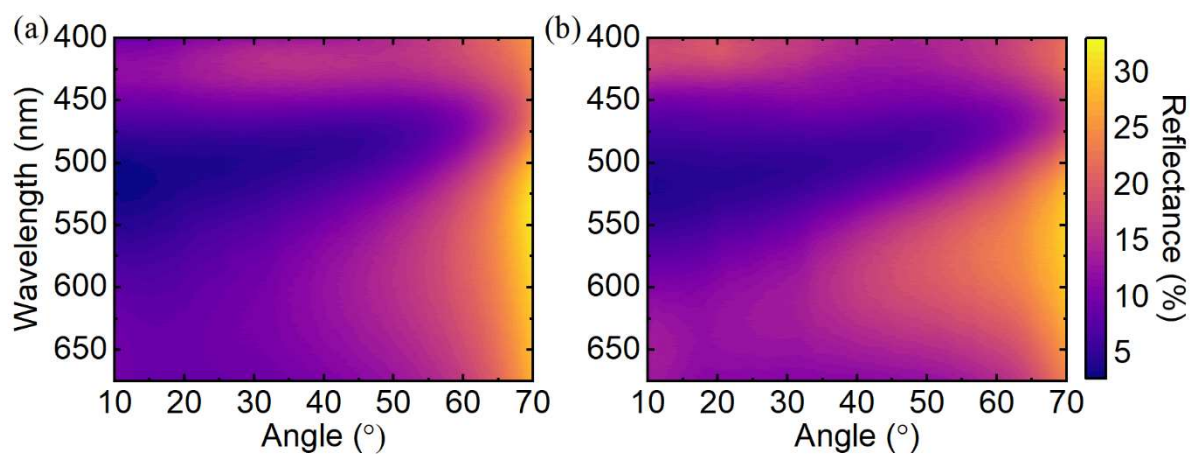


Figure S1: Angle-dependent reflectivity as a function of wavelength for bottom ITO films sputtered onto (a) glass and (b) carbon fibre-reinforced polymer (CFRP) composite substrates

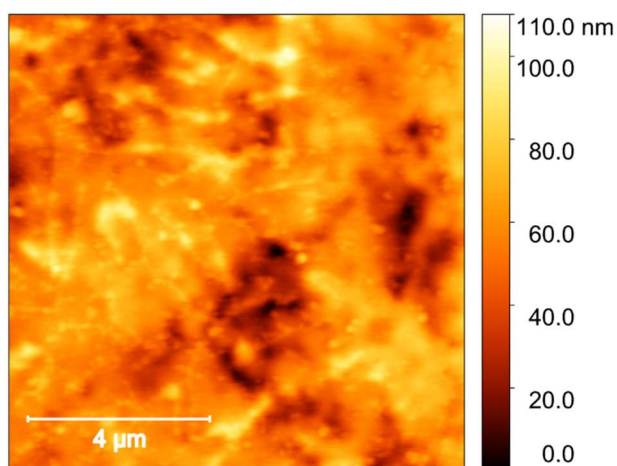


Figure S2: AFM height topography map of ITO deposited directly onto primed planarised CFRP composite substrate.

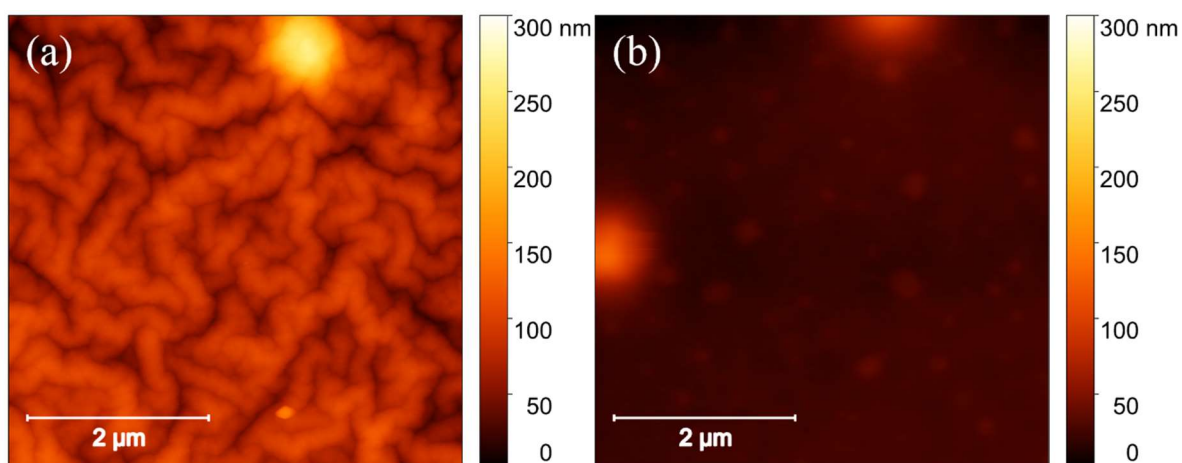


Figure S3: AFM height topography maps of ITO deposited onto (a) a SiO_2 layer, atop primer and planarised CFRP composite substrate and (b) a polished glass substrate.

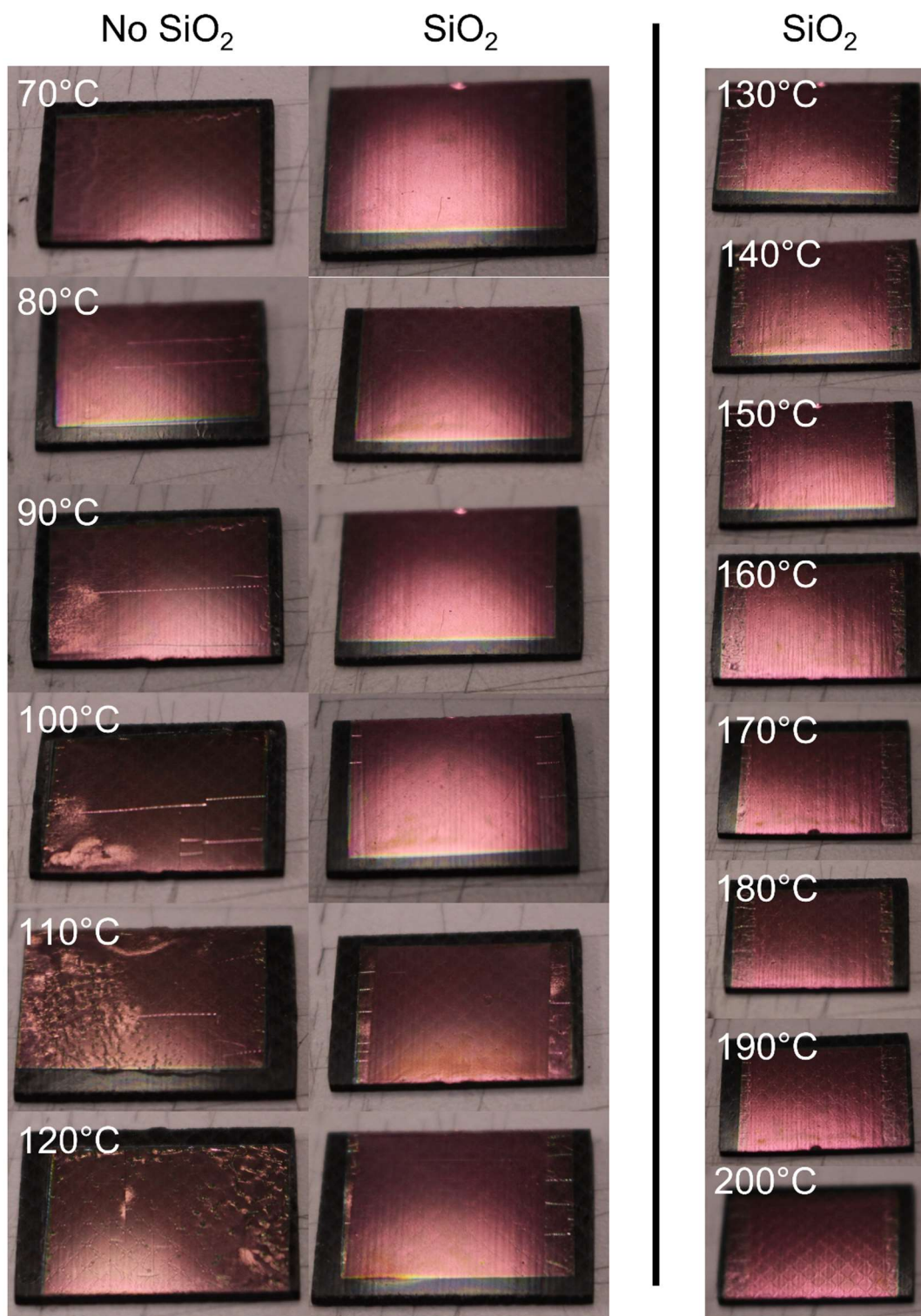


Figure S4: Comparison of ITO coated planarised CFRP composite substrates with and without the crack-prevention SiO_2 layer after being held at temperatures from 80 – 120 °C (left) to illustrate crack formation and inhibition. Also shown (right) are substrates incorporating the crack-prevention layer that have been held at temperatures up to 200 °C to illustrate stability towards thermally induced cracking.

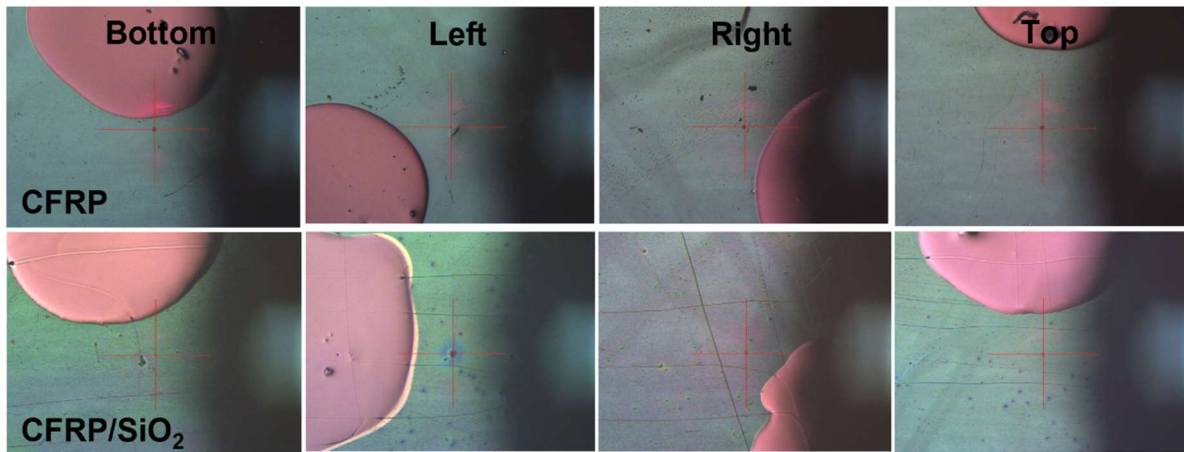


Figure S5: Optical microscope images of features used to find CTE values for bare CFRP and CFRP/primer/SiO₂ substrates. The large, approximately circular structures are dots made with a marker pen to assist in finding the features. The features used for the measurement are small surface imperfections located under the red crosshair.

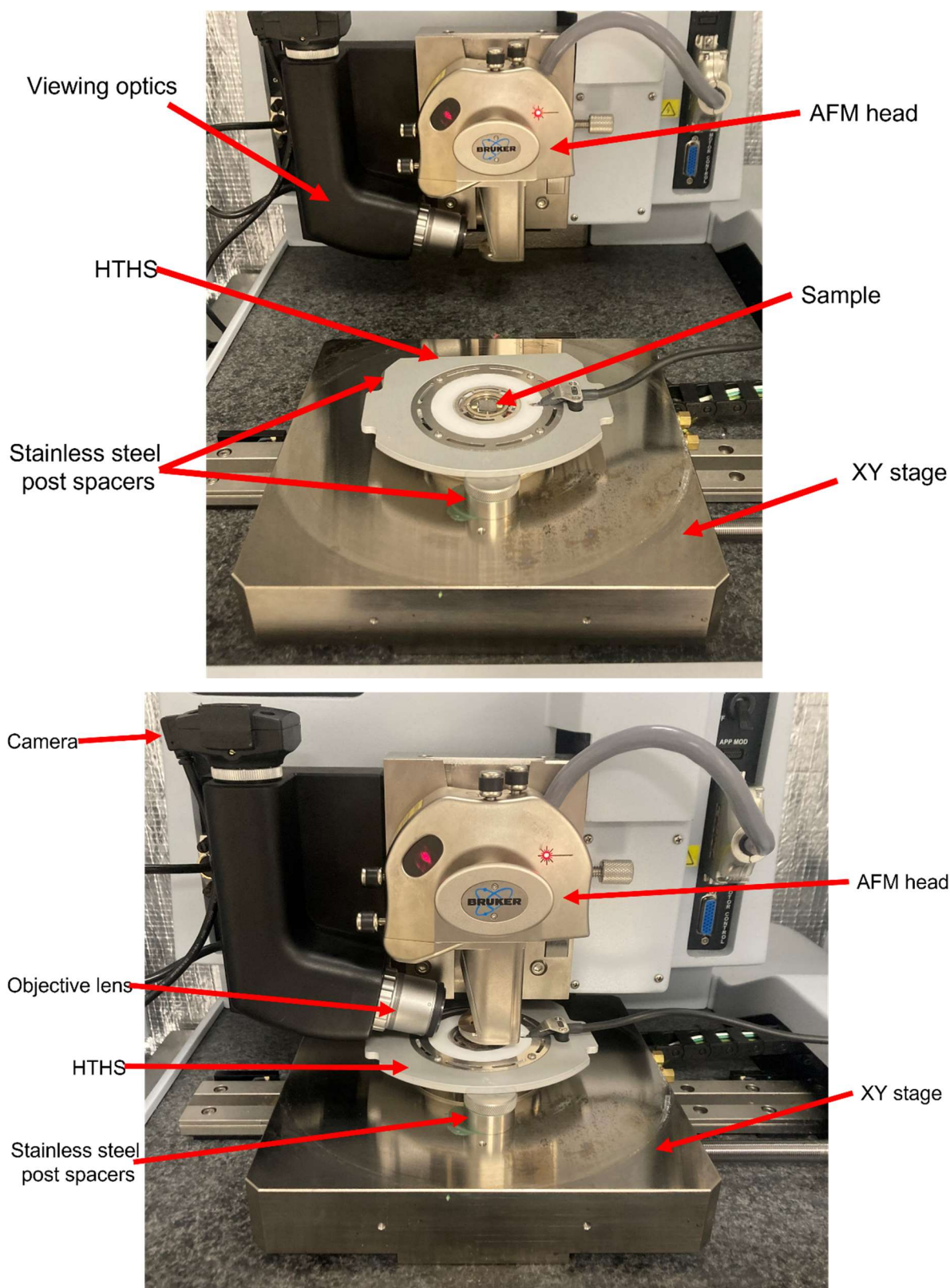


Figure S6: Experimental set up of JPK HTS / Dimension Icon AFM "Chimara" used for CTE measurements. Top image depicts sample placement with AFM head backed off for clarity, below image depicts the AFM head in position (obscuring sample) when taking measurements.

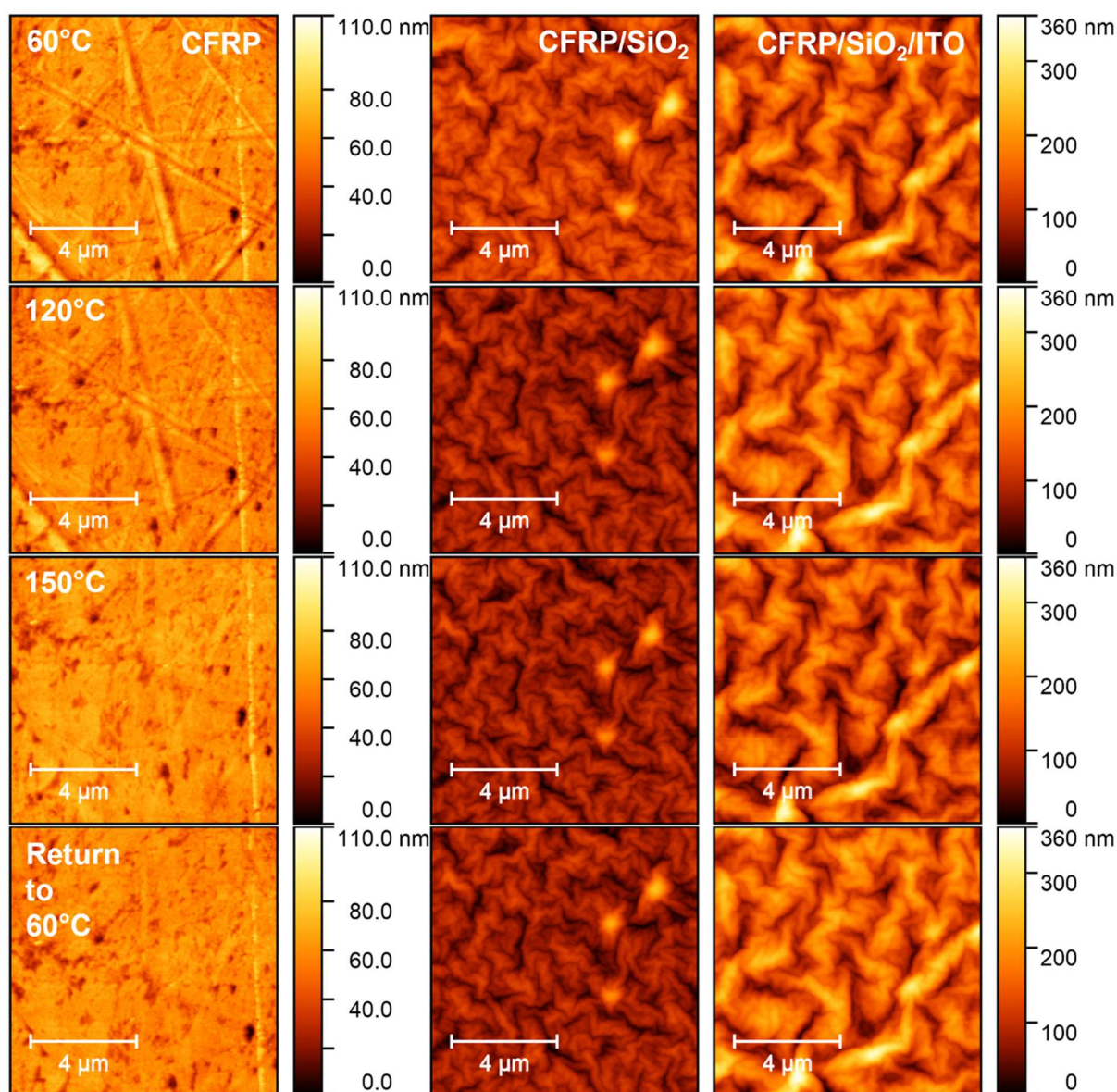


Figure S7: A selection of temperature-dependent HT-AFM scans recorded on a bare CFRP substrate (left), CFRP/primer/SiO₂ (middle) and CFRP/primer/SiO₂/ITO (right). Note that the bare CFRP undergoes irreversible changes when heated above 120 °C whereas all surface features are visible in both the CFRP/primer/SiO₂ and CFRP/primer/SiO₂/ITO samples up to 150 °C.

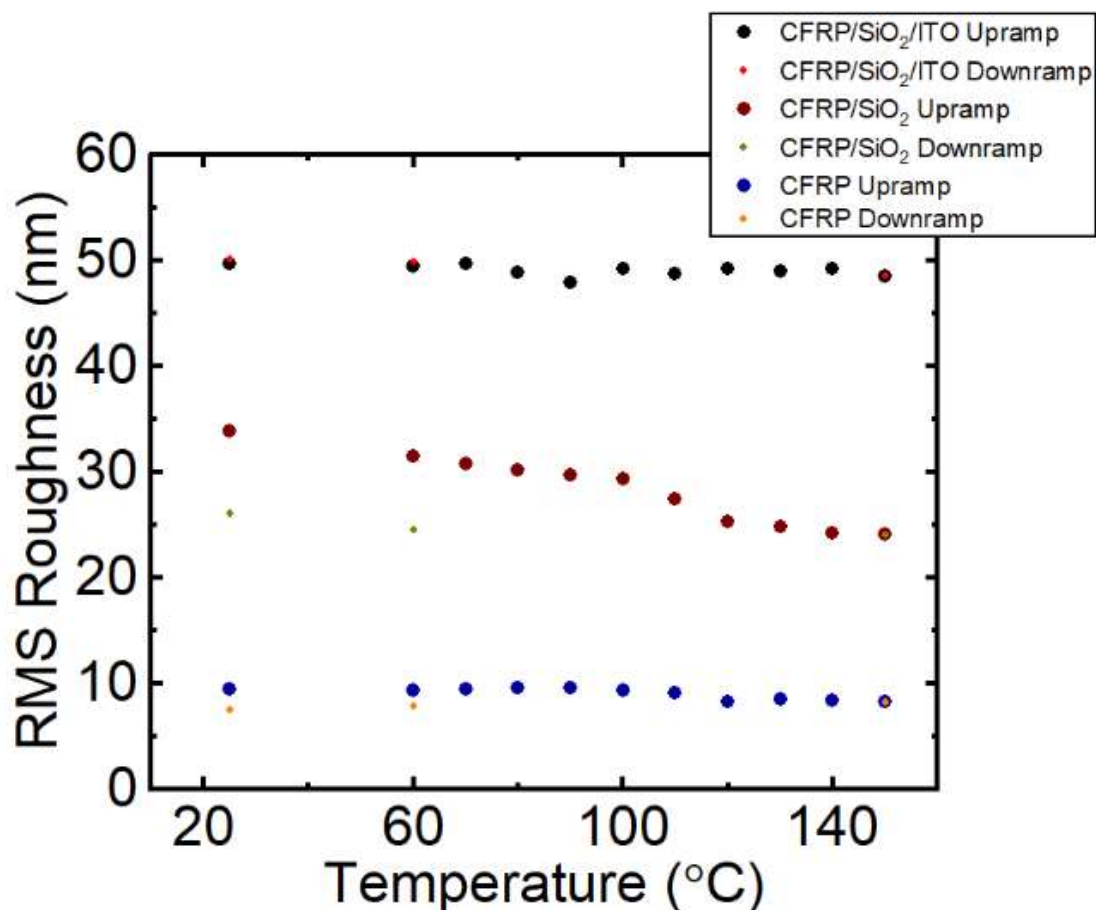


Figure S8: A measurement of RMS roughness extracted from HT-AFM for bare CFRP, CFRP/primer/SiO₂ and CFRP/primer/SiO₂/ITO substrates as a function of temperature. Note the downward trend in RMS roughness between 25 °C and 100 °C for CFRP/primer/SiO₂ substrate that is not observed in bare CFRP. Note also much larger overall plastic deformation.

High temperature AFM (HT-AFM) on CFRP substrates that are either coated with SiO₂ / ITO or are uncoated are shown in Figure S6, with Figure S7 showing the surface roughness which is extracted from the images. AFM images of CFRP samples without the SiO₂ layer (Figure S6, left hand column) indicates little change in surface morphology as films are heated to around 120 °C. Above this temperature however, surface roughness begins to reduce and by 150 °C many surface features have apparently disappeared, suggesting some form of surface / bulk modification has occurred. For samples coated by the SiO₂ layer, we observe a small reduction in surface roughness throughout the entire temperature range (see Figure S7), however wrinkles are still easily identifiable (see Figure S6 – middle column) even at 150 °C; a result that demonstrates that the film has a high degree of robustness. We propose that crack-prevention occurs due to two main mechanisms: (1) The nano-texture of the wrinkled SiO₂ acts as a roughened surface onto which the ITO binds strongly. (2) The wrinkled structure prevents the long-range propagation of cracks;

here we suspect that its highly textured nature forms a network of interconnected fissures and domains that all slightly open and as the temperature is changed, thereby eliminating the formation of large cracks. It is not possible to directly observe this effect in the high temperature AFM above, as, over a lengthscale of $10\text{ }\mu\text{m}$ the expected thermal expansion (calculated from the large scale CTE measurement above) is approximately 70 nm (~ 3.5 pixels) from $60\text{ }^{\circ}\text{C}$ to $150\text{ }^{\circ}\text{C}$, which is significantly below the level of thermal drift in the high temperature AFM setup used.

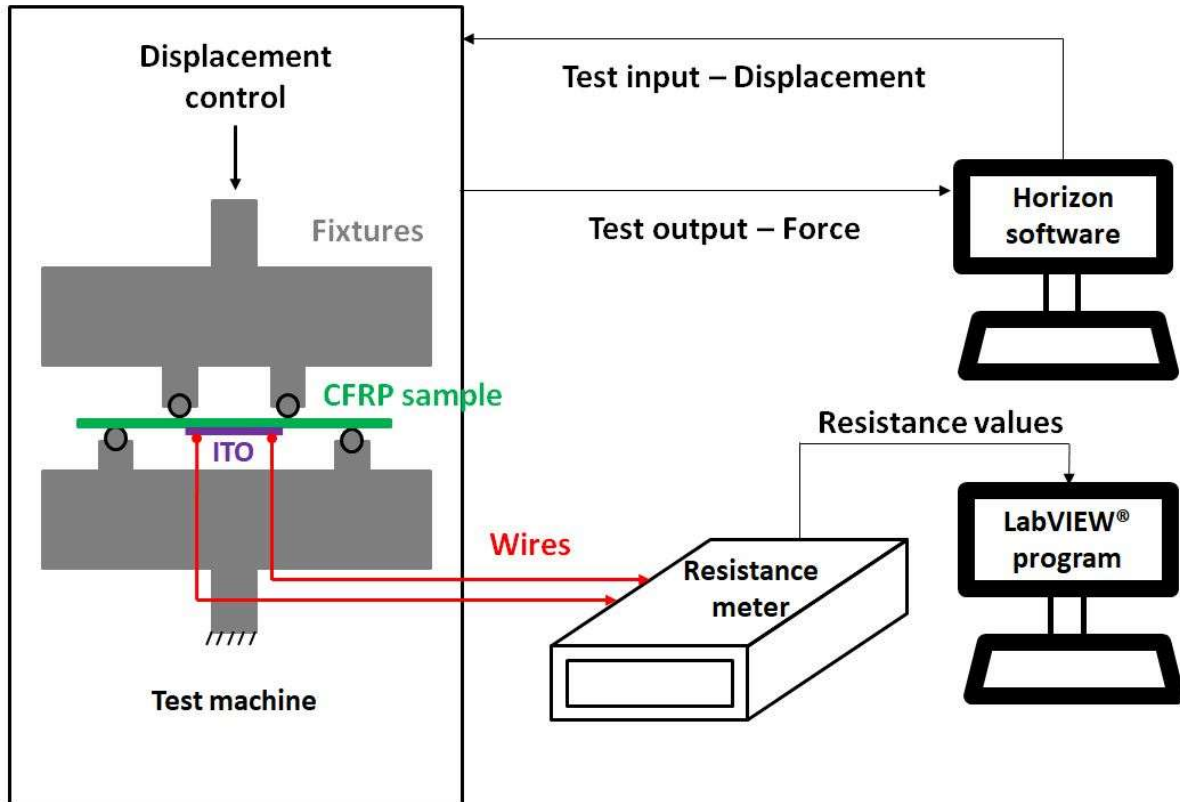


Figure S9: Schematic diagram of the four-point bend test set up.

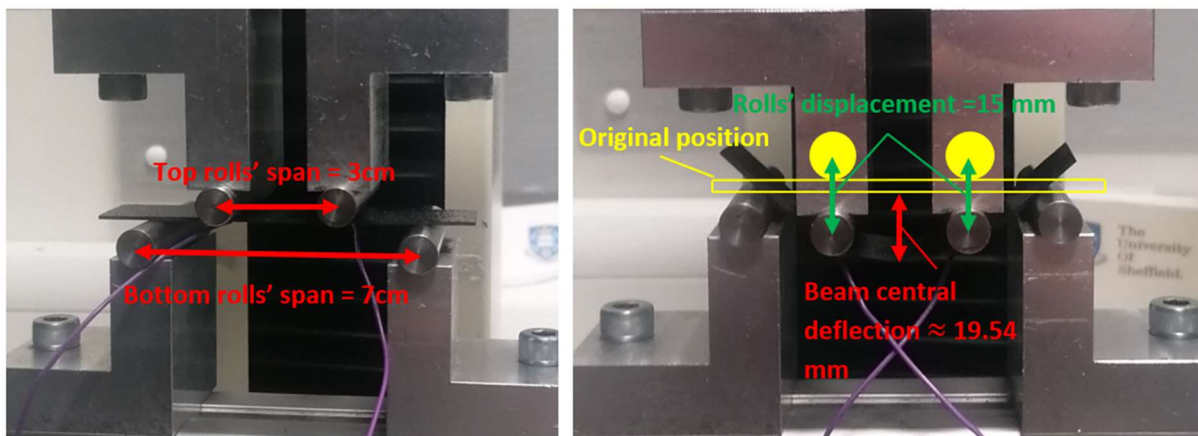


Figure S10: Annotated photographs of initial (left) and final (right) position of the four-point bend test with substrate in situ.

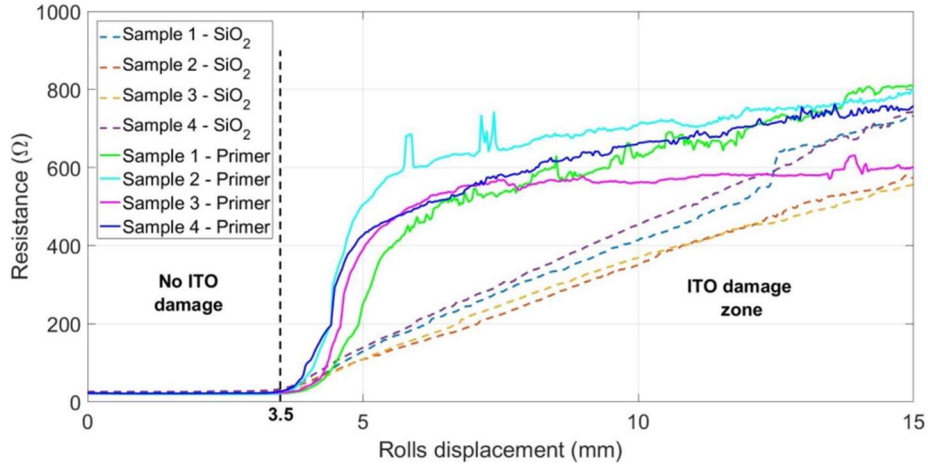


Figure S11: Measured resistance as a function of roll displacement for ITO coated CFRP composite substrates with and without the stress-release SiO_2 layer.

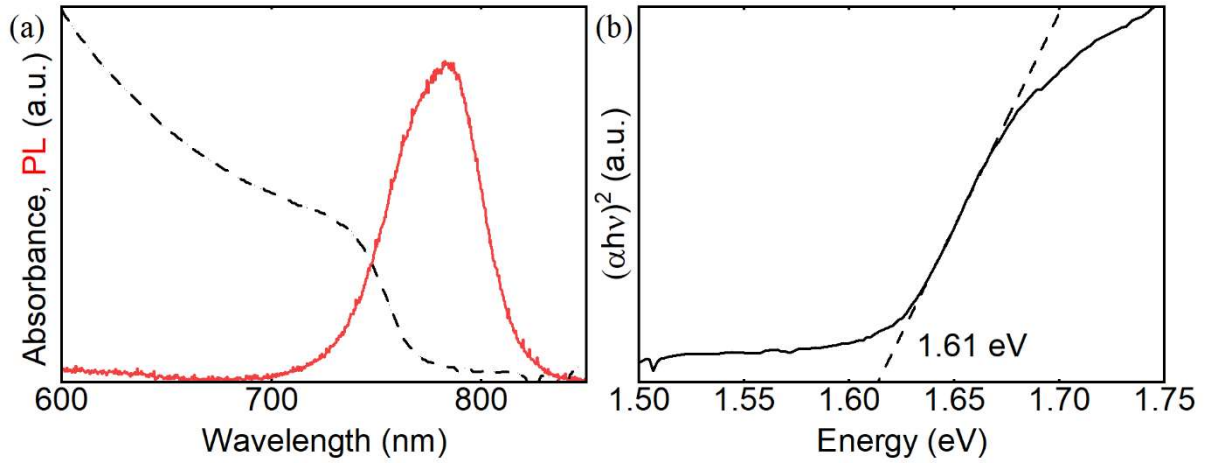


Figure S12: Part (a) depicts absorbance (black) and steady-state photoluminescence (red) spectra for the triple-cation perovskite composition deposited on a quartz substrate. Part (b) shows a Tauc plot extracted from the absorption spectrum in part (a). From this we determine an optical band gap of 1.61 eV, corresponding to a wavelength of 770 nm.

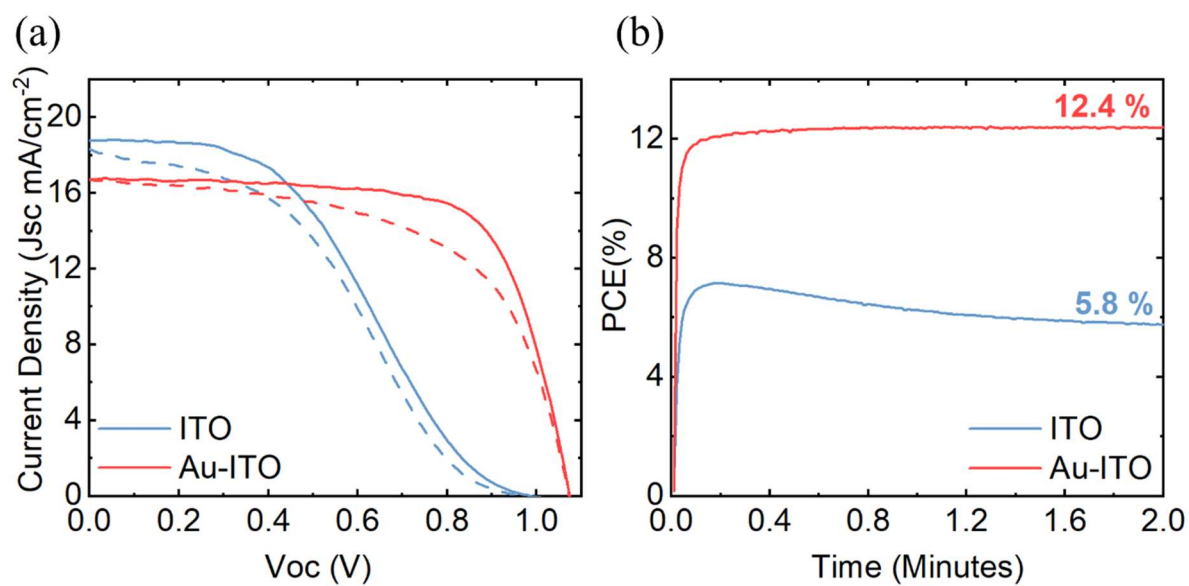


Figure S13: *JV sweeps (a) and stabilised power outputs (b) for CFRP composite PSC devices with and without the presence of a 0.8 nm gold interlayer between spiro-OMeTAD and the top ITO electrode.*

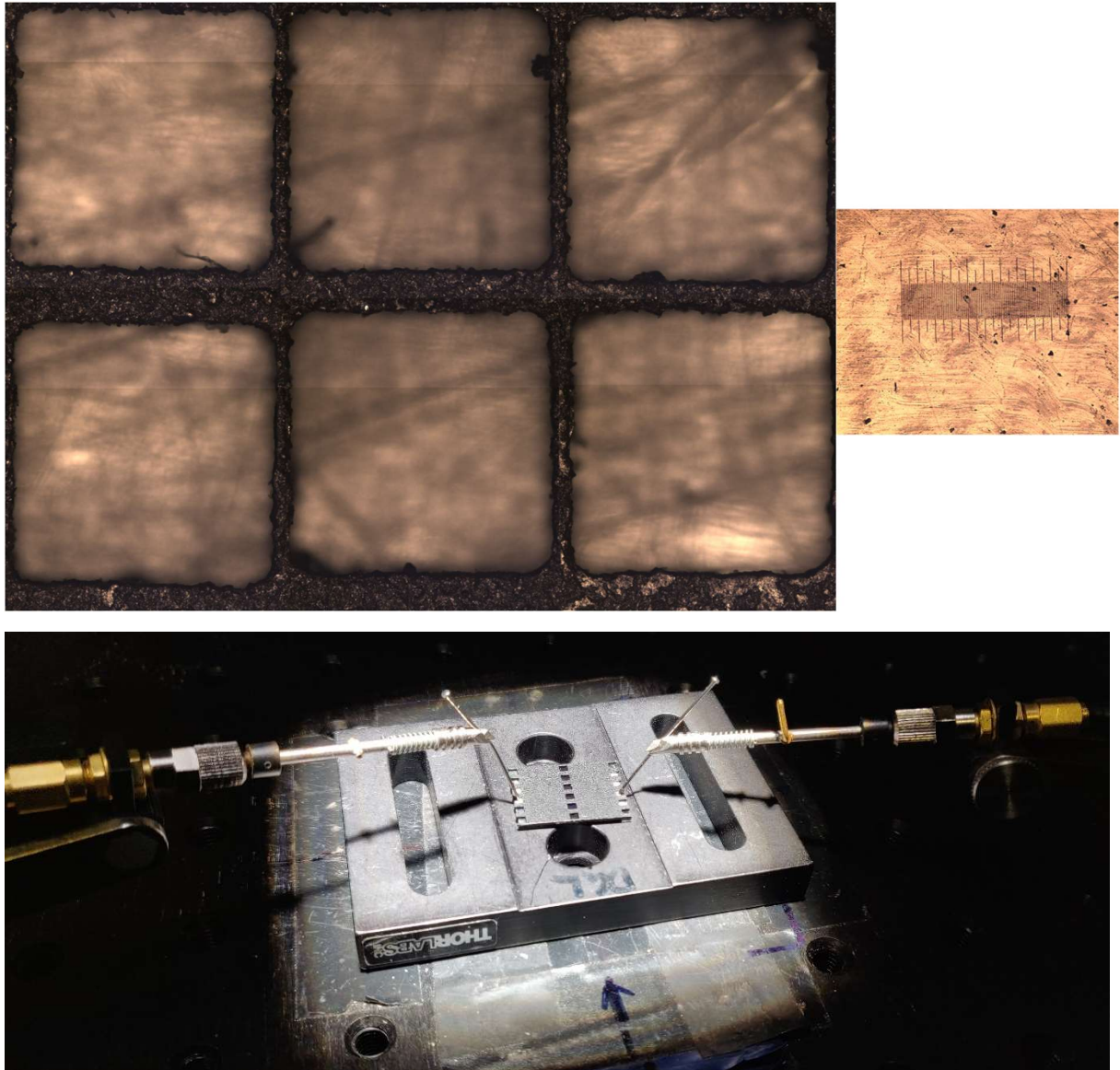


Figure S14: Composite optical microscope image of illumination mask apertures used in testing of CFRP composite PSCs. Accurate aperture areas were calculated using ImageJ, with the average area being 0.02385 cm^2 . The photograph below shows one of the CFRP-PSCs under testing.

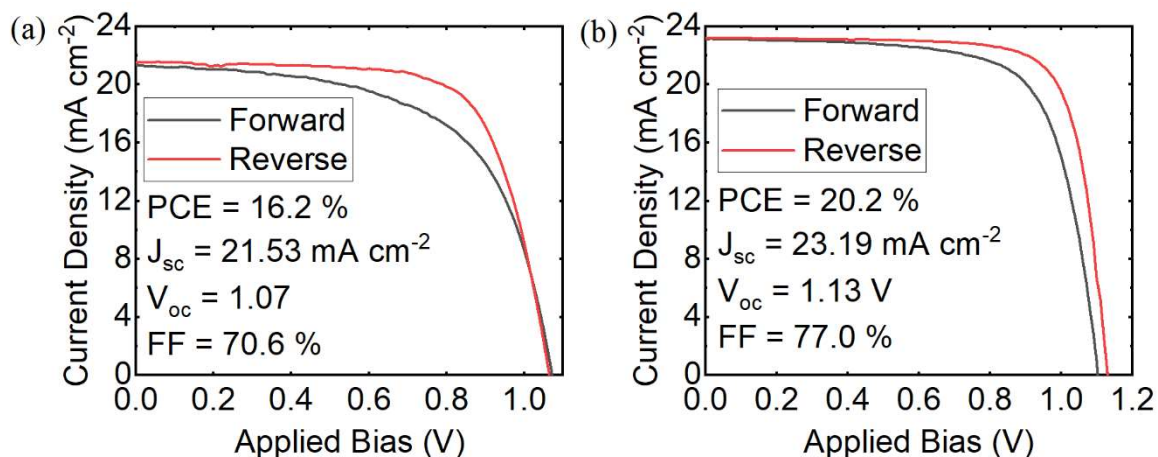


Figure S15: Part (a) represents JV data for the champion glass control device illuminated from the glass side of the device with a transparent rear ITO electrode, (b) represents JV data for the champion glass control device illuminated from the glass side of the device with an 80 nm Au rear electrode.

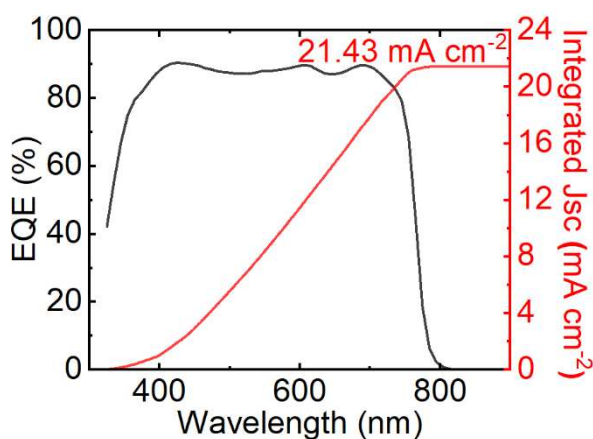


Figure S16: EQE spectrum of a standard architecture (glass/ITO/SnO₂/TC-perovskite/spiro-OMeTAD/Au) PSC illuminated through the glass substrate using the same triple-cation perovskite absorber layer composition as that used for CFRP devices. Note that we measure an enhanced EQE between 300–400 nm as compared to that recorded for devices fabricated on CFRP as discussed in the main manuscript. This improved response results from the fact that incident light is not parasitically absorbed by the spiro-OMeTAD HTL before reaching the perovskite absorber layer.

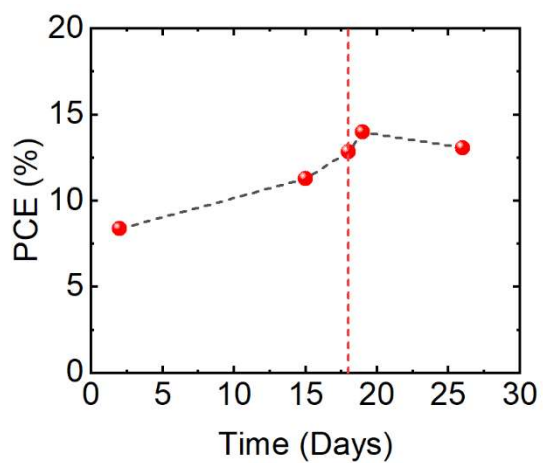


Figure S17: Average of forward and reverse sweep PCE derived from JV measurements of a single CFRP-based PSC stored in air under darkness, as a function of time. The red dashed line denotes the point in time (day 18) when an antireflection coating was deposited on the device.

5.5 References

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Chapter 6

Spray-Coated Perovskite Solar Cells Fabricated on Carbon Fibre-Reinforced Polymer Substrates

6.1 *Publication Foreword*

Having demonstrated that perovskite devices can be fabricated onto carbon fibre-reinforced polymers, and that spray coating devices onto curved substrates was indeed feasible, the next logical step was to fabricate spray coated devices onto curved carbon fibre based substrates. The first hurdle was to find a way to fabricate curved carbon fibre-reinforced polymer substrates. As we had success working on glass optical lenses in chapter 4, we elected to use these as our moulds. The prepreg layup procedure was somewhat complicated here, as in order to fabricate convex curvature, it was necessary to use concave lenses. This meant a 90° angle between the lens and the flat glass it was adhered to, along with a reflex angle greater than 270° at the rim of the lens. These angles and the circular shape of the lens created significant difficulties in conformally wrapping the relatively low elasticity prepreg layers. Coupled with shrinkage during the curing process, it was necessary to find a more benign geometric arrangement. To do this, a resin ramp was built up around each lens. Removing the as cured panels from the moulds was the next challenge. Here, curved samples were difficult to release, with resin often penetrating minute gaps between the ramp resin and the glass lens. The unidirectional carbon fibre materials would then often simply snap along their fibre axis. To solve this problem, we switched to woven carbon fibre, which we had avoided in the chapter 5 in an attempt to reduce roughness of the final substrate.

To begin with, we aimed to fabricate flat devices *via* spray coating onto the woven carbon fibre panels. It became rapidly apparent, however, that our cracking issues had returned. Indeed, the deposited ITO would begin to crack at even lower temperatures than before. Ironically, removal of the crack prevention layers actually improved the situation. It was possible to heat the substrates to 80°C before the ITO became damaged. Here, the ITO did not crack, *per se*, instead it appeared to start delaminating. We theorise this is because of an observed compressive strain along one fibre axis, but may also be related to the scrim embedded in the planarization layer, or radial expansion of carbon fibres.

In any case, ITO deposited directly onto the bare planarization layer could be heated to temperatures at which the perovskite layer could be processed. Additionally, removal of the crack

prevention layers significantly reduced areal mass, helping to boost specific power. Finally, fabrication onto curved carbon fibre-reinforced polymer substrates was attempted, although here the yield was very low, some devices did work, with the best sample displayed in the final manuscript. The final manuscript is currently undergoing peer review, having been submitted to Solar Energy Materials and Solar Cells.

6.2 *Author Contributions*

T.T fabricated all perovskite samples and devices, characterized and tested them, wrote the initial draft of the manuscript, curated all data and created all visuals. A.J-E. performed all ITO depositions. T.T and F.C-M. fabricated flat and curved carbon fibre-reinforced polymer substrates. I.A.A. performed AFM measurements. N.M.A. performed XRD measurements. R.H.G. performed angular reflectivity measurements. D.B. assisted in fabrication of devices. S.F., C.P. and S.A. assisted with sample curation. O.S.G. and E.J.C. advised on fabrication of devices. L.M.J. assisted with optoelectronic-mechanical testing. J.P.A.F., J.M.W. and D.G.L. conceptualised, funded and supervised the study. All authors contributed to editing of the manuscript.

6.3 *Publication Main Body*

Spray-Coated Perovskite Solar Cells Fabricated on Carbon Fibre-Reinforced Polymer Substrates

*Timothy Thornber, Ana Jurado-Estrada, Fernando Cepero-Mejias, Ibrahim A. Albariqi, Noor M. Alotaibi, Robert H. Gordon, Dinesh Behera, Samuel Furtado, Clara Polaco, Sajjad Ahmad, Onkar S. Game, Elena J. Cassella, Luke. M. Jones, J. Patrick A. Fairclough, J. Michael Walls and David G. Lidzey**

T. Thornber, I.A. Albariqi, N.M. Alotaibi, R.H. Gordon, D. Behera, S. Ahmad, E.J. Cassella and D.G. Lidzey

Department of Physics and Astronomy, School of Mathematical and Physical Sciences, University of Sheffield, Hicks Building, Hounsfield Road, Sheffield, S3 7RH, U.K.

Email: d.g.lidzey@sheffield.ac.uk

A. Jurado-Estrada, J.M. Walls

CREST, Wolfson School of Mechanical, Electrical and Manufacturing Engineering, Loughborough University, Loughborough, Leicestershire, LE11 3TU, U.K.

F. Cepero-Mejias

Centre for Future Transport and Cities (CTFC), Coventry University, NTDC, Swift Road, Coventry, CV1 2TL, U.K.

L.M. Jones, J.P.A. Fairclough

School of Mechanical, Aerospace and Civil Engineering, University of Sheffield, Sir Frederick Mappin Building, Mappin Street, Sheffield, S1 3JD, U.K.

I.A. Albariqi

Physics Department, Faculty of Science, Al-Baha University, Alaqiq 65779-7738, Kingdom of Saudi Arabia.

N.M. Alotaibi

Department of Physics, College of Science, Taif University, Taif 21944, Kingdom of Saudi Arabia.

S. Furtado, C. Polaco

Composite Centre, Advanced Manufacturing Research Centre, University of Sheffield, Advanced Manufacturing Park, Wallis Way, Catcliffe, Rotherham, S60 5TZ, U.K.

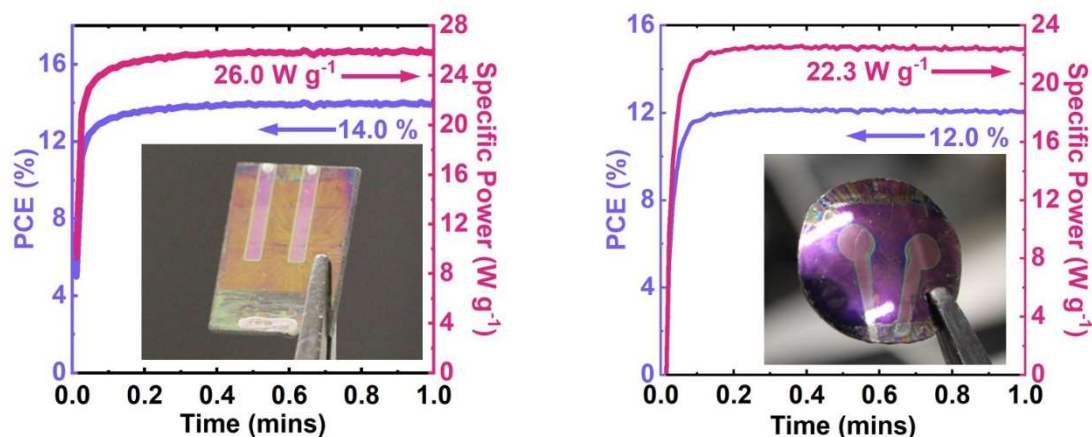
O.S. Game

Department of Physics, Indian Institute of Technology (IIT), Indore, Khandwa Road, Simrol, Indore – 453552, Madhya Pradesh, India.

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Keywords: carbon fibre-reinforced polymers, integrated photovoltaics, perovskite solar cells, high specific power, building integrated photovoltaics, mobile power generation

6.3.1 Abstract



Carbon fibre-reinforced polymers (CFRPs) combine high strength and elastic modulus with low weight, and are thus an important material within the automobile and aviation industries. Combining high performance perovskite solar cells (PSCs) with CFRP substrates presents an opportunity to create structural materials that also generate power. Here such mobile power applications require the use of devices having a high specific power in which both the efficiency and the weight of the solar cell is of critical importance. Here, we discuss the fabrication of *n-i-p* PSCs *via* ultrasonic spray coating on CFRP substrates. Our devices yield a stabilized maximum

power conversion efficiency (PCE) of 14.0 %, corresponding to a specific power of 26.0 W g⁻¹. We also spray-coat PSCs onto dome-shaped CFRP substrates having a maximum PCE of 12.3 %, equivalent to a specific power of 22.8 W g⁻¹. Importantly, we subject devices to low cycle mechanical fatigue testing, repeatedly applying a load of 50 N, with devices retaining 100 % of their prestressed PCE after 25 stress cycles. This is the first demonstration of curved, rigid, CFRP based PSCs that can bear an appreciable mechanical load, making them suitable for mobile power applications.

6.3.2 Introduction

Hybrid organic-inorganic metal halide perovskites have been the subject of intense research efforts since their first practical demonstration in 2012.^[1,2] Having high charge carrier diffusion lengths^[3] and mobilities,^[4] high defect tolerance,^[5] high optical absorption coefficients,^[1] and low exciton binding energies^[6] these materials are ideally suited for photovoltaic (PV) power generation. Single junction perovskite solar cells (PSCs) have, as of 2025, demonstrated certified power conversion efficiencies (PCEs) of up to 27.0 %, ^[7] illustrating the significant potential of these materials. Importantly, hybrid perovskites can be deposited from solution using a wide range of deposition techniques, with all processing steps performed at relatively low temperature.^[8] This critical advantage allows them to be combined with a wide variety of substrate materials, including those based on polymer films,^[9,10] metal foils,^[11-16] biodegradable substrates,^[17-19] and flexible willow glass.^[20]

Carbon fibre-reinforced polymer (CFRP) composites combine high strength and elastic modulus with low weight.^[21] Such materials find uses in a variety of applications including aerospace,^[22] automobile,^[23] construction,^[24] defence,^[25] and medical industries.^[26] In many of these industries, there are potential applications where solar-power generation by external surfaces could be beneficial, including in electric vehicles (EVs), unmanned aerial vehicles (UAVs) and the internet of things (IoT). The combination of PSCs with CFRP therefore represents an attractive approach to realise both high specific power PV devices and high specific strength materials which could be used – for example – as the monocoque of an electric vehicle or the aerofoil of a UAV. We note that CFRP is commonly used in medical imaging due to its transparency to X-rays,^[26] and so the incorporation of perovskite X-ray detectors with the curved gantry walls of a radiotherapy machine could also be used to significantly improve image resolution compared to rotating flat detectors. We also propose that lightweight CFRP based PV could find applications in the built environment in locations where the use of relatively heavy silicon-based technologies becomes impractical.^[27]

The specific power of a PV device can be significantly improved by directly integrating it onto a primary load-bearing surface. By directly fabricating a PV device stack onto a multi-functional surface, the effective functional weight of the PV system is essentially limited to the device stack itself. Here, the device shares the structural mass of the host component, eliminating the need for separate structural support and often reducing packaging requirements. This minimizes system weight and thus maximizes device specific power. In contrast, the more common approach of laminating a prefabricated, flexible PV device onto a surface of interest introduces several non-functional weight penalties, including the weight of adhesive layers, additional supporting structures often inherent to the flexible panel itself and crucially, rear-facing encapsulation.

Significant research has been conducted into the development of high specific power PSCs, typically focusing on ultrathin polymer substrates. In 2015 Kaltenbrunner *et al.* demonstrated PSCs with a high specific power. Here, PSCs were fabricated on 1.4 μm thick PET substrates with a specific power of 23 W g^{-1} reported – enough to power a lightweight solar plane.^[28] Kang et al. then created devices with a specific power of 29.4 W g^{-1} using PEN substrates combined with an orthogonal silver nanowire transparent electrode.^[29] Wu et al. subsequently demonstrated devices with a specific power of 30.3 W g^{-1} using an ultrathin 3 μm parylene substrate combined with a lift off fabrication technique.^[30] The Kaltenbrunner group have subsequently demonstrated devices with a specific power of 44 W g^{-1} utilising a quasi-2D perovskite system mounted onto $< 2.5 \mu\text{m}$ PET/ Al_2O_3 substrates, again powering an aerial vehicle.^[31] The highest specific power devices have been reported by Jia et al using colourless polyimide-based substrates with devices having a peak specific power of 50 W g^{-1} .^[32] Large area perovskite solar modules have also been deposited onto flexible polymer substrates having an area up to 117.0 cm^2 with a specific power of 1969 W kg^{-1} .^[33-35]

While the majority of research into perovskite PV focuses on PSCs in which the solution processed layers are spin coated, attention has increasingly turned to the use of deposition processes compatible with high throughput manufacture as this will be critical for the eventual commercialisation of this technology.^[36] High throughput processes are typically based on roll-to-roll (R2R) fabrication, for which a variety of solution deposition techniques can be used, including slot die,^[37] blade coating,^[38] vacuum coating,^[39] ink-jet,^[40] and ultrasonic spray coating.^[41] Of these techniques, all but spray coating relies on either forming a meniscus, or a close proximity between the deposition head and the substrate. These restrictions are straightforward to achieve when a substrate is held flat, as is common in R2R processing. In contrast, spray coating is compatible with film processing over 3D surfaces,^[42] and thus is compatible with complex surfaces that curve in more than one direction (e.g. the roof of a car or the wing of an aeroplane). Here, we note that

PV devices fabricated onto flexible substrates which are subsequently bonded to a surface of interest can only wrap around surfaces that curve in a single direction. Indeed, more complex surfaces require either a substrate to be stretched,^[43] or to otherwise include pleats to allow it to completely cover a surface.^[44] This limits the extent to which flexible PV technologies can be applied in mobile power applications.

We believe that ultrasonic spray coating represents a promising route that will permit PSCs to be directly integrated onto CFRP substrates having complex topological shapes. Our group has previously reported the successful fabrication of *n-i-p* architecture PSCs onto flat CFRP substrates,^[45] however such devices were fabricated onto unidirectional CFRP substrates *via* spin coating. The unidirectional fibre orientation of such substrates resulted in anisotropic thermal expansion which necessitated the use of crack prevention interlayers to protect the indium tin oxide (ITO) bottom electrode during the thermal annealing step used to process the perovskite thin film.

In this work, we demonstrate the fabrication of *n-i-p* PSC devices in which the perovskite absorber layer is deposited *via* ultrasonic spray coating onto both flat and curved substrates. Importantly, we utilise woven carbon fibre-reinforced polymer substrates, creating a thermally robust substrate that does not require crack prevention interlayers. This dramatically reduces the areal mass of the devices while improving the morphology of the bottom ITO electrode, allowing us to create high specific power PSCs that have improved yield and stability. We show flat CFRP devices yield champion PCEs of 14.0 %, which stabilise at 14.0 %. Such devices generate a specific power of 26.0 W g⁻¹ assuming the substrate is already extant. Having established our processes on flat CFRP substrates, we then demonstrate spray-coated curved CFRP devices which yield a maximum PCE of 12.3 %, stabilised at 12.0 %, corresponding to a maximum specific power of 22.8 W g⁻¹. We believe our work demonstrates the inherent compatibility of spray-cast PSC devices with CFRP, and suggests a promising method to create materials for mobile power applications that have both structural and energy-harvesting capabilities.

6.3.3. Results and Discussion

CFRP substrates are generally composed of a series of woven carbon fibres encased in an epoxy resin matrix. While it might be expected that the electronic properties of CFRP would be dominated by the insulating epoxy matrix, we have previously found that CFRP substrates have significant electrical conductivity as a result of individual carbon fibres that protrude through the resin matrix at the surface. This leads to the formation of substrates that are both relatively rough and have a high degree of electrical conductivity – attributes that make them unsuitable as

substrates for thin film electronics. To mitigate such issues, an epoxy planarization layer was placed between the prepreg CFRP sheets and the glass mould prior to curing in an autoclave. **Figure 1a** shows a photograph of a typical planarized, woven CFRP substrate used in this work, with Figure 1c topography measured using a surface profilometer. From this we determine a root mean squared (RMS) roughness of 180 nm over a length scale of 2 mm. Here, the diamond shaped motif apparent is due to a thermoplastic scrim set into the commercially available epoxy planarization layer. For completeness we include an atomic force microscopy (AFM) measurement of a planarized CFRP substrate, with an RMS roughness of 4.8 nm determined over a length scale of 5 μm in Figure S1.

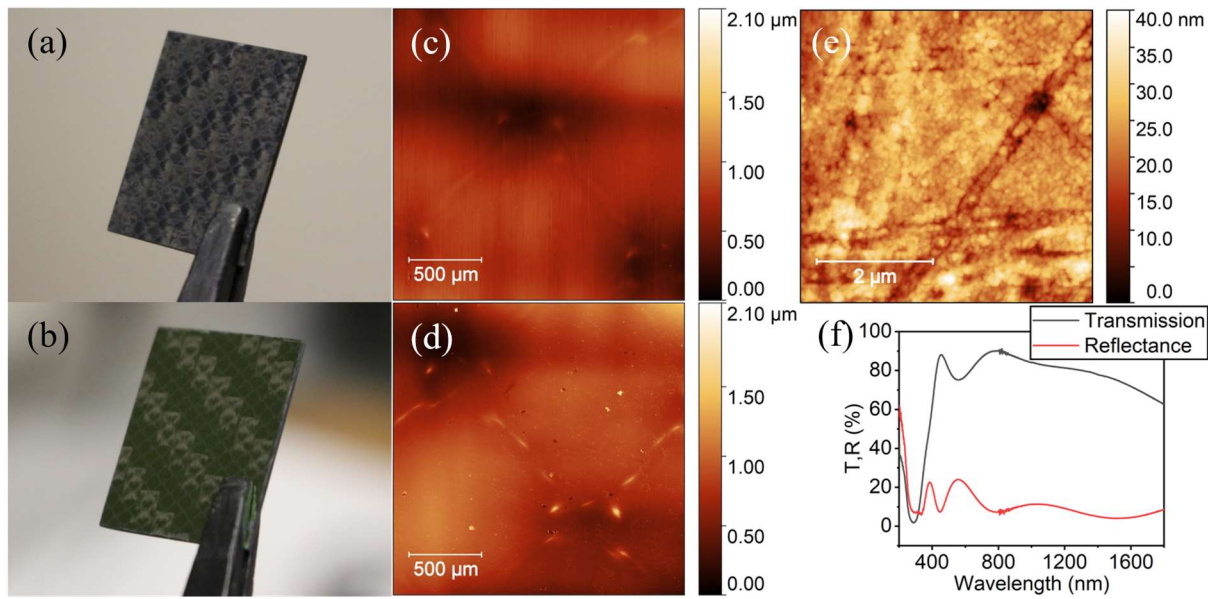


Figure 1: a) Photograph of planarized CFRP substrate, b) photograph of ITO coated planarized CFRP substrate, c) surface topography of planarized CFRP substrate, d) surface topography of ITO coated planarized CFRP substrate, e) AFM image of ITO coated directly onto planarized CFRP substrate, f) optical transmission (T) (black) and reflectance (R) (red) for the bottom ITO electrode as deposited onto glass.

We have performed measurements of the coefficient of thermal expansion (CTE) (see SI for methods) of our woven CFRP to determine its capacity to be heated as necessary for any subsequent perovskite thermal annealing steps. We determine a CTE of -0.45 and -42 ppm K^{-1} along the two fibre axes, confirming that the substrate undergoes an anisotropic compression as it is heated. We find that indium tin oxide (ITO) films deposited directly onto the planarized CFRP *via* magnetron sputtering remain stable when heated up to 80 $^{\circ}\text{C}$, and at higher temperatures begin to undergo micro-cracking and delamination (See Figure S2) in agreement with the generation of a compressive stress as temperature increases. We emphasize, however, that it is possible to

fabricate PSCs onto CFRP using process temperatures up to 80 °C without significant loss in device efficiency.

Figure 1b shows a photograph of a typical ITO coated CFRP substrate, with Figure 1d showing its surface topography from which we determine a roughness of 210 nm over a 2 mm. Figure 1e shows an AFM measurement of an ITO film on CFRP; here, we find such films have an RMS roughness of 4.5 nm over a length scale of 5 μ m. We believe that the low degree of ITO roughness contributes to the promising device yield and excellent storage stability as we discuss below. Figure 1f plots transmission and reflectance spectra recorded of control ITO films deposited onto a glass substrate, with a maximum reflectivity of 24.0 % at a wavelength of 557 nm determined. We have measured the thickness of such films on glass using a surface profiler to scan across an etched step, and determine a thickness of 200 nm. We have also measured the angular dependent reflectivity (see Figure S3a,b) for ITO films on both glass and CFRP, with closely matched results suggesting that the films on both surfaces are optically and morphologically similar.

PSC devices were fabricated onto CFRP/ITO surfaces *via* a combination of both ultrasonic spray coating and spin coating. First, a colloidal tin oxide nanoparticle solution (np-SnO₂) was ultrasonically spray-coated in air onto cleaned CFRP/ITO substrates. These were then annealed for 5 minutes at 80 °C before being transferred into a N₂ filled glovebox. A 1.2 M solution of Cs_{0.05}FA_{0.81}MA_{0.14}PbI_{2.55}Br_{0.45} (referred to as TC-perovskite) dissolved in an 80:20 v/v% DMF:DMSO solvent mixture was then ultrasonically spray-coated onto the np-SnO₂ coated substrate. The substrate was then exposed to a rough vacuum for 4 minutes to induce perovskite nucleation. The substrate was then annealed at 80 °C for 5 minutes under nitrogen followed by a further 30 minutes at 80 °C under a rough vacuum to remove all residual solvent and improve crystallinity. A doped solution of Spiro-OMeTAD was then spin coated under N₂ onto the surface and allowed to oxidise overnight. Finally, a 1 nm thick layer of Au was thermally evaporated onto the substrates before the deposition of a 120 nm thick transparent top ITO contact *via* magnetron sputtering. Full details of film processing and device and materials characterisation are presented in the *Supporting Information*.

To characterise the perovskite films, we performed AFM measurements on spray-coated films deposited onto both CFRP/ITO/np-SnO₂ and glass/ITO/np-SnO₂, with data shown in **Figure 2a,b** respectively. Here, we note that both perovskite films are similar to each other over short length scales, with an RMS roughness of 12.5 nm recorded on CFRP compared to 16.3 nm on glass. For completeness we report 5 additional AFM measurements under each condition (Figure S4) and a table reporting their overall statistics (Table S1), confirming that the TC-perovskite film is morphologically similar on both substrates. We have also performed a grain size analysis on all

6 AFM images for each sample. Here, we find an average equivalent disc radius of 96.6 ± 52.1 nm and 95.8 ± 50.7 nm for samples fabricated on CFRP and glass respectively, suggesting these films are broadly equivalent in morphology, these data are summarised in Figure S5a. Figure S6 details the surface topography of these same films measured using a surface profilometer over a length scale of 1 mm. Aside from the motif that derives from the presence of the underlying scrim, these films appear broadly similar. Here, our measurements indicate that total perovskite film thickness was around 730 nm.

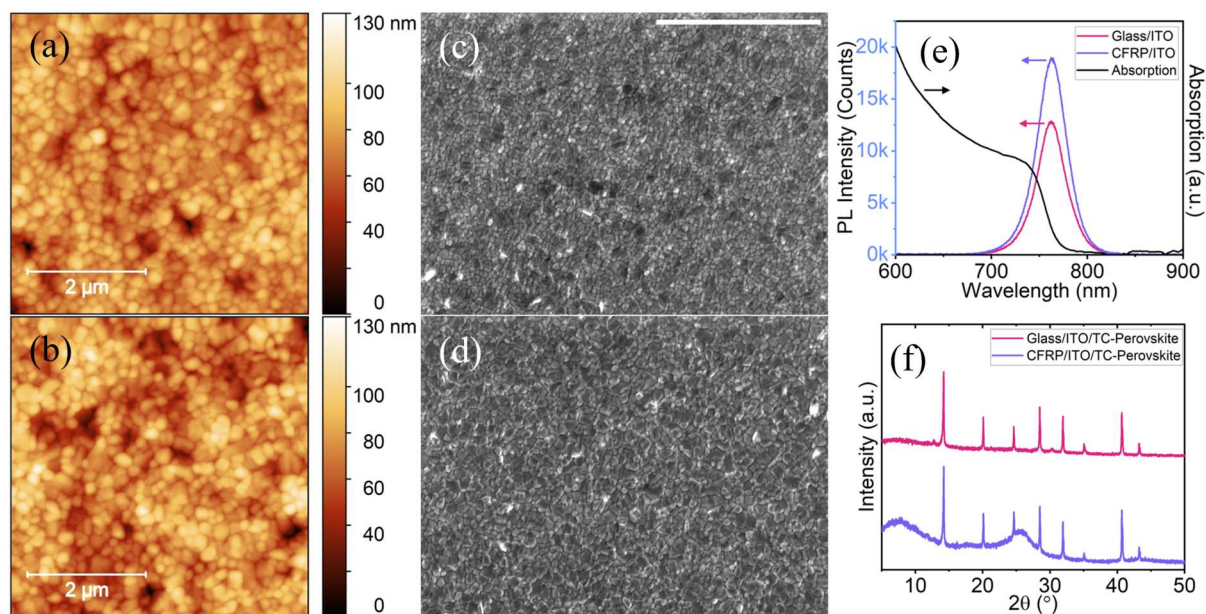


Figure 2: *a,b*) AFM images of TC-perovskite deposited onto planarized CFRP/ITO/*np*-SnO₂ and onto glass/ITO/*np*-SnO₂ respectively, *c,d*) SEM images of TC-perovskite deposited onto planarized CFRP/ITO/*np*-SnO₂ and glass/ITO/*np*-SnO₂ respectively. Here the scale bar (white) represents 5 μ m. Part *e*) shows steady state PL of TC-perovskite deposited onto planarized CFRP/ITO/*np*-SnO₂ and glass/ITO/*np*-SnO₂ together with thin-film absorption. Part *f*) shows XRD diffractograms of TC-perovskite deposited onto planarized *w*-CFRP/ITO/*np*-SnO₂ and glass/ITO/*np*-SnO₂.

Scanning electron microscopy (SEM) measurements indicate that the grain sizes of the TC-perovskite deposited onto CFRP/ITO/*np*-SnO₂ (see Figure 2c) and glass/ITO/*np*-SnO₂ (Figure 2d) are comparable, with respective average equivalent disc radii of 88.7 ± 55.1 nm and 89.2 ± 59.9 nm (see Figure S5b) again suggesting little impact on perovskite film morphology as a result of the use of a CFRP substrate. Figure 2e plots steady state photoluminescence (PL) for both perovskite films on CFRP/ITO/*np*-SnO₂ and glass/ITO/*np*-SnO₂ taken from the perovskite/air interface. The plot also includes an absorption spectrum of the TC-perovskite recorded onto glass/ITO/*np*-SnO₂. In both cases, we identify a PL emission peak maximum at 762 nm, although the PL emission intensity on the CFRP based films is slightly higher; an effect that likely results

from the comparatively high reflectivity of the ITO on CFRP compared to commercially deposited ITO on glass (see Figure S3b,c). XRD measurements (see Figure 2f) of the TC-perovskite on both CFRP/ITO/SnO₂ and glass/ITO/SnO₂ substrates confirms the same perovskite material is formed, regardless of the nature of the substrate. Here, we note that an additional amorphous signal is observed which derives from a combination of the amorphous room temperature deposited ITO and the amorphous nature of the underlying CFRP substrate (see Figure S7).

Figure 3a shows a typical image of solar cells fabricated on a CFRP substrate. We have characterised the performance of such devices using a calibrated Newport 92251A-1000 solar simulator and a Keithley 237 source-measure unit. Figure 3b shows box plots of reverse scan PCE, J_{SC}, V_{OC}, and FF, with these data taken from a total of 63 device pixels recorded over 45 individual substrates. Encouragingly, this corresponded to a device yield of over 70 %; a significant improvement on our previous work which we attribute to the relatively high level of smoothness of the CFRP/ITO films. It is probable that using a gelcoat to planarise the underlying CFRP in contrast to the scrim containing epoxy laminate used here will further reduce surface roughness, allowing us to gain additional increase in the yield of operational devices. Here, we find mean average values for PCE, J_{SC}, V_{OC}, FF, and hysteresis index (HI) of 10.7 % $\pm$ 2.2 %, 18.7 mA cm⁻² $\pm$ 1.6 mA cm⁻², 0.97 V $\pm$ 0.06 V, 59 % $\pm$ 9 % and 0.28 $\pm$ 0.17 respectively. Notably, we do not employ any passivation strategies or anti-reflection layers which could be expected to boost V_{OC} / FF / HI, and J_{SC} respectively, indicating that additional performance gains can be expected.

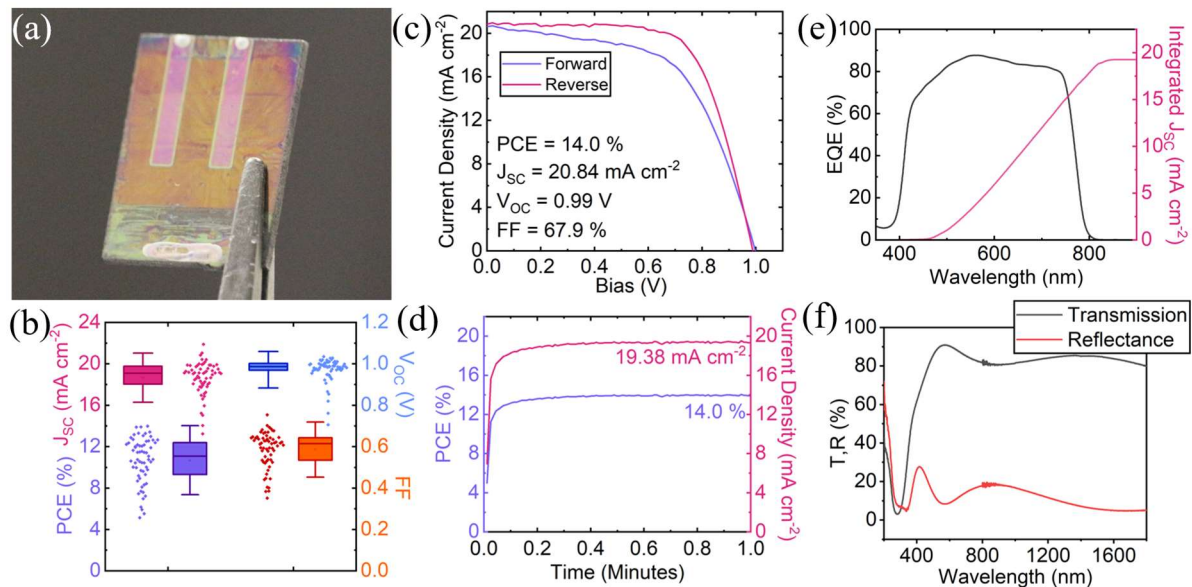


Figure 3: a) Photograph of CFRP based PSCs, b) box plots of device performance metrics based on reverse JV sweeps, c) JV data for champion flat CFRP based PSC, d) stabilised power output for champion CFRP based

PSC, e) EQE data for champion CFRP based device, f) transmission (T) (black) and reflectance (R) (red) characteristics of the top ITO electrode as measured on glass.

We plot JV characteristics for the champion device in Figure 3c where the reverse sweep yields a PCE of 14.0 %, J_{sc} of 20.8 mA cm⁻², V_{oc} of 0.99 V and FF of 68%. We find this level of performance to be in accord with our control devices fabricated on ITO/glass, which demonstrate a champion PCE of 13.1 %, J_{sc} of 21.5 mA cm⁻², V_{oc} of 0.97 V and FF of 63 % when illuminated through the top ITO electrode (see Figure S8) and a champion PCE of 13.6 %, J_{sc} of 23.0 mA cm⁻², V_{oc} of 0.99 V and FF of 60 % when illuminated through the glass/commercial-ITO electrode (see Figure S9). Figure 3d plots a stabilised power measurement for our champion device held at 0.72 V yielding a stabilised current density of 19.4 mA cm⁻² and a PCE of 14.0 %. Using an areal mass for our device as 5.39 g m⁻², we calculate a specific power for our champion cell of 26.0 W g⁻¹.

EQE data for the champion device is plotted in Figure 3e where the integrated J_{sc} is found to be 19.3 mA cm⁻²; a value in good agreement with that determined from the JV sweep. Note that our device has a limited spectral response below 400 nm as a result of parasitic absorption from the top Spiro-OMeTAD layer. Figure S8c plots EQE data for a glass control device illuminated through the glass/commercial-ITO substrate where we demonstrate an increased integrated J_{sc} due to light absorbed at wavelengths below 400 nm; a result confirming the deleterious effect of the Spiro-OMeTAD layer. Finally, the transmission and reflectivity characteristics of the top ITO electrode as deposited onto a glass substrate are plotted in Figure 3f. Here we find a peak transmission of 91.0 % at a wavelength of 572 nm.

To demonstrate the potential viability of CFRP based PSCs as load bearing structures, we have performed preliminary experiments to assess their mechanical stability. Here, we subjected devices to a three-point bend (3PB) testing regime while recording their optoelectrical properties *in-situ*. To do this, a device was mounted in a sample holder containing a silver mirror that allowed the device to be illuminated whilst a force was applied from the opposite side (see Experimental Methods section in the *Supporting Information* for further details, and Figure S10 for images depicting the full experimental set up). In this preliminary measurement, the PV device was placed under tensile stress, however we acknowledge that compression and torsional stresses are neglected. It is important to note that in these experiments the top and bottom ITO electrodes were both in contact with the bottom span points which we believe represents a potential failure mode. We anticipate that our devices would be more robust if this was not the case. Future work should include the entire range of testing profiles but with samples fabricated in such a way that the electrodes are not in contact with the testing apparatus.

In our experiments we firstly measured stabilised current output (see Figure S10a) under a 0.8 Sun simulated AM 1.5G spectrum, with devices biased at 0.7 V. Here, we found that device photocurrent output significantly deteriorated when it experienced a bending force of around 100 N, and by 150 N the devices underwent complete failure. We estimate the tensile strain on our devices at 100 N to be around 1.4 %. To further understand such effects, we selected a device and measured its JV characteristics (see Figure S10b) as a function of applied force. Here, we identify a similar outcome with the device beginning to undergo failure at around 80 N of measured force. Here, we estimate the tensile strain at 80 N to be around 1.1 %.

We then performed preliminary fatigue testing on a fresh device. Here, we subjected the device to a force of 50 N (i.e. 62.5 % of the measured force at which the devices are thought to undergo irreversible damage) over 25 stress and release cycles, with JV measurements recorded every 5 cycles. Here, we estimate the strain on our devices at maximum load to be around 0.7 %. **Figure 4a** plots the results of this test; here it can be seen that even after 25 cycles, device performance was unaffected. While it would be preferable to reach the point at which the devices failed under fatigue testing, we believe this demonstrates at least a proof of concept. Indeed, we note that PSCs fabricated on glass having a similar thickness to the CFRP used here underwent catastrophic failure (substrate fracture) at just 43 N under the same testing conditions (see Figure S12). It is clear however that extended mechanical testing studies are required in order to explore the stability of devices when subjected to millions of fatigue cycles, along with the effect of vibration, impact and variable loads that are expected in practical applications.

We have also explored the storage stability of our devices to demonstrate that neither the substrate nor the transparent top electrode is inherently incompatible with PSCs. Here, devices were stored in an inert N_2 atmosphere in the dark and the periodically subject to JV testing. We plot device efficiency as a function of storage time in Figure 4b. It can be seen that over 1000 hours, devices maintain > 100 % of their mean average initial PCE.

Having confirmed the mechanical and storage stability of our spray-coated CFRP PSCs, we have explored the fabrication of curved devices. Here, we fabricated curved CFRP substrates using optical grade convex lenses as a mould. The substrates were fabricated using the same lay-up procedure as that of the flat substrates, however the autoclave pressure was reduced to restrict resin flow during the curing stage. ITO was then directly sputtered onto the substrates in the same manner as used with the flat substrates. PSCs were fabricated following the same procedures outlined above, with the only significant difference in process being that the top transparent Au/ITO electrode was patterned through a conformal silicone evaporation mask (see Figure S12). Figure 4c shows a photograph of a curved CFRP device, demonstrating two pixels, each having

an area of around 28.3 mm^2 . Figure 4d shows a 3D schematic of the curved devices, also serving to illustrate the device architecture used for all CFRP devices explored in this work.

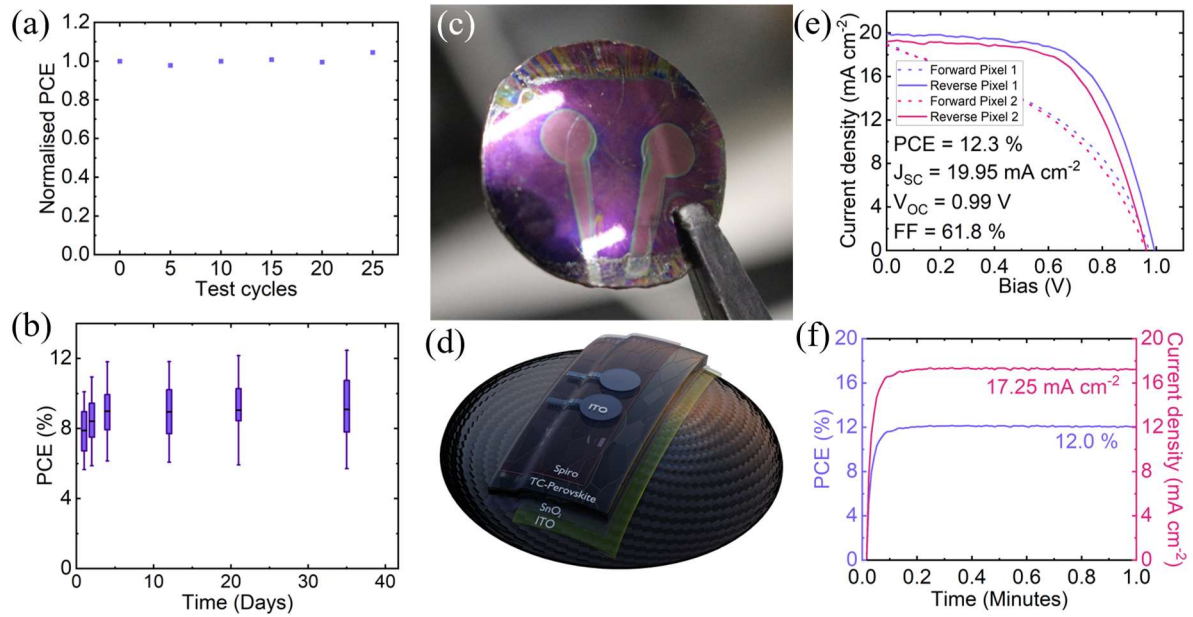


Figure 4: a) Normalised PCE of a device undergoing fatigue testing, b) box plots of measured PCE for devices stored under N₂ as a function of time, here $n = 30 - 34$, whiskers correspond to a standard deviation of 1.5. Part c) shows a photograph of curved CFRP based PSCs. In part d) we show a 3D schematic of curved CFRP based PSC structure. Parts e) and f) show JV measurements of both pixels on curved CFRP substrate and stabilised power conversion efficiency of champion curved CFRP based PSC respectively.

Devices were tested through an 8.81 mm^2 illumination mask (see Figure S14), with the JV characteristics presented in Figure 4e. Here we find that the champion device had a PCE of 12.3 %, J_{SC} of 20.0 mA cm^{-2} , V_{OC} of 0.99 V and a FF of 62 % corresponding to a specific power of 22.8 W g^{-1} . Figure 4f plots the stabilised current density and efficiency of a device when biased at 0.7 V. Here, the device generated a photocurrent of 17.3 mA cm^{-2} with a stabilised PCE of 12.0 % corresponding to a specific power of 22.3 W g^{-1} . Note that area of the illumination mask was considerably smaller than that of the device pixel (28.3 mm^2). This was done in order to ensure that the area tested was maintained at normal incidence to light from the solar simulator. If a much larger aperture mask had been used, then there would have been a range of angles between the device normal and the solar simulator, with variations in optical reflectivity (which increases at off axis angles) reducing the effective PCE of the devices. We note however that by probing a limited area of the device we likely introduce errors in our measurements as we do not account for to variations in device efficiency across the active area.

6.3.4 Discussion

We have successfully fabricated PSCs onto woven CFRP substrates, with the perovskite layer deposited *via* ultrasonic spray coating. Here the improved thermal stability of woven CFRP compared to unidirectional CFRP has allowed us to remove “crack prevention” layers that were used to reduce thermally induced damage to the ITO, with this strategy allowing us to reduce the areal weight of devices and thereby improve specific power.⁴⁵ By fabricating devices *via* spray coating we have also shown that our process is compatible with coating objects having complex, 3D shapes.

The CFRP substrates explored here are expected to be able to provide another primary, structural function, and thus we disregard the mass of the substrate when calculating specific power, instead accounting only for the materials contained within the PSC stack. Using the known densities of each material, along with their measured thickness, we calculate the areal mass of each material, and therefore determine the areal mass of the total device structure. Using this methodology (see Table S2 for details), we calculate the stabilised specific power output of our flat and curved CFRP devices to be 26.0 W g⁻¹ and 22.3 W g⁻¹ respectively. These numbers exceed the specific power of *a*-Si devices at 8.31 W g⁻¹,^[46] or commercial GaAs devices at 3.8 W g⁻¹,^[47] and are competitive with flexible organic PV at 32.1 W g⁻¹,^[48] and within a factor of two of flexible PSCs at 50 W g⁻¹.^[32] It is important to note, however, that flexible PSC devices would need to be attached to a surface of interest, increasing effective mass and reducing the effective specific power through the use of adhesives or supporting structures. Furthermore, for practical application, it will be necessary to use encapsulation films to protect our devices from the atmosphere. We estimate that a 100 nm Al₂O₃ barrier layer used in conjunction with a 1.4 µm thick polyurethane (PU) topcoat would reduce specific power to around 19.4 W g⁻¹. The inclusion of both rear and front 100 nm thick Al₂O₃ layers, together with a 20 µm PU clearcoat would reduce specific power to around 4.0 W g⁻¹; a value which still remains competitive with commercial GaAs. We are in fact confident that further gains in our device efficiency and thus specific power can be achieved through the use of improved light management schemes; here our top ITO contact has an optical reflectivity in excess of 25%, with light passing through the perovskite active layer likely being absorbed within the black carbon fibre substrate. Such loss mechanisms can straightforwardly be reduced using a top anti-reflection coating and by placing reflective gel-coat layers on to the top of the CFRP substrate to scatter light back into the device.

We have also demonstrated that our CFRP PSC based devices have promising mechanical stability. Typically, for aerospace applications the design load limit (DLL) for a composite material under tension is between 0.4 % and 0.5 % strain.^[49-51] As such, any component expected to experience a

load during service would necessarily be designed to limit maximum strain to such values. Importantly, such components would also need to undergo repeated stresses due to vibrations, pressure changes (e.g. fuselages), and loading/unloading (e.g. aerofoils during take-off and landing). We have shown that our devices can repeatedly withstand loads of up to 50 N without any degradation in performance. Such a force corresponds to a strain of around 0.7 %; a value well above that which might be expected from CFRP members which meet aerospace standards. These results suggest therefore that such devices could reasonably be integrated onto structural composites for mobile power applications with no modification to component design. We also expect further improvements in strain tolerance from the application of encapsulation layers which are likely to bring the neutral plane closer to that of the devices. We note that our fatigue testing was carried out at forces larger than those necessary to induce catastrophic failure in a glass device of similar thickness. This suggests that CFRP based PSCs could be used to reduce or eliminate the need for the additional reinforcements required when retrofitting PV fabricated onto glass substrates onto existing roofs. It is clear however that a more comprehensive series of mechanical tests are necessary to fully characterise the structural robustness of our devices. We propose to undertake such work in a follow-up study, which will also include compressional, torsional, shear, vibrational, thermal-mechanical testing, and extended fatigue testing. Future work will also include the incorporation of improved bottom contacts to enhance charge extraction, a switch to a p-i-n architecture to reduce parasitic absorption from the Spiro-OMeTAD hole transport layer, device scale up *via* modularisation, and the development of ultralightweight encapsulation.

6.3.5 Conclusion

We have demonstrated the fabrication of CFRP based PSCs in which the perovskite absorber layer was deposited onto both flat and curved substrates *via* ultrasonic spray coating, with flat devices having stabilised PCEs of up to 14.0 %, corresponding to a specific power of 26.0 W g⁻¹. We have also fabricated devices onto dome-shaped substrates, with devices having PCEs of up to 12.3 % and a specific power of 22.8 W g⁻¹. A preliminary study of the mechanical strength of flat CFRP PSC devices demonstrates they can undergo repeated bending cycles when exposed to a mechanical force of 50 N without compromising optoelectronic performance. Our work is an important step towards the direct integration of perovskite PV with the working surfaces of, for example, the aerofoils of a UAV or the body of an EV. We believe further improvements in device specific power will be possible through the use of light management strategies to enhance optical absorption within the PV active layer.

6.3.6 Acknowledgements

T. Thornber, A. Jurado-Estrada and F. Cepero-Mejias contributed equally to this work. The authors are especially grateful to Dr Nic Mullin for assistance with CTE measurements. R.H.G and D.B. thank the EPSRC for PhD studentships. T.T. thanks the University of Sheffield for the provision of a PhD studentship, while I.A.A. and N.M.A. thank the Saudi Arabian government for PhD scholarships.

6.3.7 Conflict of interest

D.G.L. is a co-director of the company Ossila Ltd. which retails materials and equipment used in thin film optoelectronic device research and development.

6.3.8 Data Availability Statement

The data supporting the findings of this work are available from the corresponding author upon reasonable request.

6.4 Supporting Information

6.4.1 Experimental Methods

6.4.1.1 Device fabrication

Carbon fibre-reinforced polymer substrate fabrication: Flat woven carbon fibre-reinforced polymer (CFRP) substrates were prepared on a glass sheet with the following layers sequentially stacked: release agent (Marbocote Fastcote), one layer of 20 x 20 cm XC120 epoxy laminate (XPREG), three layers of 20 x 20 cm XC130 210g 2x2 Twill 3k prepreg carbon fibre (XPREG), and a breather fabric. This was then sealed and evacuated before insertion into an autoclave. The pressure of the autoclave was set to 6 bar, with the composite materials heated to 100 °C at a rate of 2 °C/min before being held at this temperature for 4 hours. After 4 hours, the pressure was reduced at a rate of 0.2 bar min⁻¹ and the temperature at 2 °C/min until ambient. Curved CFRP was fabricated using an LC1120 N-BK7 Plano-Concave Lens (Thorlabs) with the same lay up stack. Here, the autoclave pressure was reduced to 4 bar during the curing process.

Flat CFRP substrates were cut from the 20 x 20 cm w-CFRP panels using either waterjet cutting or computer numerical control cutting. The curved CFRP substrate was cut by hand using heavy duty composite material shears (Whitely, Sheffield) and sanded to remove sharp edges. CFRP substrates were cleaned by hand using Hellmanex (Hellma) and rinsed in deionised (DI) water and isopropyl alcohol (IPA) before being loaded into an AJA ATC 2200 magnetron sputter coater, with a 200 nm thick layer of indium tin oxide (ITO) deposited at a power of 155 W and an argon flow rate of 7 SCCM.

Perovskite solar cell fabrication: Glass control devices were fabricated from unpatterned glass/ITO (Ossila) substrates which were etched using zinc and 4M HCl. These were then cleaned via ultrasonication in Hellmanex, DI water and IPA prior to treatment under UV ozone for 20 mins. For CFRP devices, substrates were etched using zinc and 4M HCl before being cleaned by hand with Hellmanex and rinsed in DI water and IPA prior to UV ozone treatment for 20 mins.

A np-SnO₂ electron transport layer was deposited onto the ITO in air from a 15 wt% aqueous solution of tin oxide nanoparticles (Alfa Aesar), diluted at a ratio of 1:70 with deionised water. This solution was filtered and spray-coated using a Prism Ultra-coat 300 ultrasonic spray coater in air. The spray head traversed across the substrate at 180 mm s⁻¹ at a height of 30 mm above the sample stage which was held at 30 °C. Fluid flow rate was controlled by N₂ flow into the fluid reservoir at a pressure of 10 mbar. The np-SnO₂ coated samples were then annealed at 80 °C for 5 minutes before being exposed to UV ozone treatment.

Samples were then transferred into a nitrogen-filled glovebox for perovskite layer deposition *via* spray coating. A Sonotek Exactacoat ultrasonic spray coater with an Impact head was used to spray coat a 1.2 M solution of $\text{Cs}_{0.05}\text{FA}_{0.81}\text{MA}_{0.14}\text{PbI}_{2.55}\text{Br}_{0.45}$ triple cation perovskite solution dissolved in a 4:1 solvent mixture of DMF:DMSO in a single pass at a head height of 100 mm, with the sample stage held at 40 °C. Here, the spray head traversed across the substrate at a velocity of 60 mm s⁻¹ with the fluid flow rate set to 1 mL min⁻¹ and the tip power set to 2 W, with the resultant mist guided to the substrates by a N₂ shaping gas at 3 psi. The wet films were then subjected to a rough vacuum for 4 minutes, before being annealed for 5 minutes at 80 °C and finally further annealed at 80 °C under a rough vacuum for 30 minutes.

Following perovskite deposition, a solution of 2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD) was prepared in anhydrous chlorobenzene at a concentration of 86 mg mL⁻¹. For each mL of this solution, 11 µL of Co(II) (trifluoromethanesulphonyl)imide in acetonitrile (300 mg mL⁻¹), 20 µL of lithium bis(trifluoromethanesulphonyl)imide in acetonitrile (500 mg mL⁻¹) and 34 µL of 4-tertbutylpyridine was added. This solution was then spin coated onto the perovskite films at 4000 rpm for 30 s before being allowed to oxidise in dry air overnight. A 1 nm layer of Au was then deposited *via* thermal evaporation in an Edwards 306 bell-jar evaporator.

For flat devices, the top ITO electrode was deposited in an AJA ATC 2200 magnetron sputter coater through a shadow mask. Here, the first 30 nm was deposited at a power of 40 W with the remaining 80 nm deposited at a power of 200 W, the argon flow rate was held at 10 SCCM throughout the deposition. For the curved device, an AJA Orion 8 HV magnetron sputter coater was used to deposit the top ITO through a conformal silicone shadow mask, with the first 30 nm sputtered at 60 W before the remaining 80 nm was deposited at 200 W, the argon flow rate was controlled at 10 SCCM throughout the deposition.

6.4.1.2 Characterisation

Current-voltage measurements: AM 1.5G illumination was generated using a Newport 92251A-1000 solar simulator and calibrated using a Newport silicon reference cell to 1000 W m⁻². For flat devices measured through the top ITO electrode, a matte black illumination mask with a measured aperture area of 2.385 mm² was used to define the illumination area. Flat control glass based devices were measured through the substrate using an illumination mask with a measured aperture area of 2.365 mm². For curved devices, a matte black illumination mask with a measured aperture area of 8.814 mm² was used to define active area, with this fabricated from opaque cardboard. Flat and curved CFRP devices were contacted using a semiconductor probe station together with an Ag conductive paste to improve electrical connection. Flat glass based devices were measured

though the substrate using an Ossila test board. Again, an Ag conductive paste was used to improve electrical connection. For all measurements a Keithley 237 source measurement unit was used to record current-voltage measurements under illumination. Current-voltage measurements were recorded by scanning the applied bias between -0.2 V and 1.2 V at a rate of 0.2 V s⁻¹ and recording current density. Stabilised power output measurements were measured using the same testing methodology with the devices held at the maximum power point voltage as determined from the JV sweeps.

External quantum efficiency (EQE) measurements: EQE measurements were recorded using a QuantX-300 Quantum Efficiency Measurement System (Newport, Oriel). An optical chopper operating at 25 Hz referenced to a virtual lock-in amplifier was used to modulate a Xe arc lamp light source prior to passing through an Oriel CS130B monochromator using a step size of 10 nm. The spectral response was measured over wavelength range 325 – 900 nm. For CFRP devices measured through the top ITO electrode, a semiconductor probe station was used to make electrical connect. For flat control devices measured through the substrate an Ossila test board was used to make electrical connection.

Surface profilometry: A Bruker DektakXT equipped with a 12.5 µm stylus with an applied force of 3 mg was used for all large area topographical measurements. Topographical maps were produced with a vertical resolution of 15 nm per point, comprised of 200 line scans spaced 10 µm apart. Each line scan was recorded over 2 mm with a linear resolution of 0.333 µm. All images were processed in Gwyddion 2.58 to calculate statistical quantities and generate images.¹

Atomic force microscopy (AFM): A Veeco Dimension 3100 scanning force microscope was used in tapping mode to record AFM images in air. Here, the cantilever tip (SCOUT 350 - Si AFM probe - Al reflective backside coating) was resonating at a frequency of 350 kHz with a spring constant of 42 N m⁻¹. Data were processed using Gwyddion 2.58, with images leveled by mean plan subtraction and rows aligned by median of differences, for image generation and calculation of statistical quantities.⁵²

Scanning electron microscopy (SEM): SEM measurements were recorded using an FEI Nova Nano-SEM 450 field emission gun at a working distance of 4.7 – 5.2 mm operating at an acceleration voltage of 5 kV.

X-ray diffractometry: X-ray diffractograms were recorded using a Panalytical X'pert³ diffractometer equipped with a Cu line focus X-ray tube operating at a voltage of 45 kV and a current of 40 mA. Data was collected from 5° – 50° 2θ via a 1D-detector in Bragg–Brentano geometry.

Steady state photoluminescence: An Ocean Insight Flame spectrometer was used to collect PL emission from samples excited by a 405 nm continuous wave laser.

Absorption, transmission and reflectivity: Absorption measurement of the TC-perovskite was recorded using an Horiba Fluoromax. Transmission/Reflectivity measurements of the sputtered ITO films deposited onto glass were measured using a Varian Cary 5000 UV-VIS-NIR spectrophotometer with an integrating sphere attachment. Measurements were made across wavelengths ranging from 200 nm to 1800 nm, with a step size of 1 nm. Measurements were recorded on top and bottom ITO films deposited on 5 cm x 5 cm x 1.1 cm thick Corning Eagle XG® Borosilicate LCD Glass. Transmission measurements were taken by placing the sample on the front aperture of the integrating sphere while reflection measurements were taken by placing the sample on the rear aperture of the integrating sphere. For both measurements, the samples were positioned with the ITO film facing away from the incident light. Angle-resolved white light reflectivity measurements used incident radiation from an Ocean Optics DH-2000-BAL deuterium–tungsten lamp delivered via optical fiber to a motorised goniometer. The light was focused onto the sample and collected from 10 to 70 degrees with 1 degree angular resolution, where the reflected light was coupled via fiber optic to an Andor Shamrock SR-303i-A triple-grating CCD spectrometer for spectral analysis. To calculate the absolute reflectance, all measured angle-resolved intensity spectra were calibrated against the known reflectance of a planar silver standard.

Coefficient of thermal expansion (CTE): A fine marker pen was used to mark the sample at the midpoint of each side. The sample was mounted on a Linkam TP93 Heating Stage using thermal coupling compound (HTSP, Electrolube). The heating stage was then positioned on the sample stage of a Dimension Icon AFM (Bruker) and secured using removable silicone moulding rubber adhesive (ReproRubber Thin Pour, Flexbar). The motorised stage and optics of the AFM were used as a travelling microscope to measure the location of small features adjacent to the fine marker marks using the inbuilt position encoder (specified bidirectional repeatability 3 μm). The (x,y) positions of each feature were measured 5 times at 50°C and 5 times at 150°C. The separation between points on opposite edges of the sample was calculated at each temperature and the thermally induced strain calculated from these. The CTE was then estimated assuming a linear strain per unit temperature.

Optoelectrical-Mechanical testing: Samples were mounted in a 3D printed test rig, with a silver mirror positioned underneath at an angle of 45°. This test rig was positioned in a Tinius Olsen H5K-S Tensile and Compression machine equipped with a 5 kN load cell of repeatability and hysteresis >0.1 %, with a test span of 16 mm. Electrical connection was made to the devices *via* a combination of Ag conducting paste and Cu tape. Crocodile clips were used to make electrical connection to the Cu tape, and were connected to an Ossila source measurement unit. In front of the test rig, an Ossila LED solar simulator was positioned such that the emitted AM1.5G spectrum

was reflected upwards onto the down facing solar cell. A Newport silicon reference cell was used to show that the resultant light incident on the device was 0.8 Suns. Figure S9 depicts the experimental set up. Devices were subjected to a three point bend test regime where a force of 5 N was applied at a rate of 2 N min^{-1} . Upon reaching a force of 5 N, the position of the test head was held static and the device was characterised either by recording a JV measurement or the stabilised current output while held at a bias of 0.7 V. This process was repeated until the measured force reached 200 N. For fatigue testing, the devices were subjected to a force of 50 N at a rate of 20 N min^{-1} before being reduced to 0 N at a rate of 20 N min^{-1} , in a sawtooth loading pattern, with JV measurements recorded every 5 cycles.

6.4.2 Supporting Information Figures

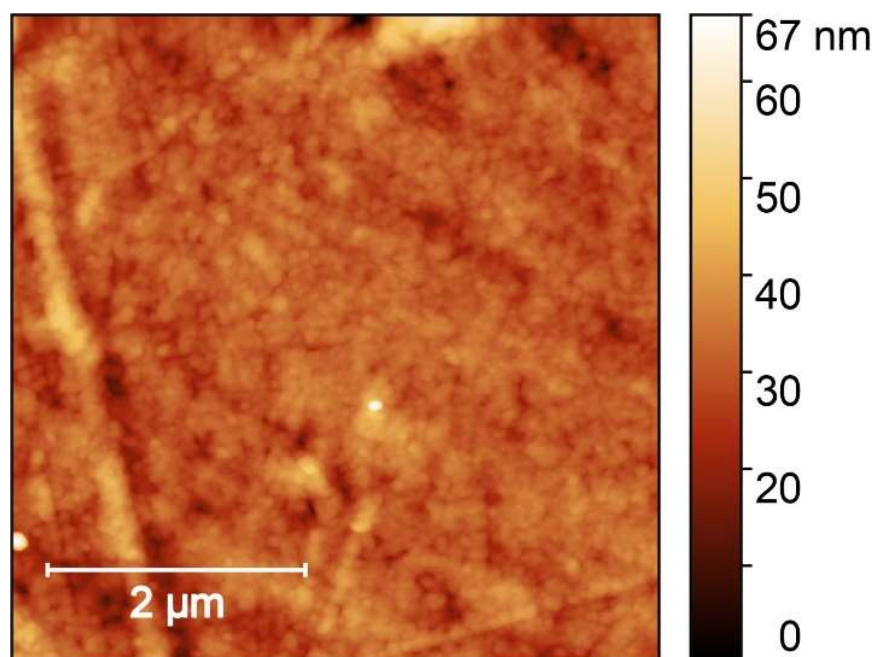


Figure S1: AFM of planarized w-CFRP substrate, here the root mean squared (RMS) roughness was 4.8 nm, the maximum peak height 36.3 nm and maximum pit depth 30.4 nm.

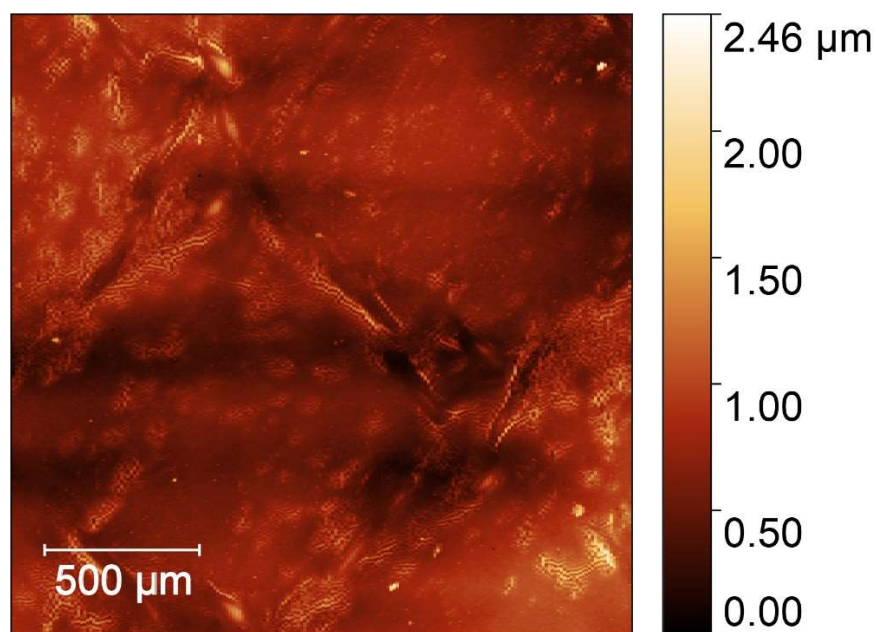


Figure S2: Dektak surface profilometry map of a CFRP/ITO substrate heated to 100 °C. Note evidence of microcracking, likely caused as a result of negative CTE.

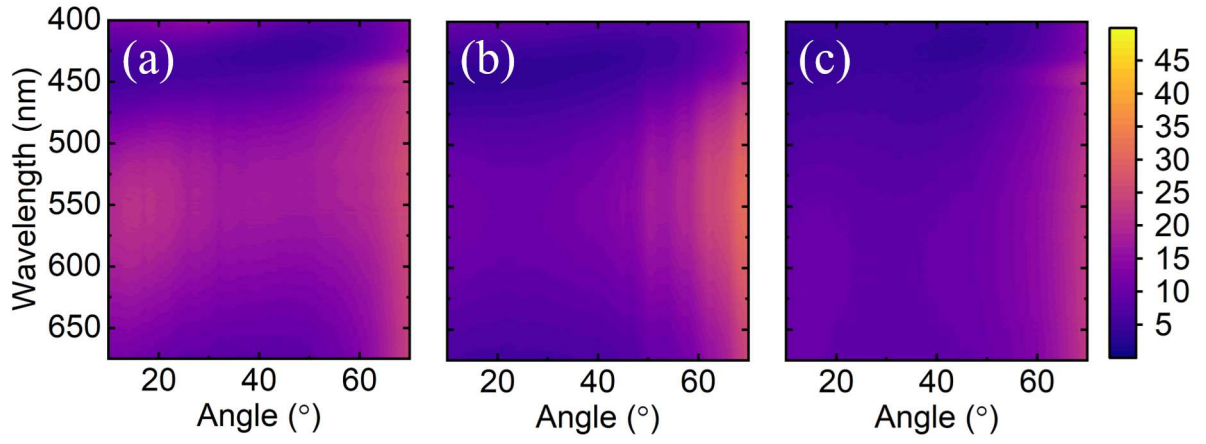


Figure S3: Absolute (%) angular dependent reflectivity of a) bottom ITO deposited onto Eagle glass and b) bottom ITO deposited directly onto CFRP. Here we note a slight increase in reflectivity for the sample deposited onto Eagle glass, however the wavelength dependency is similar, suggesting the same material was deposited in both cases and the overall reflectivity is decreased due to absorption by the underlying CFRP substrate. Part c) plots the same measurement for commercial ITO deposited onto glass. Here, it can be seen there is a reduced overall reflectivity compared to ITO deposited either onto Eagle glass or CFRP.

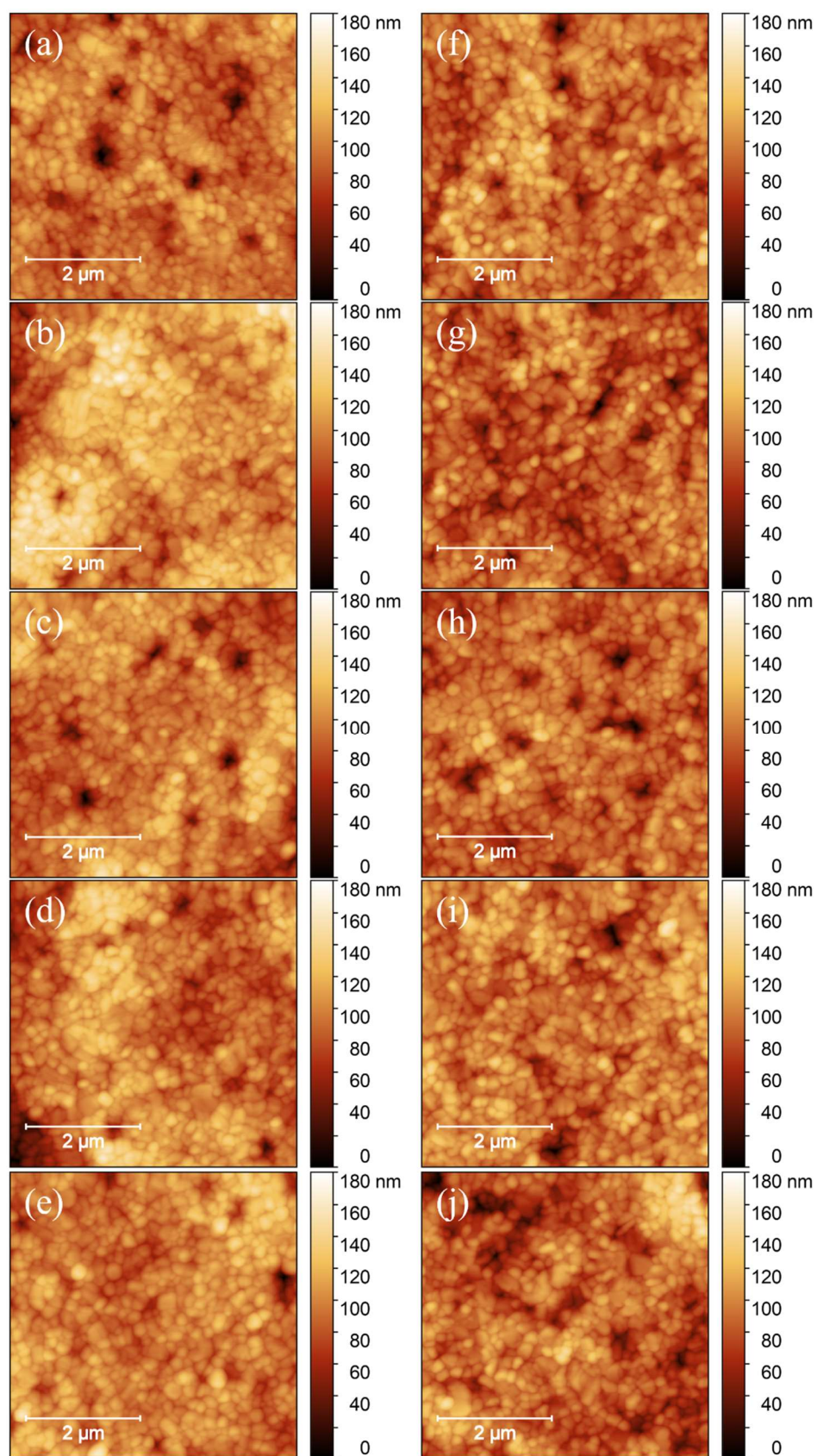


Figure S4: Additional AFM images of TC-perovskite deposited onto (a-e) CFRP/ITO/np-SnO₂ and (f-j) glass/ITO/np-SnO₂. Here, we find that the films on either substrate are broadly similar.

	w-CFRP/ITO/np-SnO ₂ /TC-perovskite		glass/ITO/np-SnO ₂ /TC-perovskite	
	Mean average	Standard deviation	Mean average	Standard deviation
RMS roughness (nm)	17.5	3.0	17.7	1.7
Max peak height (nm)	59.4	8.4	60.7	5.0
Max pit depth (nm)	91.5	10.5	84.0	6.8

Table S1: Statistical quantities derived from the AFM images in Figure 2 and Figure S6.

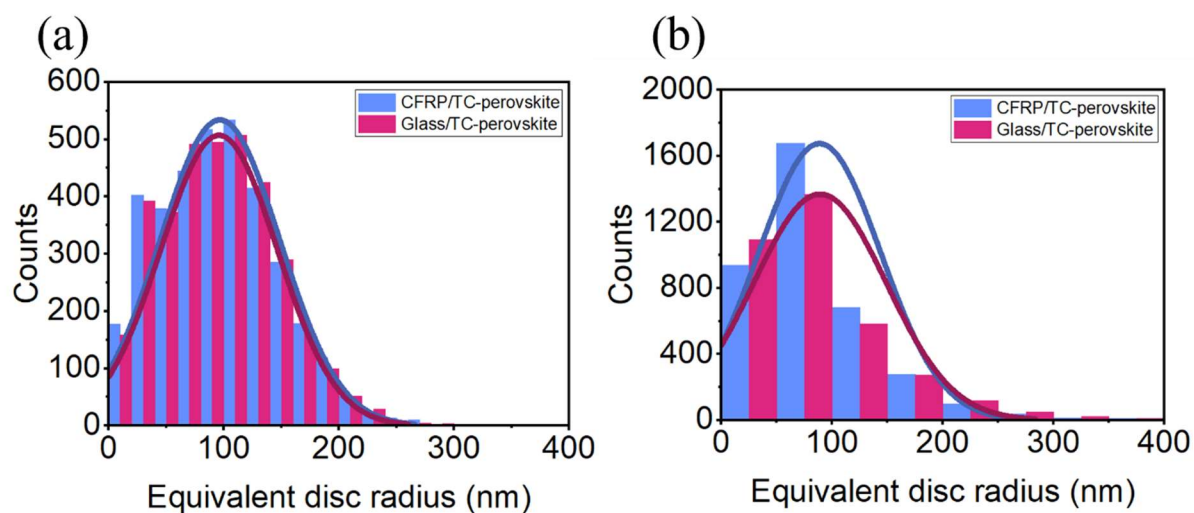


Figure S5: Grain size analyses of both a) AFM and b) SEM images of perovskite films deposited onto CFRP and glass.

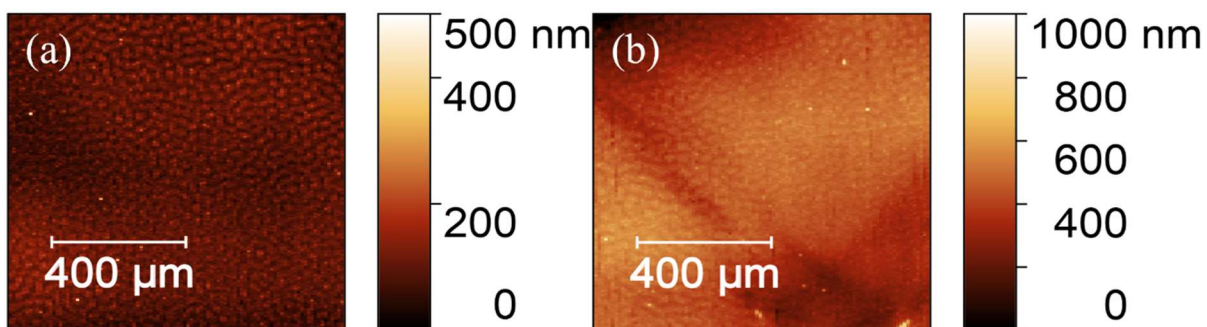


Figure S6: Dektak of perovskite on a) glass/ITO/np-SnO₂ and b) CFRP/ITO/SnO₂. Note the scale has been changed for clarity. We find that the morphology of both films is similar with the underlying scrim present in the w-CFRP sample responsible for the broad variation in height.

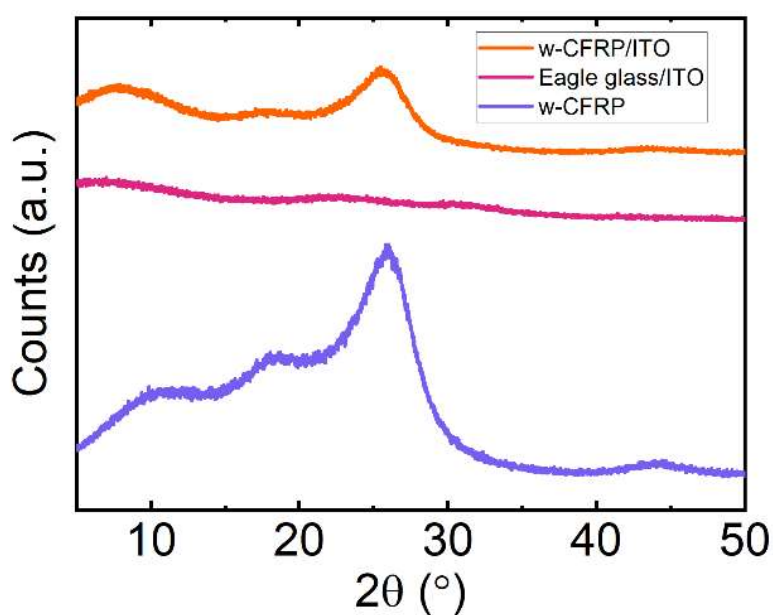


Figure S7: XRD diffractograms for CFRP, ITO deposited onto Eagle glass and ITO deposited onto CFRP. Here both the substrate and the ITO film are amorphous, contributing to the amorphous background signal in Figure 2f.

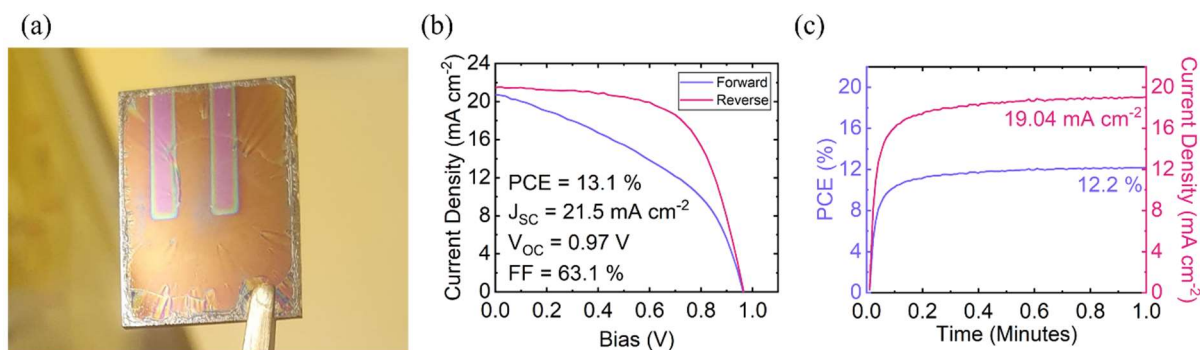


Figure S8: a) Photograph of a glass control device, b) JV data for the champion glass control device as recorded through the top ITO electrode with device metrics derived from the reverse JV scan, c) stabilised charge density and power output of the same device recorded through the top ITO electrode under a bias of 0.64 V.

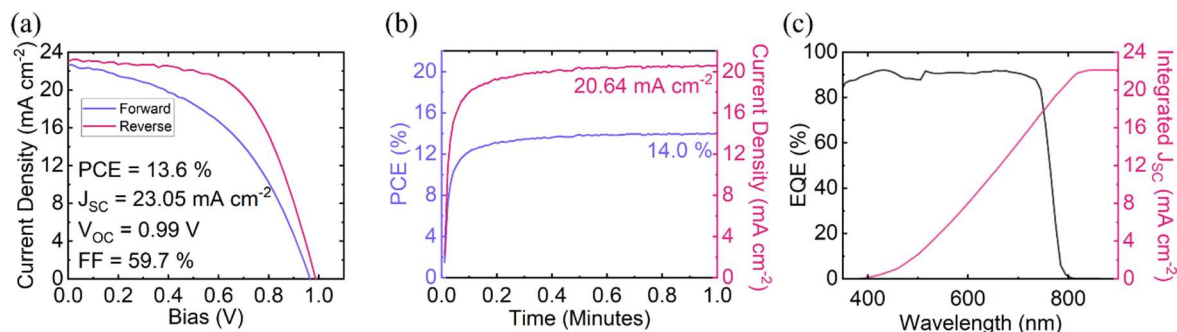


Figure S9: Part a) shows JV data for the champion glass control device as recorded through the bottom, commercial, ITO electrode with device metrics derived from the reverse JV scan. Part b) stabilised current density and power output of the same device recorded through the bottom ITO electrode under a bias of 0.68 V, c) EQE measurement of the same device measured through the bottom electrode. Note the increased spectral response below 400 nm due to the absence of the UV/blue absorbing Spiro-OMeTAD layer. The integrated J_{SC} is calculated as 22.1 mA cm^{-2} .

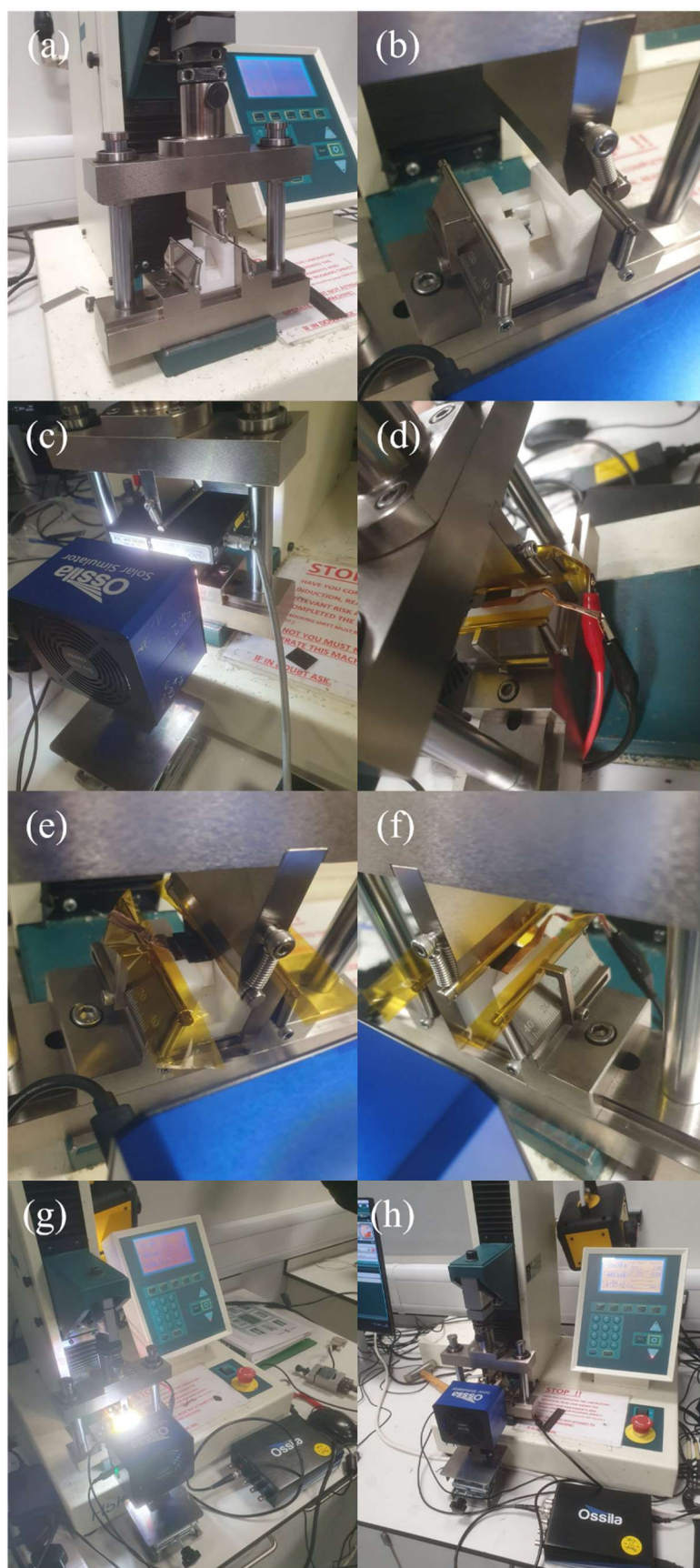


Figure S10: Photographs of a) the test rig situated within the 3 point bend set up, b) close up of the test rig showing 45° angled Ag mirror, c) measurement of intensity using a Newport silicon reference cell, d) electrical connection via crocodile clips, e) sample in situ taken from the left side of the span, f) sample in situ taken from the right side of the span, g) full experimental set up with devices in situ and measurements being recorded, h) full experimental set up prior to commencement.

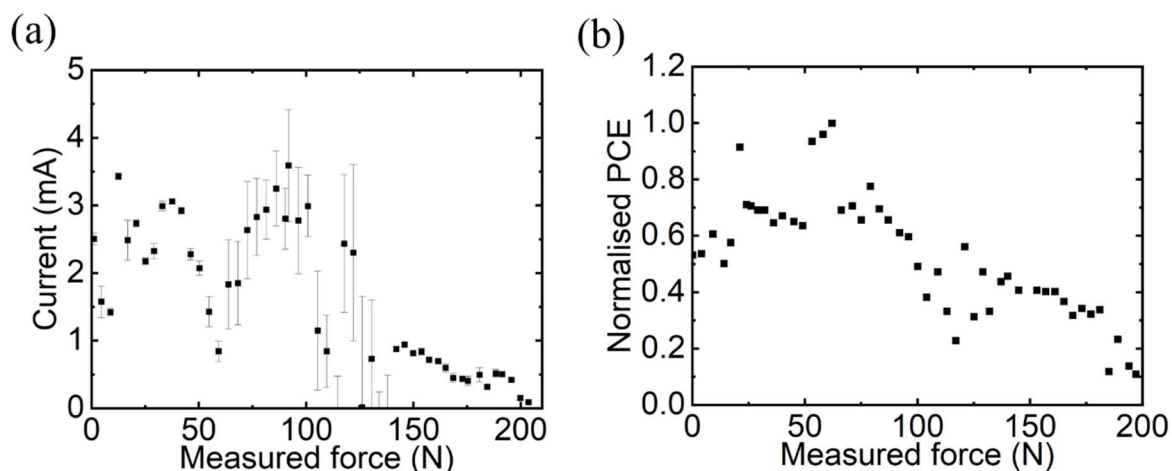


Figure S11: Preliminary mechanical testing data. Here, part a) presents the stabilised current output of a device biased at 0.7 V, recorded over 60 seconds as a function of measured force applied. In these measurements the error bars record the standard deviation of the current across the individual measurement. Part b) shows the normalised PCE of a device as a function of measured force applied, derived from recording JV sweeps, with PCE determined from the average PCE of the forward and reverse sweeps.

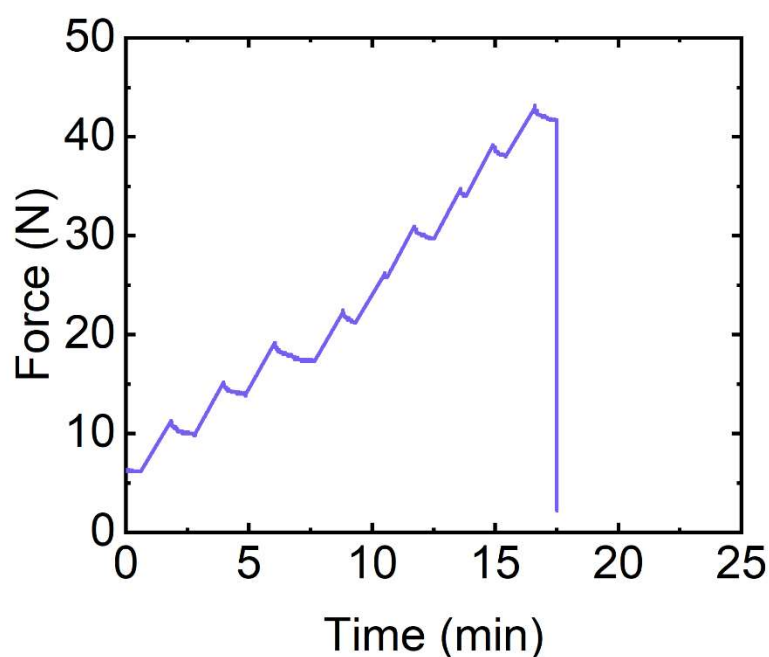


Figure S12: Force – distance plot demonstrating the complete failure of a PSC device on a glass substrate.



Figure S13: Silicone evaporation mask used to define device pixels on a curved CFRP substrate, note this image recorded after the ITO deposition.

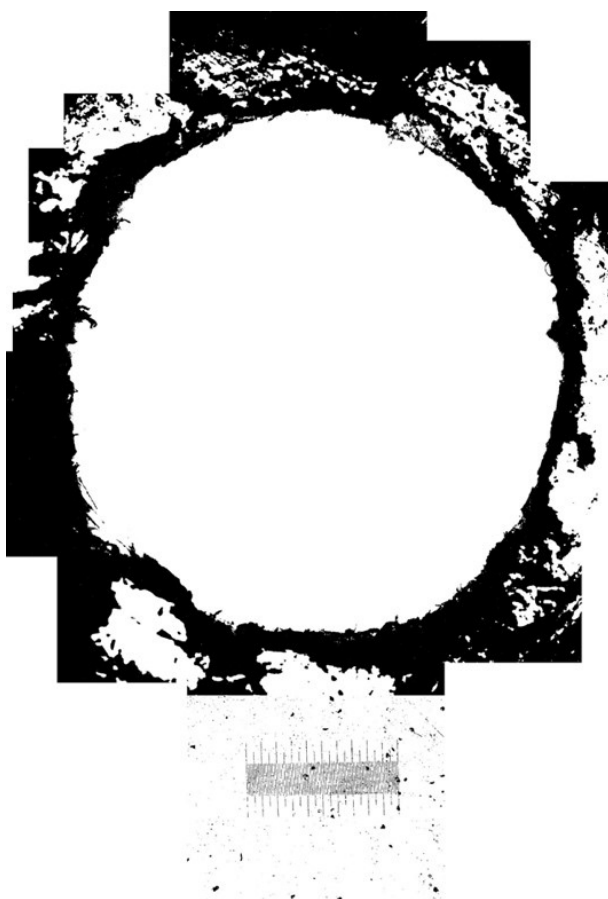


Figure S14: Composite image of the aperture area of the black cardboard illumination mask used to characterise curved CFRP devices. Here an area of 8.814 mm^2 was determined using image processing in ImageJ.

Material	Density (kg/m ³) ⁵²⁻⁵⁶	Thickness (m)	Areal mass (kg/m ²)	Specific Power (W g ⁻¹)
ITO	6800	2 x10 ⁻⁷		
np-SnO ₂	6900	3 x10 ⁻⁸		
Perovskite	4000	7 x10 ⁻⁷		
Spiro- OMeTAD	1020	2 x10 ⁻⁷		
ITO	6800	1.2 x10 ⁻⁷		
		Total	5.39	26.0

Table S2: Film densities extracted from the literature for each material in the device stack. The areal mass is then calculated via the known thickness of each layer. For a PCE of 14.0 % we find a specific power of 26.0 Wg⁻¹.

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Chapter 7

Conclusions

To summarise, we have first demonstrated the applicability of spray coating towards the fabrication of curved, rigid PSCs on glass substrates, reporting PCEs up to 12.5 %. We then found that it was possible to fabricate PSCs onto CFRP substrates, provided that a planarization layer is used to provide a smooth enough surface to avoid device shorting. Here, we demonstrated PCEs up to 14.5 %, and specific powers up to 21.4 W g^{-1} , competitive with other thin film technologies. Finally, we demonstrated the successful deposition of spray coated PSCs onto curved CFRP substrates, demonstrating a specific power of 22.3 W g^{-1} , and on flat surfaces we achieve specific powers up to 26.0 W g^{-1} .

7.1 *Future work*

We note that there are numerous avenues by which we should be able to improve on these results. Our best CFRP devices register PCEs between 14 and 15 %, this lags significantly behind the state of the art in the field. Notably, f-PSCs routinely demonstrate $> 20 \%$ efficiencies, and likewise for spray coated PSCs on rigid substrates. We believe that improvements to the perovskite absorber layer, is likely to significantly improve performance. Inclusion of bulk passivation additives, and the use of quasi 2D perovskites have been demonstrated to significantly improve device performance and stability, both techniques absent in this work. In addition to this, interfacial passivation is another technique finding use in all high performance PSCs which has been neglected here. Improvements in total efficiency are essential for mobile power applications where peak power is just as important as specific power, especially with limited space upon which to place solar PV.

There are of course other routes to improving device efficiency. Reducing series resistance by moving to higher conductivity metal bottom electrodes should significantly improve performance, and can reflect photons back into the device to improve J_{sc} . This would have the additional benefit of reducing the thickness of the perovskite layer, reducing areal mass and improving specific power. If the bottom electrode was to remain a TCO such as ITO, then the use of a pigmented, or reflective, gelcoat instead of the transparent planarization layer could also improve light management in the devices. We also postulate that moving to a gelcoat is likely to reduce roughness and provide improved thermal stability via the removal of the troublesome polymer

scrim and the inclusion of inorganic pigments. Finally, it should also be possible to improve light management by the inclusion of an antireflective layer above the transparent top electrode.

The transparent top electrode could also be improved upon by finding materials with higher transmission and lower sheet resistance. The use of solution processed materials such as AgNWs or carbon based inks are attractive prospects, capable of reducing fabrication complexity and areal mass while achieving the above, and should be areas of immediate further research.

It will also be necessary to upscale devices; while many of the processing steps used in this thesis are scalable, the devices presented are still of a very small scale. Improvements in surface roughness should improve on this limitation. The use of laser scribing will need to be explored in relation to CFRP based devices, as the fabrication of modules will be essential towards generating high efficiency, high peak and specific power devices. It is likely that such modules will need to tessellate so as to achieve the highest geometric fill factor on surfaces which are unlikely to be rectilinear in plan view, such as aerofoils.

Another route towards improving device efficiency would be the inclusion of tandem, or even triple junction devices. Perovskite-perovskite multijunction devices fabricated onto CFRP via spray coating would represent a significant leap for this technology and in light of concerns regarding peak power output will undoubtedly become essential for mobile power generation.

There are significant obstacles which will require overcoming before CFRP based PSCs can realistically become a commercial technology. Chief among these is operational stability. We have already alluded to improving stability of the perovskite layers themselves via the use of 2D forming additives, and passivation techniques, however as with all solar cells encapsulation will be necessary.

Thin film polymer based encapsulation, which can withstand UV radiation and multiple, rapid, wide range thermal cycling will need to be developed. Materials such as polyurethanes or polysiloxanes are likely to be the ideal contenders, in combination with barrier layers such as Al_2O_3 or high crosslink density polymers. It will be essential to investigate stability of devices *in-situ*, as in addition to thermal and radiation based degradation, there will also be significant flexural, compressive and tensile forces acting upon the devices when applied to vehicles and aircraft. Devices will also have to be able to withstand forces acting to literally pull them apart as well, due to the effects of drag, lift and leading edge shear forces, making adhesion of layers and encapsulation paramount.

Finally, it may also be possible to fabricate back contact solar cells onto CFRP. For example, groove based PSCs such as those demonstrated by PowerRoll may find improved stability due to

CFRP being significantly more robust than flexible polymers, thus improving back contact stability. In principle, it should be possible to emboss grooves into a gelcoat, and such devices would still have very low areal mass, making them suitable for stationary power generation on older roofs which cannot support heavy PV.

7.2 *Challenges*

This project has not been without its challenges. The first of which was coming to an understanding of exactly what was required out of a CFRP/ITO substrate, and then how to source them adequately with respect to both lead times and sheer volume. Certainly, during the first half of the project this was greatly helped by the presence of our colleagues in the mechanical engineering department, however in the latter half the burden of this fell solely upon the author. This meant that much work would need to be practised first on proxy substrates, with the hope that the findings would translate onto the CFRP based substrates – this was, regrettably, rarely the case. The next challenge was getting ITO deposited, which required its own degree of preparation, and then lead times associated with postage, collaborator availability and then the return journey. All this considerably delayed progress, and meant that at any given time the number of substrates available to work with was very limited, upping the stakes with respect to any deposition process, or decisions made regarding optimisation routes. Towards the end of the project, the author started personally delivering substrates for ITO depositions, and then ferrying the coated substrates back themselves. All in all, to get substrates ready for device fabrication from scratch would take 3 full days, spread out over 4 - compare and contrast with glass/ITO substrates which could be readied in the space of a couple of hours, with no travel involved. It would not be inaccurate to state that a commercial source of CFRP/ITO would have significantly alleviated the strain.

Fortunately, the author contributed significantly to improving on these issues for subsequent researchers here in Sheffield who might be minded to work on CFRP based PSCs. We worked hard to build connections at the Advanced Manufacturing Research Centre, and together with them successfully were granted funding so they could use their composite department's expertise to fabricate larger CFRP panels at a much higher rate, and then to fund a UK company, Diamond Coatings, to deposit large areas of homogenous ITO. This has meant that since the author exited the lab, a reliable and consistent supply of CFRP/ITO substrates has been established, these demonstrating higher thermal stability, smoother ITO and superior wetting properties.

7.3 *Final thoughts*

The work presented in this thesis is intended to demonstrate an alternative application of perovskite solar cell technology. Within the vast range of research into these materials for energy generation, precious little has been focused on the idea of fabricating such devices onto arbitrary surfaces of interest. Perhaps thousands of human-hours have been spent on optimising them using techniques with little hope of commercial viability (e.g. spin coating), or by using increasing numbers of additives and interlayers which represent significant complexity expansion. An equal amount of work has been expended on demonstrating the route from “lab to fab”, mostly focused on a transition from spin-coated devices to those which are Roll-to-Roll (R2R) compatible. Finally, vast amounts of research has been spent on utilising perovskites for tandem solar cells based on crystalline silicon and wide band gap perovskite layers.

All these approaches are valid and constitute essential research, in that improving device performance is always beneficial, and that without vastly upscaled methodologies the technology would likely never become competitive cost-wise with crystalline silicon. Silicon/perovskite tandems represent their own niche, boosting performance and taking advantage of the technological maturity of crystalline silicon.

However, the work introduced here represents an almost entirely untapped theatre of operations for perovskite solar cells. Here, we propose that an entirely new application, taking advantage of the unique solution processed, low temperature fabrication properties of metal halide perovskites, is extant. That there is another model for perovskite solar cell commercialisation beyond silicon/perovskite tandems or high throughput R2R fabricated devices. That a bespoke, niche market might exist whereby the marriage of photovoltaics with the body form of vehicles, personal electronics or architectural surfaces is celebrated.

No other PV technology is suited for direct integration with rigid, non-developable surfaces quite like that of perovskites. Organic PV may be the only one which might compete, but currently lags behind with respect to performance. The application of devices fabricated onto flexible, or elastomeric, surfaces which are then adhered to rigid, non-developable surfaces, introduces new failure modes, and unnecessary additional mass and complexity. No other fabrication ideology is therefore suited to the fabrication of perovskite solar cells onto rigid, non-developable surfaces quite like that of direct integration.

It is somewhat astonishing to the author that this area of research has been so wholly neglected, and the author contends that if even half the amount of work had been directed in this heading as

has been expended on f-PSCs, that we would undoubtedly be demonstrating comparable PCEs, device areas, and stabilities on curved, rigid substrates. Indeed, it might even be somewhat concerning for the f-PSC community that such a small group could have achieved so much progress on a totally new substrate material and geometry.

Of course, we do not aim to compete with f-PSCs when it comes to fabrication at volume, and low cost. Instead, we aim to compete with state of the art high-specific power devices such as GaAs, but with the added advantages of even higher specific power, and seamless integration with body form, coupled with significantly reduced costs. The devices we propose necessarily can only be fabricated batchwise, however, for the applications we envisage, this should not necessarily be an impediment to commercialisation. Of course, as capacity grows, the additional costs associated with batch-to-batch fabrication would trend downwards and thus, if the niche benefits of our approach were to gain traction, it is likely that one day most working surfaces will enjoy the fruits of photovoltaic power generation.

Appendix A:

Doping, p-n Junctions, & Extraction

Doping of semiconductors serves to shift the Fermi level of an intrinsic semiconductor closer to a band such that conductivity can be increased. Consider crystalline silicon (c-Si) which has a tetragonal structure in which each Si atom is bonded to four others. If an atom of Si was replaced with, for example, an atom of boron which is trivalent, we still find a tetragonal structure but here one of the bonds is deficient by an electron. The effect of this is that holes are introduced into the valence band of the semiconductor and the semiconductor is classed as p-type. Equally, if an atom of Si is replaced with an atom of phosphorus, we now have an additional electron present which resides in the conduction band. Strictly speaking, these electrons and holes are bound to their donor or acceptor atoms, however the binding energy is of an order of tens of millivolts, easily overcome by thermal energy at room temperature. Holes move freely in the valence band, and electrons freely in the conduction band, so in both cases doping increases the conductivity of the semiconductor. We can envision this as a change in the Fermi level, wherein n-type doping shifts E_f towards the conduction band, and p-type doping shifts it closer to the valence band.

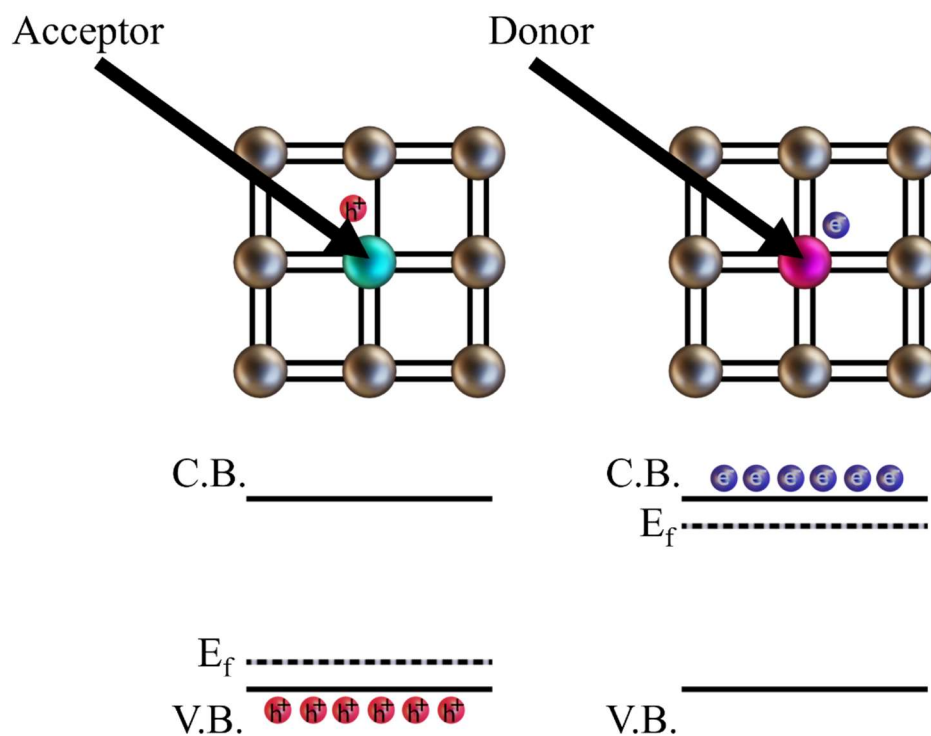


Figure A1.1: Schematic representation of doping in p/n type lattices, and associated energy level diagrams.

If a p-type and an n-type semiconductor are brought together, we form what is called a p-n junction. A diffusion current is set up, where majority carriers (electrons in the n-type, holes in the p-type) diffuse to areas in which they are deficient. That is to say, electrons diffuse towards the p-type semiconductor and holes diffuse towards the n-type. This results in electrons and holes meeting and recombining, thus annihilating them and creating a region where all carriers are depleted, creatively named the depletion region. This has the effect of equilibrating the Fermi level across the junction. Recall the dopant atoms, the action of majority carriers recombining results in these becoming charged, however these are fixed within the lattice and therefore cannot move. We therefore have a depletion region characterised by fixed positive charges on the n-type side, and fixed negative charges on the p-type side, and a general dearth of free carriers. The fixed charges create an electric field across the junction, and this causes a drift current. As the field increases, the drift current increases such that eventually it is equal and opposite to the diffusion current and we reach equilibrium. This balance effectively governs the width of the depletion region.

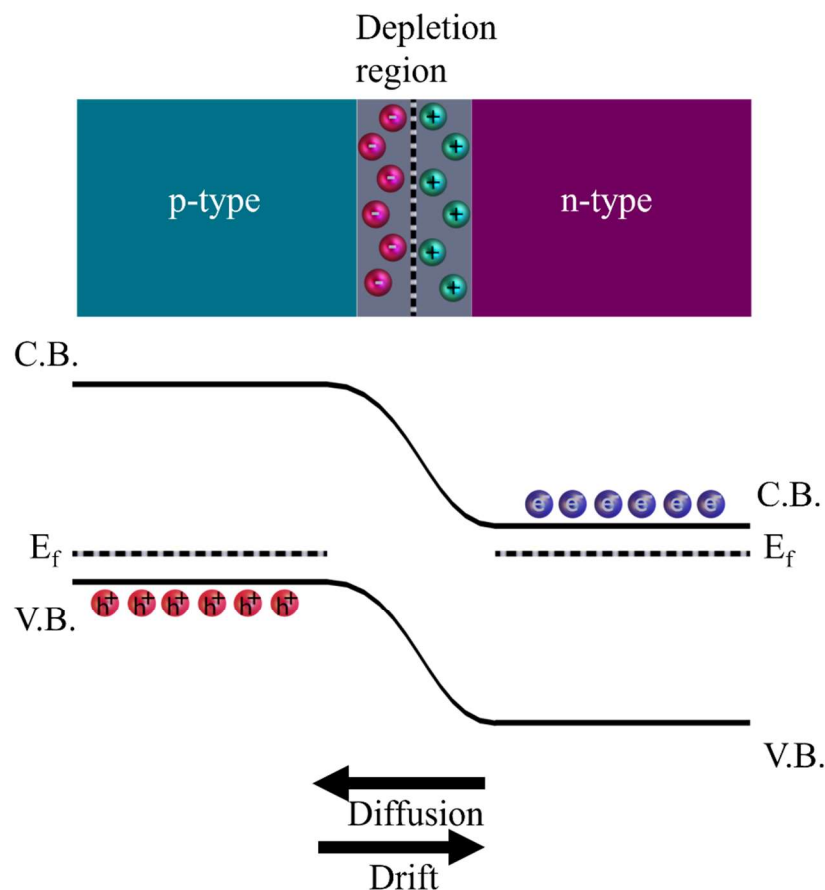


Figure A1.2: Schematic representation of an unbiased p-n junction, illustrating the depletion region formed by balance of diffusion and drift currents. The band diagram illustrates the energetic barrier to majority carriers formed

by equalisation of Fermi levels. Note, the diffusion and drift currents exactly oppose each other, and no current flows.

If the p-n junction is, in the dark, reverse biased, the voltage across the device exacerbates the built in electric field increasing the energetic barrier that majority carriers must overcome to diffuse across the junction. This can be thought of as majority carriers being extracted, thus widening the depletion region and therefore *via* Gauss's law increasing the electric field generated. In this scenario, the diffusion current is significantly reduced, but the drift current is increased slightly, resulting in a small net current as minority carriers are swept across the junction. If, instead, the device is forward biased, majority carriers are effectively pushed towards the depletion zone, shrinking it and reducing the energetic barrier they must overcome for a current to flow. In this scenario, the drift current is essentially eradicated, and a large diffusion current is induced, resulting in a large net current as majority carriers diffuse across the junction. We can see from this asymmetric behaviour with respect to bias that a p-n junction is essentially a diode.

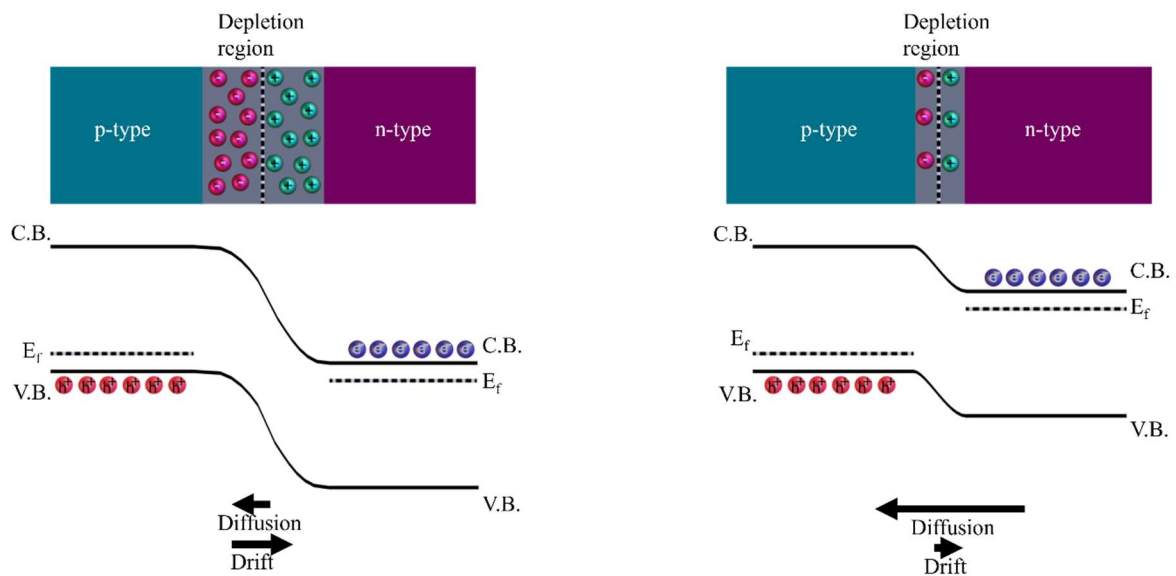


Figure A1.3: Schematic representations of, left, p-n junction under reverse bias and right, p-n junction under forward bias. Note widening of depletion region and increased energetic barrier to majority carriers under reverse bias, resulting in small net drift current, and narrowing of depletion region and decreased energetic barrier under forward bias leading to large net diffusion current.

Under irradiation, as photons are absorbed on both sides of the junction, additional electron hole pairs are formed, however as the population of majority carriers is so high, the change in these is negligible. However, there is an appreciable change in the number of minority carriers. At short circuit, these minority carriers are swept across the junction due to the built in field. This adds a

photocurrent to the balanced drift and diffusion currents, resulting in a net current flow in the same direction as the drift current. When the device under illumination is reverse biased, as in the dark a slight net drift current flows, and this is the same under illumination but with the notable addition of the photocurrent; both currents are driven by minority carriers diffusing over the junction. If the p-n junction is forward biased under illumination, the built in field is reduced in magnitude, at first photocurrent continues to flow but as the forward bias increases eventually the current flow reverses as the dark diffusion current first equals and then exceeds the photocurrent. The point at which the photocurrent and the dark current equal each other is the open circuit voltage (V_{OC}). At a certain point there will be a balance between the photocurrent and the bias voltage such that a maximum power is being extracted. In actual operating conditions, the maximum power extracted from the cell would require a close matching of illumination (photocurrent generation) and load, such that the chemical potential on one side of the device is raised (effectively forward biasing the device), and it is the potential difference between the Fermi levels on each side of the device that ultimately governs V_{OC} .