



Doctoral dissertation submitted to obtain the degree of Doctor of Sciences: Physics, to be defended by

Allyson Robert

DOCTORAL DISSERTATION

Advancing Methodologies to Assess the
Physical and Aesthetic Properties of
Patterned Solar Cells:

A Case Study on "Photovoltaic Photographs"

Promoter:

Prof. Dr Jean Manca | UHasselt



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KNOWLEDGE IN ACTION

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X-LAB
WHERE SCIENCE MEETS ART

D/2026/Allyson Robert, uitgever

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Pour Mamy

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When I embarked on this journey, I thought research and paper writing would be the hardest part of a PhD in Physics. As I started my thesis, I realized that the introduction would be most difficult. I wrote chapters one by one, as publications, procrastinating on the introduction. But after finishing my draft, I found myself with an unexpected writing block, different from any other. Finally, after one of the many wonderful evenings at the Fitlink, inspired by my colleagues and thinking about my friends, I can finally start writing. Realising I needed the most important thing I discovered these past four years: **community**.

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—

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Merci,

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Samenvatting

Kunst en esthetiek zijn ongebruikelijke onderwerpen binnen een fysicadepartement. Toch zijn zij relevant bij het aanpakken van complexe uitdagingen met een groot maatschappelijk belang. De mondiale klimaatcrisis vereist dat fossiele brandstoffen worden vervangen door hernieuwbare alternatieven. De productie van zonne-energie is een van de belangrijkste instrumenten in deze transitie, maar natuurlijke habitats worden vaak gebruikt voor de installatie ervan. Een aantoonbaar betere oplossing bestaat uit een nauwe integratie van fotonvoltaïsche panelen in reeds bestaande stedelijke omgevingen. Toch blijft stedelijke ruimte onderbenut voor energieproductie, deels vanwege esthetische en toepassingsbeperkingen van bestaande panelen. Nieuwe soorten fotonvoltaïsche technologieën bieden vele voordelen op het gebied van esthetiek en toepassingsflexibiliteit. Ze kunnen flexibel, semi-transparant en zelfs kleurrijk worden gemaakt. Dit maakt hen uitermate geschikt voor esthetische toepassingen en zelfs voor de integratie van kunst.

Een dergelijke esthetische toepassing, de zogenaamde "Photovoltaic Photograph", werd in 2022 geïntroduceerd door collega's. Hierbij wordt een afbeelding rechtstreeks in de actieve laag van het fotonvoltaïsche apparaat aangebracht via een extra patroonvormingsstap die tijdens de fabricage wordt toegevoegd. Hoewel deze toepassing veelbelovend is, moet zij grondig worden gevalideerd voordat commerciële toepassing kan worden overwogen. Proof-of-concept-apparaten werden voorbereid en gekarakteriseerd door Hustings et al. in hun oorspronkelijke publicatie. Er bleven echter belangrijke wetenschappelijke vragen bestaan met betrekking tot procescontrole en werking. In dit werk wordt een fundamentele multidisciplinaire aanpak toegepast om de wetenschappelijke vra-

gen voortvloeiend uit een esthetische toepassing te beantwoorden. Deze thesis verfijnt en combineert daarom methodologieën die nodig zijn om de fysische en esthetische eigenschappen van "Photovoltaic Photographs" te begrijpen, te karakteriseren en te evalueren.

Het inleidende hoofdstuk van dit werk positioneert "Photovoltaic Photographs" en de bijbehorende onderzoeksvragen zowel binnen het bredere onderzoeksveld van zonne-energie als binnen hun maatschappelijke context.

Hoofdstuk twee biedt experimentele details die relevant zijn voor dit werk en als referentie voor toekomstige onderzoekers fungeren. Eerst wordt de voorbereiding van "Photovoltaic Photographs" uitvoerig besproken, waarna een fundamentele beschrijving volgt van de meettechnieken en experimentele opstellingen die in dit werk werden gebruikt. Tot slot beschrijft het hoofdstuk drie ontwikkelingen van dit onderzoek, waarvan twee inmiddels als aanvullende instrumenten beschikbaar zijn in X-LAB en het derde een open-sourceframework is voor gegevensbeheer en -analyse, geschreven in Python. Samen benadrukken deze ontwikkelingen het verkennende karakter van het onderzoek en schetsen zij de methodologische vooruitgang die gedurende dit werk werd geboekt.

In hoofdstuk drie wordt het voorbereidingsproces onderzocht. Meer specifiek worden de chemische en fysische veranderingen bestudeerd die tijdens de patroonvorming optreden in "Photovoltaic Photographs" die werden vervaardigd met de huidige standaardkleurstof N719. Hiervoor werden verschillende complementaire chemische analysetechnieken gebruikt. Wij tonen aan dat het isothiocyanaatligand van deze kleurstof wordt gewijzigd en vervangen via een degradatieproces in twee stappen. Deze bevindingen zijn niet alleen relevant voor een beter begrip van het voorbereidingsproces, maar dragen ook bij aan het algemene begrip van de degradatie van deze kleurstof. Bovendien kunnen deze resultaten worden gebruikt om de techniek over te dragen naar nieuwere fotonische materialen, zoals perovskietzonnecellen.

Hoofdstuk vier richt zich op de bepaling van de lokale foto-elektrische eigenschappen van fotonische apparaten. Het beschrijft de constructie van een betaalbaar meetsysteem voor laser beam-induced current op basis van commercieel verkrijgbare componenten en standaardapparatuur

voor fotovoltaïsch onderzoek, gevolgd door metingen van typische "Photovoltaic Photographs". Details van de karakterisering worden besproken, inclusief meetartefacten, en er wordt aangetoond dat pixelgroottes kleiner dan $50\text{ }\mu\text{m}$ eenvoudig haalbaar zijn, terwijl redelijke scantijden behouden blijven, zelfs voor kleurstofzonnecellen. De visuele patronen die in "Photovoltaic Photographs" zijn opgenomen, zijn duidelijk zichtbaar in de stroommetingen, wat bevestigt dat de imprintmethode niet alleen het uiterlijk van het apparaat veranderde, maar ook lokaal de foto-elektrische omzettingseigenschappen beïnvloedde.

Het vijfde hoofdstuk is gewijd aan de methodologie die nodig is om de stabiliteit van "Photovoltaic Photographs" te beoordelen. Deze stabiliteit wordt gedefinieerd als een combinatie van een stabiele energieproductie in de tijd en de kleurvastheid van de aangebrachte afbeelding. Daarom wordt een combinatie van traditionele meettechnieken met de eerder besproken stroomscanning en kleurenfotografie voorgesteld en getest. Hoewel de resultaten door de beperkte statistiek van de monstervoorbereiding nog slechts een eerste indicatie vormen, toont de voorgestelde combinatie van methoden een groot potentieel voor het systematisch beoordelen van de stabiliteit van "Photovoltaic Photographs", en van gepatroneerde fotovoltaïsche apparaten in het algemeen, zowel vanuit esthetisch als operationeel oogpunt.

Ten slotte vat een afsluitend hoofdstuk deze bevindingen samen en behandelt het aanvullende onderzoeksvragen die tijdens dit werk naar voren kwamen. Er worden eerste aanzetten en experimenten gepresenteerd die wijzen op toekomstige onderzoeksrichtingen. Deze omvatten de uitbreiding van het laser beam-induced current-meetsysteem naar meerdere operationele golflengten en verdere verkenningen van het concept van de "Photovoltaic Photograph".

Summary

Art and aesthetics are unusual topics in a physics department. Yet, these are relevant when addressing complex challenges of significant societal importance. The global climate crisis requires fossil fuels to be replaced with renewable alternatives. Solar energy production is one of the most significant tools in this transition, but natural habitats are being depleted for their installation. An arguably better solution involves a tight integration of photovoltaic panels into already existing urban environments. Still, urban area remains underutilised for energy production, in part due to aesthetic and application constraints of existing panels. New types of photovoltaic technologies offer many advantages regarding aesthetics and application flexibility. They can be made flexible, semi-transparent, and even colourful. This makes them prime candidates for aesthetic consideration and even to integrate art.

One such aesthetic application, the so-called “Photovoltaic Photograph” was introduced by colleagues in 2022. Here, an image is imprinted directly into the active layer of the photovoltaic device by an additional patterning step introduced during preparation. While promising, the application must be thoroughly validated before it can be considered for commercial deployment. Proof-of-concept devices were prepared and characterised by Hustings et al. in their initial publication. However, relevant scientific questions towards process control and operation remained. A fundamentally cross-disciplinary approach is applied in this work to address the scientific questions arising from an aesthetic application. This thesis thus advances and combines methodologies required to understand, characterise, and evaluate the physical and aesthetic properties of “Photovoltaic Photographs”.

The introductory chapter of this work positions “Photovoltaic Photographs” and the related questions within the broader solar energy research field as well as societally.

Chapter two provides experimental details relevant to this work as a reference for future researchers. The preparation of “Photovoltaic Photographs” is discussed in detail first, before moving to a fundamental description of the measurement techniques and experimental setups used in this work. Finally, the chapter describes three tools developed during this work, two of which are additional instruments now available at X-LAB and the third is an open-source framework for data management and analysis written in Python. Together, these developments emphasise the exploratory nature of the research and outline the methodological advances made throughout this work.

In chapter three, the preparation process is investigated. More specifically, the chemical and physical changes induced during patterning are studied for “Photovoltaic Photographs” prepared using the state-of-the-art N719 synthetic dye. This was done using different complementary chemical analysis tools. We show that the isothiocyanate ligand of this dye is altered and replaced in a two-step degradation process. These findings are not only relevant for a better understanding of the preparation process but also contribute to the understanding of the dye’s degradation in general. Furthermore, these findings can be used to transfer the technique to newer photovoltaic materials, such as perovskite solar cells.

Chapter four centers on the determination of the local photoelectric properties of photovoltaic devices. It describes the construction of an affordable laser beam-induced current measurement device from off-the-shelf components and standard photovoltaic research equipment, followed by measurements done on example “Photovoltaic Photographs”. Details on the characterisation are given, discussing artifacts and showing that pixel sizes below $50\text{ }\mu\text{m}$ can be readily achieved, while maintaining reasonable scan times, even for dye-sensitized solar cells. The visual images included in “Photovoltaic Photographs” are clearly seen in the current measurements, confirming that the imprinting method not only visually altered the device but also locally affected its photoelectric conversion properties.

The fifth chapter is devoted to the methodology required to assess the stability of "Photovoltaic Photographs". This stability is defined as a combination of stable energy production over time and the colour fastness of the imprinted image. Consequently, a combination of traditional measurement techniques with the previously discussed current mapping as well as colour photography is proposed and tested. Although the results are preliminary as they are limited by sample preparation statistics, the proposed combination of methods demonstrates strong potential for systematically assessing the stability of "Photovoltaic Photographs", and patterned photovoltaic devices in general, both aesthetically and operationally.

Finally, a concluding chapter summarises these findings and explores additional research questions raised during this work. Initial exploration and experiments are presented that point towards future research directions. These include the expansion of the laser beam-induced current measurement device to multiple operational wavelengths and additional explorations of the "Photovoltaic Photograph" concept.

Résumé

L'art et l'esthétique sont des sujets inhabituels au sein d'un département de physique. Ils sont pourtant pertinents lorsqu'il s'agit de relever des défis complexes et de grande importance sociétale. La crise climatique mondiale exige en effet le remplacement des combustibles fossiles par des alternatives renouvelables. La production d'énergie solaire constitue l'un des outils les plus importants dans cette transition. Malheureusement, des habitats naturels sont régulièrement détruits pour faciliter son déploiement. Une solution sans doute préférable consiste à intégrer les panneaux photovoltaïques dans les environnements urbains déjà existants. Néanmoins, les zones urbaines restent sous-exploitées pour la production d'énergie, notamment en raison des contraintes esthétiques et fonctionnelles des panneaux existants. Les nouvelles technologies photovoltaïques offrent de nombreux avantages en matière d'esthétique et de flexibilité d'utilisation. Elles peuvent être flexibles, semi-transparentes et même colorées. Elles constituent ainsi des candidates idéales pour des applications esthétiques et même pour intégrer l'art.

L'une de ces applications esthétiques, appelée "Photovoltaic Photograph", a été introduite par des collègues en 2022. Dans cette approche, une image est directement intégrée dans la couche active de l'appareil photovoltaïque grâce à une étape supplémentaire introduite lors de la fabrication. Cette application présente un potentiel important, mais doit rigoureusement être validée avant qu'un déploiement commercial puisse être envisagé. Des démonstrateurs de principe ont été préparés et caractérisés par Hustings et al. dans leur publication originale. Cependant, des questions scientifiques importantes relatives au contrôle du procédé et au fonctionnement des appareils restaient ouvertes. Dans ce travail, une ap-

proche fondamentalement interdisciplinaire est adoptée afin de répondre aux questions scientifiques découlant d'une application esthétique. Cette thèse développe et combine ainsi les méthodologies nécessaires à la compréhension, à la caractérisation et à l'évaluation des propriétés physiques et esthétiques des "Photovoltaic Photographs".

L'introduction situe les "Photovoltaic Photographs" et les questions de recherche associées autant dans le contexte général de la recherche sur l'énergie solaire que dans leur contexte sociétal.

Le deuxième chapitre fournit les détails expérimentaux pertinents à ce travail et constitue une référence aux futurs chercheurs. La préparation des "Photovoltaic Photographs" est d'abord détaillée, avant de présenter une description fondamentale des techniques de mesure et des méthodes expérimentales utilisées dans cette étude. Le chapitre décrit trois outils développés lors de ce travail, dont deux sont désormais disponibles comme instruments supplémentaires au sein de X-LAB, tandis que le troisième est un logiciel open source de gestion et d'analyse de données développé en Python. Collectivement, ces développements soulignent la nature exploratoire de cette recherche et mettent en évidence les avancées méthodologiques réalisées tout au long de ce travail.

Le chapitre suivant étudie le procédé de préparation. Plus précisément, les modifications chimiques et physiques induites sont examinées pour des "Photovoltaic Photographs" préparées à l'aide du colorant synthétique N719, colorant de référence dans ce domaine. Plusieurs techniques complémentaires d'analyse chimique ont été utilisées dans cette étude. Nous démontrons que le ligand isothiocyanate de ce colorant se dégrade en deux étapes. Ces résultats sont non seulement pertinents pour une meilleure compréhension du procédé de préparation, mais contribuent également à la compréhension générale de la dégradation de ce colorant. En outre, ils peuvent être utilisés pour transférer cette technique vers des matériaux photovoltaïques plus récents, tels que les cellules solaires à pérovskite.

Le quatrième chapitre est consacré à la détermination des propriétés photoélectriques locales des appareils photovoltaïques. Il décrit la construction d'un système de mesure appelé "laser beam-induced current" réalisé à partir de composants disponibles dans le commerce et d'équipements standards de recherche photovoltaïque, puis son application à des exem-

ples de "Photovoltaic Photographs". Les détails de la caractérisation sont présentés, notamment les artefacts de mesure, et il est démontré que des tailles de pixels inférieures à 50 μm peuvent être obtenues aisément tout en conservant des temps de balayage raisonnables, même pour les cellules solaires sensibilisées par colorant. Les images visuelles intégrées dans les "Photovoltaic Photographs" apparaissent dans les mesures de courant, confirmant que la méthode d'impression a non seulement modifié l'apparence de l'appareil, mais a aussi affecté localement ses propriétés de conversion photoélectrique.

Le cinquième chapitre est consacré à la méthodologie nécessaire pour évaluer la stabilité des "Photovoltaic Photographs". Cette stabilité est définie comme la combinaison d'une production d'énergie stable au cours du temps et de la tenue des couleurs de l'image intégrée. Une combinaison de techniques de mesure traditionnelles, de la cartographie de courant précédemment décrite et de la photographie couleur est donc proposée et évaluée. Bien que les résultats demeurent préliminaires en raison des contraintes liées à la fabrication des échantillons, cette combinaison de méthodes présente un fort potentiel pour l'évaluation systématique de la stabilité des "Photovoltaic Photographs" et, plus généralement, des appareils photovoltaïques à motif visuel, tant du point de vue esthétique qu'opérationnel.

Enfin, un chapitre de conclusion résume ces résultats et explore de nouvelles questions de recherche soulevées dans le cadre de ce travail. Des explorations préliminaires et des expériences sont présentées afin d'identifier de futures orientations de recherche. Celles-ci comprennent l'extension du dispositif de mesure par courant induit par faisceau laser à plusieurs longueurs d'onde de fonctionnement ainsi que de nouvelles explorations du concept de "Photovoltaic Photograph".

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Conference contributions

- Presentation: **Robert A.**, Hustings J., Fransaert N., Awouters W., Vereycken M., Romano A., Valcke R., Manca J. V., *Painting Aesthetic Solar Cells with Light*, Next-Generation PV Materials, 15-17 July 2024, Groningen, The Netherlands.
- Poster: **Robert A.**, Manca J. V., *Python GUI for Custom Data Analysis*, UHasselt Research Day.
- Poster: **Robert A.**, Manca J. V., *Python GUI for Custom Data Analysis*, 4 December 2025, Research Software Engineer Day 2025.

List of Acronyms

I_{sc} short-circuit current. 19, 43, 54, 137, 144, 146, 147

P_{max} maximum power point. 44, 54

V_{oc} open-circuit voltage. 43, 45, 54

η efficiency. 44

ANSI American National Standards Institute. 52, 121

ATR attenuated total reflectance. 67

BIPV building-integrated photovoltaics. 14, 18, 86

C-AFM conductive atomic force microscopy. 86

CAD computer-aided design. 91

CIE International Commission on Illumination. 116, 130

CNC computer numerical control. 90, 92

COM common. 45

DSSC dye-sensitized solar cell. 17, 18, 20–24, 31–33, 37, 40, 46, 60, 61, 63, 65, 66, 69, 73, 86, 88, 89, 94, 98–104, 106, 115–117, 119, 125–130, 136, 137, 143, 144, 146–148, 150, 151

EMI Energy Materials & Interfaces. 51

EQE external quantum efficiency. 148

FF fill factor. 44, 54

FTIR Fourier-transform infrared spectroscopy. 54, 58, 65, 68, 71, 73, 74, 77, 145, 151

FTO fluorine-doped tin oxide. 32, 38, 63, 66, 99

GC gas chromatography. 67

GC-MS gas chromatography–mass spectrometry. 58

GUI graphical user interface. 53

HOMO highest occupied molecular orbital. 20

ILCT intraligand charge transfer. 69

IoT Internet of Things. 18

IPCC Intergovernmental Panel on Climate Change. 13

IRENA International Renewable Energy Agency. 13

IV current-voltage. 24, 36, 41, 43–45, 47, 54, 115, 120, 124–126, 133, 136, 137, 147

JSON JavaScript Object Notation. 53, 94

LBIC laser-beam-induced current. 23, 49, 50, 54, 85, 86, 89–91, 100, 102–106, 115, 118, 124, 133–135, 137, 146–149, 151

LED light-emitting diode. 41, 47, 51, 120

LUMO lowest unoccupied molecular orbital. 20

LUT look-up table. 122

MCT mercury cadmium telluride. 67

MLCT metal-to-ligand charge transfer. 69, 77, 145

NC normally closed. 45

NO normally open. 45, 46

- OPV** organic photovoltaic. 17, 86, 116
- PA** polyamide. 34, 35, 63, 64, 99, 100
- Pb** lead. 17
- PCB** printed circuit board. 45, 46, 48
- PMMA** poly(methyl methacrylate). 43, 48, 64
- PSC** perovskite solar cell. 17, 86, 116
- PV** photovoltaic. 14, 15, 17, 18, 22–24, 41, 51, 59, 85, 86, 88, 90, 101, 115–118, 120, 125, 126, 136, 148
- PV photograph** photovoltaic photograph. 18–20, 22–24, 31–33, 37, 38, 52, 59–66, 68, 73, 76, 77, 85, 88–90, 94, 99, 101–106, 115, 117–119, 122–130, 132, 136, 137, 143–151
- PY-GC/MS** pyrolysis gas chromatography–mass spectrometry. 67, 68, 72, 73, 77, 145, 151
- SC** solar cell. 15, 17, 18, 22, 44, 49, 86, 115, 118, 128, 135–137, 147, 148
- SMT** surface-mount technology. 48
- SMU** source measure unit. 45, 46, 49, 120, 124
- TBA** tetrabutylammonium. 72
- TCO** transparent conductive oxide. 20
- ToF-SIMS** time-of-flight secondary ion mass spectrometry. 59, 62, 67, 68, 73, 74, 76, 77, 145
- TR UV-vis** time-resolved UV-vis spectroscopy. 63, 64, 68, 69, 76, 145
- UV** ultraviolet. 67, 129, 137
- UV-vis** ultraviolet-visible absorbance spectroscopy. 40, 54
- VI** virtual instrument. 93, 120
- X-LAB PM** X-LAB Plotting Manager. 53, 54

Chapter 1

Introduction

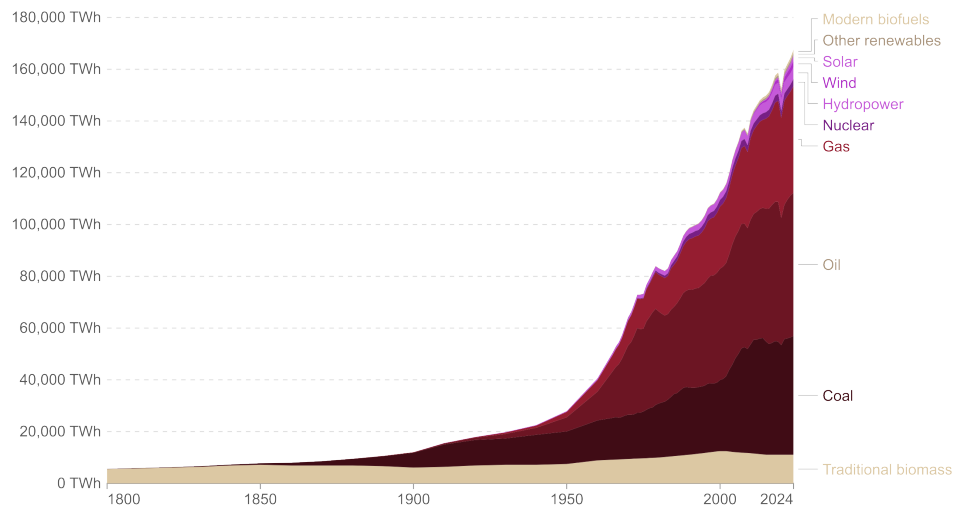
Art has a long history of coexistence with humanity [1]. A history which can be admired in museums, galleries, and collections around the world, with works spanning thousands of years of human civilizations. Today the value that we assign to art can, as most endeavors, be measured through a monetary lens. Creative industries even employ an estimated 6% of the global population, according to the United Nations Creative Economy Outlook [2]. This appreciation for the creative can reach far beyond its own industry by, among other, playing a significant role in the desirability of technological products and solutions through narrative and design. The development of consumer electronics [3], deployment of renewable energy [4], and architectural norms [5] are driven, in part, by the aesthetic choices of individuals. Embracing this dimension can play a crucial role in leveraging the cumulative effect of these choices to aid in solving issues on a global scale. One problem of such magnitude lies in our global energy consumption.

1.1 Addressing the Climate Crisis

Sustaining human activities has, over time, required increasing amounts of energy to be produced. A significant portion of our energy has historically been extracted by burning biomass. However, for the past two centuries the main source for this energy production has involved the consumption of fossil fuels. Figure 1.1 shows this increase in energy production, labelled by energy source. Here we can see that in 2024 an estimated 85% of our energy was still produced from coal, oil and gas [6]. This reliance on fossil fuels for energy has significant geopolitical consequences, e.g. between 1980 and 2018 the EU increased reliance on Russian oil supplies affecting our diplomatic freedom [7]. The discovery of oil reserves in the Middle-East had a large impact on our history in the past century [8]. Furthermore, the consumption of this oil has had catastrophic effects on our environment, already increasing average global temperatures by more than a full 1 °C, as shown in fig. 1.2.

Global direct primary energy consumption

Energy consumption is measured in terawatt-hours¹, in terms of direct primary energy². This means that fossil fuels include the energy lost due to inefficiencies in energy production.



Data source: Energy Institute - Statistical Review of World Energy (2025); Smil (2017)

OurWorldInData.org/energy | CC BY

Note: In the absence of more recent data, traditional biomass is assumed constant since 2015.

Figure 1.1: Rise in global energy consumption since 1800, by source [6].

The contribution of working group II to the sixth assessment report of the Intergovernmental Panel on Climate Change (IPCC), published in 2022, concludes that these rising temperatures have and will continue to lead to, among others:

1. Increased frequency and intensity of extreme weather events
2. Substantial damage or irreversible loss of natural ecosystems
3. Reduction in food and water security
4. Adverse health effects

These effects are not only detrimental in their own right but are additionally associated with significant economic costs [9]. It is therefore crucial to step away from fossil fuels as fast as possible in favour of more sustainable alternatives.

Renewable sources have already proven to be very effective, leveraging abundant natural cycles to extract useful work. Many such sources are continually being deployed with great success, leading to a doubling of the renewable electricity capacity in the last decade [10]. However, the adoption (or rejections) of large scale renewable energy production parks, such as wind turbines and solar farms is often affected by public opinion [11, 12].

In addition to this common opposition, valid concerns are being raised regarding the displacement of a significant amount of natural real-estate by renewable energy farms [14, 15]. This highlights the importance of integrating renewables as much as possible into already converted landscapes such as farms and cities. A clear example hereof is solar energy, on which this thesis will focus. An estimated 173 000 TW of power is being delivered to Earth by the sun [16]. In theory, harvesting this energy for 1 h would cover humanity's energy needs for an entire year.

Solar energy is currently the most widely deployed source of renewable energy and has already been significantly installed on rooftops by individuals, consisting of a third of globally deployed solar energy production in 2024 [17]. This choice is typically economic in nature as solar power now costs less than fossil fuels. The International Renewable Energy Agency (IRENA)

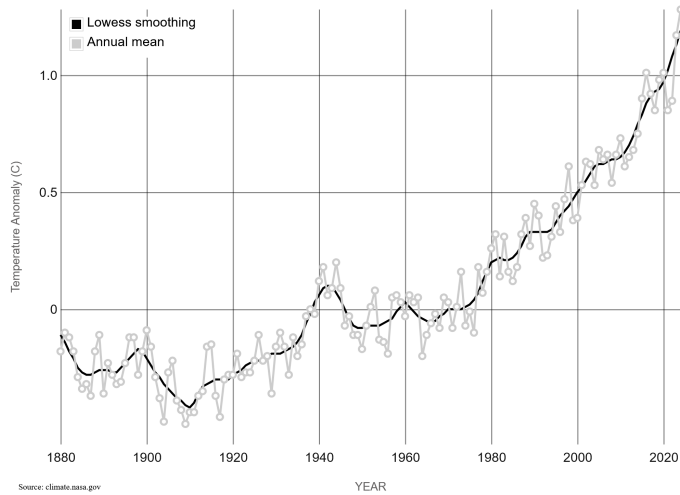


Figure 1.2: Global temperature from 1881 to 2024 relative to the baseline average for the 30-year period 1951 to 1980 [13].

reports a global weighted average levelised cost of electricity (LCOE) below 0.05 €/kWh, compared to a fuel and CO₂ cost of fossil gas of 0.27 €/kWh [18].

Rooftop solar however is not the only available avenue for a more efficient implementation of photovoltaic (PV) panels in urban areas. Another avenue involves the replacement of conventional construction materials with PV modules. For example one can replace roofing shingles or building facade linings with solar panels, greatly increasing the productive area of a building [19, 20]. This use of PV, replace construction materials rather than its addition to a completed building, is known in the literature as building-integrated photovoltaics (BIPV). While BIPV are conceptually promising, the adoption is still limited, representing “around 0.5% of the total PV market in Europe in 2023” [21]. This adoption is affected, in part, by the costs currently associated with BIPV installations, but also by awareness among architects [22].

As solar energy and PV technologies play a central role in this work I wish to take a detour to introduce recent trends in this field. Following this, I will narrow in on an application with enhanced aesthetic properties and creative possibilities with the potential to increase BIPV awareness and



Figure 1.3: Example of photovoltaic roofing shingles [23]

adoption.

1.2 New Trends in Photovoltaics

Currently, mono- and polycrystalline Si-based solar panels are dominating commercial markets [24]. These have benefited from a head start in research, enabled in part by existing semiconductor manufacturing capabilities and know-how [25]. Their commercial success also serves a significant sign-posting role by proving that solar energy harvesting is economically sensible. However, their production remained costly for a long time, incentivizing researchers to develop new technologies as alternatives. Figure 1.4 shows the adoption of PV technologies in the past decades, colour-coded by generation/type, with the first generation consisting of the well known mono-crystalline Si-solar cell (SC).

However, these SCs are costly to produce as they require a significant amount of high purity material as well energy-intensive processing steps. Attempting to mitigate these disadvantages naturally leads to research into alternate material properties, lowering processing steps, or into new materials altogether. Both avenues of inquiry led the field to the second generation of SCs, so-called thin-film PV [26]. This new generation reached excellent efficiencies over time while simultaneously showing versatility in design and fabrication. However, scaling these up to large areas, suitable for deployment, increased the complexity of fabrication significantly [27].

Best Research-Cell Efficiencies

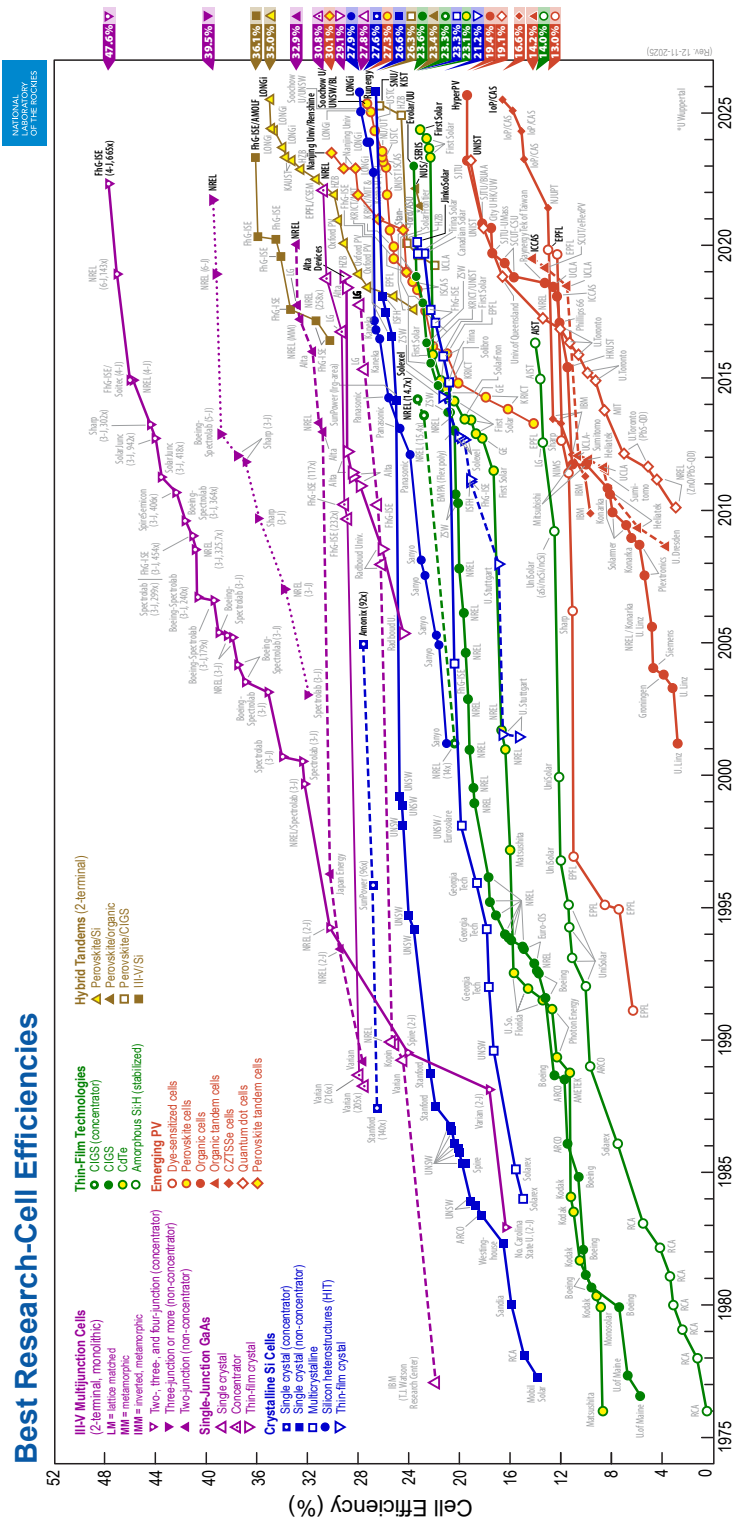


Figure 1.4: NREL chart showing the evolution of champion efficiencies over time.

These constraints motivated researchers to move away from inorganic materials, searching for different material types that would be cheaper to produce and process, such as organic or mixed organic-inorganic PV materials. This trend has led to the third generation of SCs, also called Emerging PV, characterised by the great variety in material types and significant tunability of their properties [28].

Among these organic photovoltaic (OPV), dye-sensitized solar cell (DSSC), and perovskite solar cell (PSC) have generated a significant amount of research interest spread over several decades.

OPV are characterised by the use of organic, carbon-based, materials [29]. Their active layer is prepared from a blend of electron-donating and electron-accepting materials such as fullerene-based or small-molecule acceptors or even acceptor-donor-acceptor molecular frameworks [30]. An important physical property of this technology relies on the exact morphology of the active layer deposited from solution-processed blends, as these greatly affect the properties of the final device [31].

Introduced in 1991, DSSC are a particularly effective type of photo-electrochemical cell [32]. In these hybrid cells, a semiconductor material acts as an electron transporting layer, not directly absorbing in the visible part of the solar spectrum. Absorption is achieved by the sensitisation of the semiconductor through the use of colourful pigments. Research surrounding these pigments has often been inspired by photosynthesis, as nature has developed many efficient light-harvesting molecules [33].

Most recently, research into alternate sensitizers for DSSC led to the development of PSC [34]. These are organic-inorganic hybrid devices with efficiencies rivaling the best Si-SC. While PSCs are currently in a strong position to become a significant commercial player, significant disadvantages currently delay their deployment: the use of lead (Pb) and their stability [35].

A prominent benefit shared among most emerging PV types is the breadth of potential applications for which they can be optimized [28]. These cells are in principle simple to produce [36, 37], show remarkable performance in extreme operating conditions such as extreme temperatures [38], can be applied to flexible substrates [39], and their bandgap tunability enables

optimization towards specific colourful or semi-transparent appearances [40, 41]. This versatility means emerging PV have a significant potential to be deployed in a wide area of applications, from deployment in space, to wearable PV as well as BIPV or for use on agricultural land [42, 43]. Specific examples include rollable PV for space [44], power generation and temperature management from windows [45], and the use of indoor light conversion to power household electronics or Internet of Things (IoT) devices [46]. In addition to their power generation and unique tunability emerging-PV have the potential to be aesthetically customised by incorporating visual patterns directly in their photoactive layer [47, 48].

One could imagine a museum dedicated to Van Gogh whose facade is an immense rendition of his starry night that provides part of the energy needs of the building.

1.3 Photovoltaic Photographs

Combining art and energy production in PV technologies can be achieved through various means. One approach, involving the creation of a visual pattern, has already been explored in various ways: SC can be arranged in mosaic patterns [49], materials can be selectively deposited using ink-jet printing techniques [47], or be removed from the photoactive layer after deposition [48].

In 2022, Hustings et al. [50] proposed an additional method: a photolithographic patterning of the absorbing layer in SCs, thus introducing photovoltaic photograph (PV photograph). This method was originally conceptualised when our group was approached by artist Kristof Vrancken, who is working with anthotype photography [51, 52]. This is a centuries old type of photography relying on the selective discolouration of dyed paper by masked exposure to sunlight. This collaboration led to an attempt at replicating this method using DSSC, due to their reliance on dyes for solar energy conversion. Figure 1.5 shows two examples of PV photograph prepared in the second (left) and last (right) year of my PhD, depicting the Japanese cartoon character Pikachu and my favourite Van Gogh painting respectively.



Figure 1.5: Example N719 photovoltaic photographs prepared for this dissertation in July of 2024 and May of 2026.

In their original publication, the authors showed that imprinting led to images whose contrast depends on the dye chosen to prepare the device. The achieved optical resolution was shown to reach 45 line pairs per millimeter, roughly corresponding to a minimum line width of $11\mu\text{m}$. However, imprinting reduced the short-circuit current (I_{sc}), and consequently the efficiency of the cell by a factor hypothesised to be proportional to the discoloured area. This was, however, deemed acceptable for proof-of-principle devices given the scalability of the light-induced patterning step and potential impact of the application. However, two important research questions were raised by Hustings et al. in their original publication [50]. First, the physical or chemical mechanism enabling the dye to change colour remained to be investigated specifically. Inspired by the similar process in anthotype photography, oxygenic photobleaching was hypothesised. Finally, while an initial reduction in efficiency can be considered justifiable based on the application, the long-term stability remains to be investigated. These questions will bring me to the aims of this thesis at the end of this chapter.

1.4 Dye-Sensitized Solar Cells

Before discussing the aims of this thesis, the following section is dedicated to working principles of DSSC, illustrated in fig. 1.6, as they provide the relevant technical context and are crucial in the exploration of PV photographs.

These cells can be described as consisting of three main parts: an electron-generating photo-anode responsible for light absorption, an electron-collecting cathode, and the typically liquid redox electrolyte chemically and electrically connecting the two [32, 33, 53]. The photo-anode itself consists of a substrate with a transparent conductive oxide (TCO) layer followed by a semiconductor layer, often anatase TiO_2 . The semiconductor is prepared by sintering nanoparticles, around 15 nm-20 nm in diameter, into a mesoporous structure to maximise its available surface area and acts as an electron transport layer. It can then be sensitized with dyes to absorb visible light. A well-suited dye must be able to significantly absorb light broadly in the visible and near-infrared ranges of the electromagnetic spectrum, as well as attach to the semiconductor with fast charge-transfer properties into the semiconductor's conduction band. When the dye absorbs a photon, an electron is promoted from the dye highest occupied molecular orbital (HOMO) to its lowest unoccupied molecular orbital (LUMO). The excited dye is subsequently oxidized through rapid charge transfer of this electron to the conduction band of the semiconductor. Electrons then percolate through the mesoporous layer to reach a TCO layer, which is connected to an external circuit.[54].

Meanwhile, at the cathode, electrons are injected by the external circuit into another TCO layer, having provided useful work. There they are transferred to a catalyst layer (often Pt) which promotes a redox reaction enabling efficient transfer of these electrons to the electrolyte. These charges eventually reach the oxidised dye through ionic diffusion, and a second redox reaction resets the electrolyte while reducing the dye back down to its ground state.

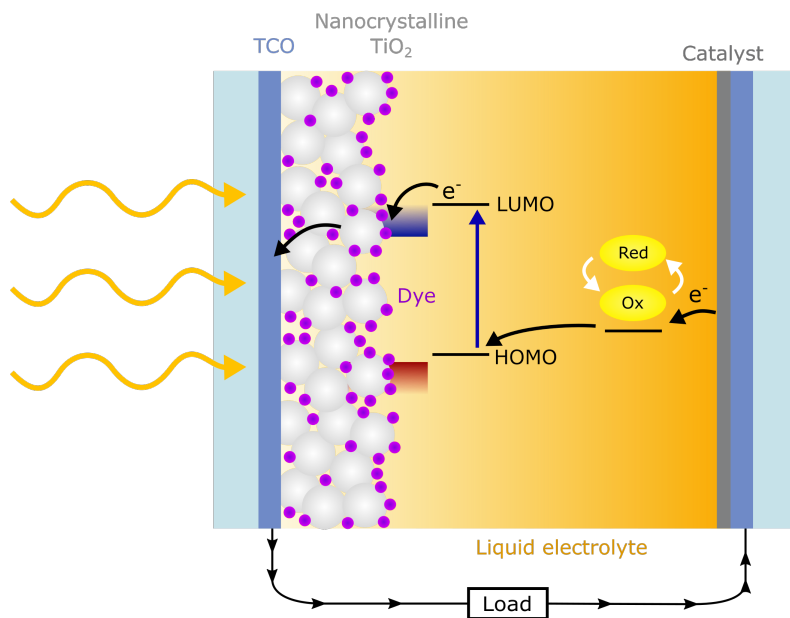


Figure 1.6: Schematic representation of a DSSC and its main working principle. Figure copied from Hustings J. (thesis).

Every aspect of the DSSC is still actively being researched, with many publications focusing on the search for new and more efficient dyes or testing natural dyes extracted from biomass. Alternative sensitisation [55], electron transport layer deposition methods [56], different electrolyte compositions [57], additives [58], etc are lines of research currently being explored worldwide. Despite this significant interest, DSSCs have yet to reach commercial maturity as their efficiency is still rather low compared to other technologies. For example, state-of-the-art co-sensitized devices have reportedly reached 15.2% efficiency under AM1.5G illumination [59]. Recent publications, however, have shown excellent efficiencies in indoor lighting conditions, reaching reported values above 35% [60]. In comparison, crystalline-Si SC are known to struggle in these conditions [46] with a reported 15.6% for a commercially available module [61]. Encapsulation has remained an important topic in this field, as oxygen and water ingress are known to affect their long-term stability in dramatic ways. Survival in 1000 h light-soaking accelerated aging tests has been reported several times so far, but combined stress tests still remain challenging [62].

1.5 Aims of the Thesis

Properly addressing the challenges created by our increasing demand for energy requires an approach on multiple fronts. Exploring and adopting new and more effective ways to convert readily available and renewable sources of energy into a form that is economically exploitable is paramount. Unfortunately, this very adoption is a complex problem reaching far beyond simple material science and engineering. Solutions can consequently only be found by approaching the problem as a whole and by bridging seemingly disparate fields.

It is here that I believe photovoltaic photographs are most powerful. This new application is a direct result of an unconventional collaboration between artists and scientists. With these new SC we might be able to leverage humanity's appreciation for creative expression to increase integrated use of PV technologies. However, doing so requires a thorough understanding of their properties, potential limitations and long-term operation. These are tangible scientific questions that are central to this thesis. In

more concrete terms, I wish to address the following research questions:

1. Which mechanisms underlie the visual changes enabling patterning in PV photographs?
2. How can we assess the local photoelectric properties affected by the visual pattern in PV photographs using readily available PV equipment?
3. Which methodology can reliably determine the stability of operation in PV photographs?

Structurally, this thesis continues in chapter 2 with a technical overview of the experimental methods that were used to answer the above research questions. Substantial original work was devoted to the development of new devices and approaches which are instrumental in addressing the complexities of these questions.

The first research question is treated in chapter 3. This chapter is a published article that investigates the exact chemical origin behind the colour change in N719 DSSC. The N719 dye is chosen for its commercial availability and wide use by researchers. We believe that the insights gained in this article will enable better control of the patterning methodology as well as facilitate attempts at transferring the method to other classes of PV. Additionally, new insights into the photochemistry of the dye were obtained, showing that its degradation in the presence of light, O_2 , and TiO_2 happens in stages.

Subsequently, chapter 4 provides a technical overview on the design and operation of a custom-built laser-beam-induced current (LBIC) device as a prepared manuscript. This device is also used to examine example PV photographs, showing that this method can successfully be applied in DSSC to study non-uniform dye properties, such as locally altered dye chemistry.

Then, a combined methodology to test the stability of PV photographs, and thus patterned PVs in general, under a 1000 h light-soaking aging test, is described in chapter 5. This chapter is written as an article draft intended for publication. Here, stability is defined by two metrics: the PV-parameters must remain constant over time, and no significant change in colour and

contrast should occur from device operation. Local photocurrent mapping and digital photography, using a custom imaging cabinet and colour correction methods, were consequently leveraged in addition to typical in-situ current-voltage (IV)-characterisation. It is argued that this combined approach is necessary to study PV photograph and patterned PV in general but can also provide a more nuanced understanding of the system can be achieved.

Finally, chapter 6 provides a combined summary of the main conclusions of this work as well as additional research questions to be investigated in the future. This chapter emphasizes the broader reach of methodological developments and insights beyond their own specific niche, impacting DSSC and visually patterned PV research in general.

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Chapter 2

Experimental Methods

Preparing photovoltaic photographs (PV photographs) and characterising them is of crucial importance to explore their properties and limitations. This chapter aims to provide details on the experimental methods central to answering the research questions posed at the end of the previous chapter.

In the following sections, the preparation of dye-sensitized solar cells (DSSCs) towards PV photographs, as well as aspects specific to the additional light-induced patterning step will be described. The second section of this chapter discusses various relevant analytical measurement techniques, with the inclusion of equipment upgrades developed for this work. Finally, the third section of this chapter is dedicated to instruments and tools which I specifically designed and built.

2.1 Preparation of Photovoltaic Photographs

The preparation of PV photographs for this thesis largely follows the established preparation protocols of DSSC, summarized in fig. 2.1 [1]. Before diving into a detailed description, it is useful to outline the general steps involved.

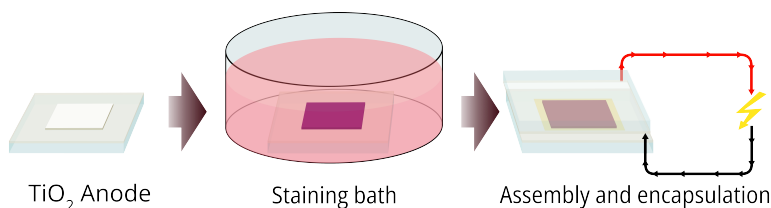


Figure 2.1: Schematic representation of the main steps involved in the preparation of DSSC. Prepared photoanodes are stained in a dye solution before the cell is completed. Image adapted from Hustings et al. [2].

Photoanodes consisting of fluorine-doped tin oxide (FTO) and TiO₂ covered glass substrates are stained by placing them in a dye solution. After staining, these are washed, dried, and subjected to the additional light-induced patterning step described by Hustings et al. [2]. A heat-meltable sealing gasket is subsequently placed around the photoactive part of the anode before an FTO and Pt covered glass substrate is placed on top as a cathode. This stack, shown in fig. 2.2, is sealed using a heat press, and the solar cell is completed by filling it with a I⁻/I₃⁻-based liquid electrolyte through pre-drilled holes in the cathodes before being sealed using epoxy and a glass cap.

2.1.1 Dye-sensitised solar cell preparation

Undyed photoanodes are purchased fully prepared from Solaronix (Switzerland). A number of different types and sizes of anodes are used throughout this thesis. The available types are listed in table 2.1. All anodes are produced by Solaronix as follows. A thin layer of conductive FTO is deposited onto sodalime glass substrates (here 2 mm thick) before an absorbing layer (8 μm - 10 μm thick) of anatase TiO₂ nanoparticles (15 nm - 20 nm in diame-

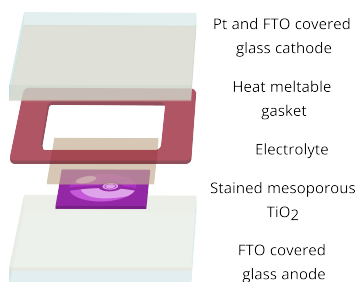


Figure 2.2: Schematic rendering of a typical DSSC/ PV photograph stack, showing electrodes (top and bottom), a stained TiO_2 layer (violet), electrolyte (yellow) and gasket (red). Not shown: cathode pre-drilled holes, epoxy and sealing cap.

ter) is applied by screenprinting using a 61-64 mesh (61 threads/cm, $64\ \mu\text{m}$ thread diameter). These substrates are semi-transparent in nature as the TiO_2 nanoparticles are significantly smaller than typical visible wavelengths. Opaque anodes are available with an additional reflective layer of larger, and thus diffusive, TiO_2 nanoparticles, with diameters above $100\ \text{nm}$. This layer is typically only $2\ \mu\text{m}$ - $3\ \mu\text{m}$ thick [3, 4]. Note that both anodes and cathodes are prepared by Solaronix from larger glass panels. These are coated, scored, and cut into individual electrodes, meaning that close visual inspection of the electrode edges reveals the conductive side. It is recommended to confirm the conductive side of the substrates electrically, using a multimeter.

Table 2.1: Photoanode types used in this work, including substrate dimensions, active area dimensions, and optical properties.

Dimensions (mm^2)	Active Area (mm^2)	Transparency
20×20	6×6	Transparent
20×20	6×6	Opaque
50×50	40×40	Transparent
100×100	90×90	Transparent

The received anodes may contain pollutants and are best reactivated, using a heat treatment step. Anodes are removed from their packaging and placed in a SNOL 8,2/1100 laboratory furnace with the TiO_2 layer facing up. The TiO_2 layer on the anodes is readily visible by the contrasting texture

of reflected features. The furnace is set to increase the temperature from ambient to 450°C at a rate of $5^{\circ}\text{Cmin}^{-1}$. The maximum temperature is held for a total of 30 min before the heating elements are turned off and the furnace is allowed to cool passively. This procedure allows removal of possible contaminants as well as residual water adsorbed onto the TiO_2 . Once the temperature indicates 60°C - 80°C , a process that usually takes about half a day, the anodes are removed from the furnace using heat resistant plastic tweezers and submerged in a 0.3 mmol L^{-1} dye-solution.

Subsequently, dye-solutions must be prepared by weighing an appropriate amount of dry powder, tabulated in table 2.2, in a borosilicate glass weighing boat using an Ohaus AX 224 scale with 0.1 mg precision. The powder is then transferred to a volumetric flask by rinsing the weighing boat with solvent. The volumetric flask is topped with the same solvent to its fill line, a magnetic stir bar is added and the flask is sealed using parafilm before being wrapped in aluminium foil to protect the solution from light. Unless otherwise specified, solutions for this work were prepared with TechniSolv® ethanol euro denatured (96%, CE Emb 28007A), purchased from VWR International. This wrapped flask is then placed onto a magnetic stirrer and the solution is left to stir gently overnight to ensure full dissolution of the dye powder in the solvent. The concentration of the solution can be verified by taking an absorption spectrum against neat solvent.

Table 2.2: Typical dye solutions prepared for sensitization experiments. All solutions are prepared at identical concentration and using ethanol, unless otherwise specified.

Dye	Solution volume (mL)	Target dye mass (mg)
RK1	25	5.6
SQ2	25	4.7
N719	250	89.2

Depending on their size, anodes are placed in small glass beakers or Solaronix staining baths with the TiO_2 layer facing down to prevent potential precipitation on the photoactive surface. This is achieved for the test cells by sliding them into 3D-printed BASF neutral polyamide (PA) holders developed for this work, shown in fig. 2.3. For larger cells, rubber standoffs

are placed on the edges of the anode. In both cases, anodes are then submerged in the dye solution baths, which are covered, placed in the dark, and left to stain overnight. Once stained, the anodes are removed from their bath and rinsed with the solvent used in the dye solution (ethanol) before being fully dried with a nitrogen gun. This ensures that any dye not adsorbed on the TiO_2 surface is removed.

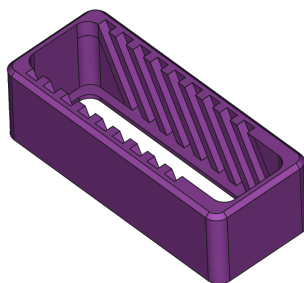


Figure 2.3: 3D rendered image of the custom anode holders, 3D printed in BASF neutral PA filament using a 1 cm brim to improve bed adhesion.

Stained photoanodes are now ready to be integrated into completed solar cells. To achieve this, the photoanodes are placed, facing up, on the bottom plate of a temperature controlled heat press capable of reaching $120\text{ }^{\circ}\text{C}$. Meltonix 1170-60 gaskets, $60\text{ }\mu\text{m}$ in thickness, are made from SurlynTM, a proprietary thermoplastic resin, and purchased from Solaronix. These are square with a cutout slightly larger than the active area of the corresponding anode and are manually placed and aligned to be concentric with the active area. Cathodes, previously heated identically to the anodes, are then placed with the conductive layer facing down, on top of the gasket. In addition to the previously mentioned score line visible on the side of cathodes the Pt layer can also be faintly recognised as a blue/violet reflection. Visual inspection ensures the alignment of the pre-drilled holes with the TiO_2 . The orientation of both electrodes is verified by performing a resistance measurement before applying firm pressure and heat using the press. A timer automatically starts upon closure of the press and notifies the user after an elapsed time of 25 s. Opening the press must be done slowly to allow cells to detach from the top plate, to which they often statically attach and from which they can slide out of the press and get damaged.

The effectiveness of the seal is verified visually by inspecting the gasket for air bubbles. It is crucial to obtain a continuous seal around the TiO_2 to ensure the integrity of the solar cell. Additional heating cycles can be performed to melt the gasket again and improve the seal, but this is also likely to cause the gasket to spread through excessive melting, providing a smaller volume inside the cell.

After this step the cells can be completed by filling them with a iodide/triiodide ionic liquid electrolyte (Mosalyte TDE-S125, purchased from Solaronix) and sealing the pre-drilled hole. This is achieved by using Vac-n-Fill syringes, purchased from Solaronix. The best results are obtained when filling the syringes approximately halfway with electrolyte before attempting to fill a solar cell. They are placed on top of (one of) the pre-drilled hole(s) and the air is replaced with electrolyte. Particular care must be taken to ensure electrolyte presence throughout the complete solar cell volume. The small ($20\text{ mm} \times 20\text{ mm}$) cells can be particularly tricky as their cathodes only contain one pre-drilled hole, as opposed to two for larger sizes. This means air must first be removed from the enclosed volume by pulling on the syringe before they can be filled with electrolyte by applying pressure. This must often be repeated as air is difficult to eliminate completely with this method. The electrolyte used is based on the I^-/I_3^- redox couple common in the field and is not a parameter under study in this research. Specifically, an ionic liquid formulation was used, as recommended by Solaronix, for its low volatility compared to acetonitrile solutions.

Finally, a two-part epoxy is mixed and carefully applied over the pre-drilled hole to seal it. A glass cap is then pressed on top to complete the seal, and the cells are left for 24 h to allow the epoxy to fully cure. The very last step in this preparation protocol involves applying silver-painted contacts to both electrodes to lower the contact resistance of cells with the various measurement devices. RS PRO Silver Conductive Lacquer is used in this step.

Preparing these samples takes approximately 3.5 days from preparing the solutions to the first current-voltage (IV) measurements.

2.1.2 Additional light-induced patterning step

An additional step was added by Hustings et al. [2] to prepare DSSC PV photographs. This step is highlighted in fig. 2.4 and is performed after the photoanodes have been stained and dried but before the cell is completed. The anodes are placed behind a patterning mask and in front of a Xenon short arc lamp (Thermo Oriel Instruments, model 66902, USA), which is operated at 150 W, powered by an Oriel Instruments power supply (model 6890, USA).

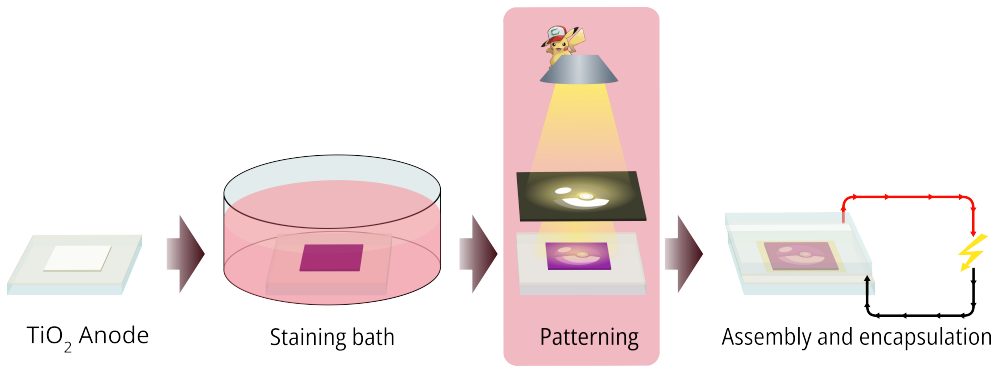


Figure 2.4: Schematic representation of the steps involved in the preparation of PV photographs. The highlighted patterning step shows the additional light-induced patterning step. Image adapted from Hustings et al. [2].

Masks prepared for this patterning step are usually one of three types, with a tradeoff between experimental control and aesthetic design freedom:

1. Metal plates are chosen when simple binary images are required and provide perfect opacity.
2. Black sticker material are used for two-tone thick line art images, these are not perfectly opaque.
3. Grayscale images are printed on commercial transparency sheets when the aesthetic impact of the finished device can be used to its full potential.

Table 2.3: Typical bleaching times required to achieve a distinct change in colour. The contrast achievable from various dyes is different in nature and in strength.

Dye	Bleaching time (h)	Resulting contrast
RK1	>30	Very weak
SQ2	4	Strikingly different colour
N719	21	Modest change in lightness

Figure 2.5 shows the different mask placements during illumination, with masks placed as close as is practical to the TiO_2 to achieve optimal contrast. It is assumed that the discoloured areas in a completed device will contribute less to the overall photocurrent production of the device. Consequently, masks are usually prepared in such a way as to remain as opaque as possible while remaining faithful to the aesthetic goal of the desired image. Note that lighter areas of the image will result in transparent areas of the mask and will thus let more light through. These areas are then exposed to more light during the bleaching step. Given that the change in colour typically leads to lighter colours, the resulting PV photographs are usually a direct representation of their corresponding mask.

Masks are selected and prepared depending on the experiment and are placed on a sheet of borosilicate glass acting as support. Photoanodes are then placed in such a way that the stained (absorbing) layer faces the light source, leading to the configurations illustrated in fig. 2.5. For opaque solar cells, this means that in addition to the glass support, the substrate glass + FTO layers are between the light source and the active layer.

This configuration is then left to bleach for a duration depending on the chosen dye, whose structures are shown in fig. 2.6. Typical bleaching times are shown in table 2.3. The nature and strength of the contrast that can be reached depends strongly on the dye under consideration. As described by Hustings et al. [2], the N719 dye allows for modest contrast to be obtained as the dye seems to produce lighter colours when bleached. Interestingly enough, the fully organic SQ2 quickly and dramatically changes from a deep blue to a vivid green under bleaching conditions, while RK1 hardly

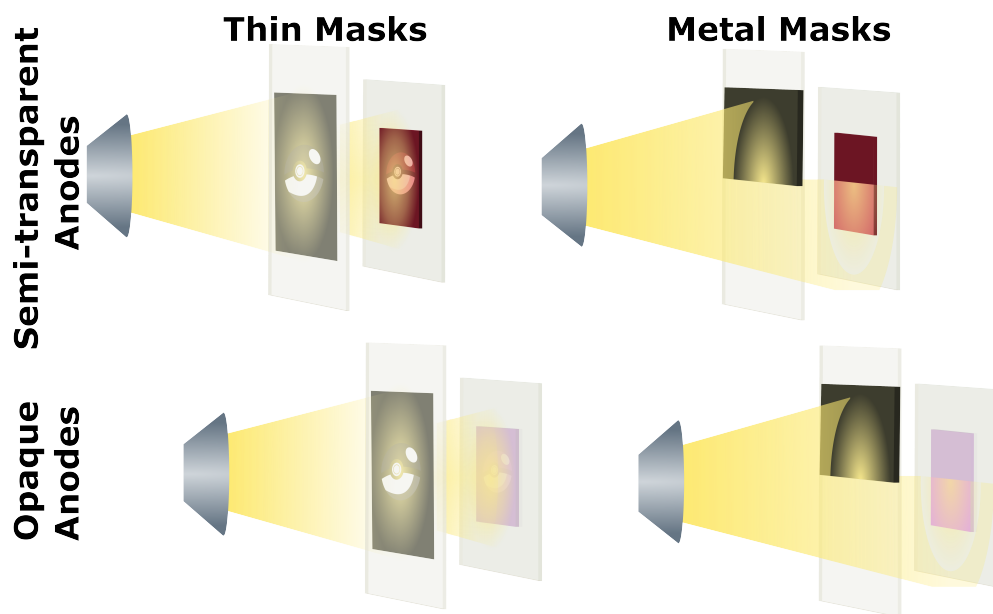


Figure 2.5: Schematic representation of mask, support, and photoanodes during the photobleaching step. Top: The semi-transparent anodes, facing towards the lamp for the most direct path, are given a red colour; Bottom: Opaque anodes, which have an additional reflective TiO_2 layer, must face away from the lamp to avoid scattering incoming light before it reaches the pigmented layer; Top: Thin (sticker or printed) masks can be placed as close as possible to the anode, behind the support glass; Bottom: Thick (Metal) masks are placed before the support glass. The shown thin masks represent printed image masks with multiple gray values.

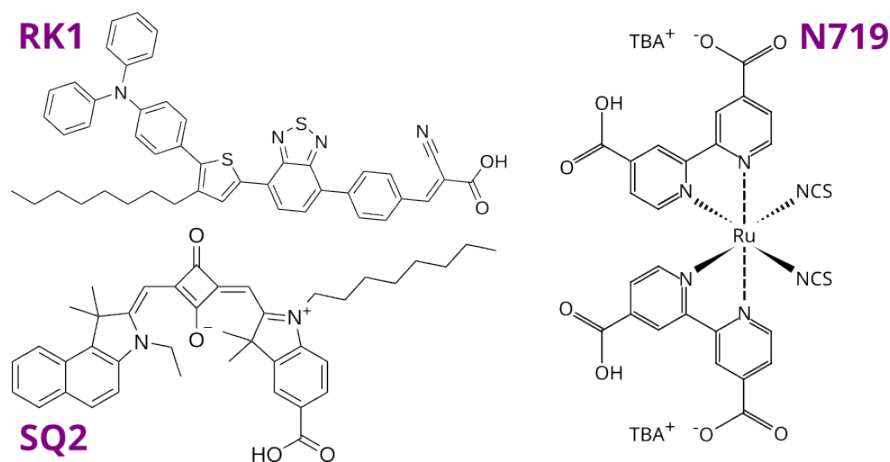


Figure 2.6: Chemical structure formulae of all three dyes used throughout this work.

shows any change at all, even after 30 h.

After this bleaching time is reached, the lamp is turned off, the photoanodes are removed from their support, and the preparation can be continued as is typical for DSSC. Consequently, this step can add significantly to the total preparation time. When using N719, cells are typically prepared over the course of 1 week.

It should be noted that the visual properties of the final device typically differ slightly from the bare photoanode. The main difference follows from the yellow colour of the electrolyte. The colour of final devices thus depends on the interaction of the visual properties of the TiO₂ layer, the dye's intrinsic colour and the electrolyte's semi-transparent yellow hue.

2.2 Measurement Techniques

A few measurement techniques were used in this work to study the materials and device properties. Examining dye absorption properties in various experimental conditions as well as verifying prepared solutions was done using ultraviolet-visible absorbance spectroscopy (UV-vis) spectroscopy.

The characterisation of photovoltaic (PV) devices requires the use of IV measurements, both in the dark and under controlled illumination, using a state-of-the-art a light-emitting diode (LED) solar simulator. Given the focus on aesthetics and colour in this research, it is also important to specify exactly how these are quantified and analysed. This is primarily done based on digital photographs, allowing time-reproducible colourimetry.

All these techniques are described in this section before briefly touching on the methodology applied to perform thorough qualitative and quantitative analysis of the data generated using the techniques.

2.2.1 Ultraviolet and visible absorbance spectroscopy

Absorbance spectra in the ultraviolet and visible ranges of the electromagnetic spectrum were performed using a DW2000 spectrophotometer from SLM Instruments Inc. (USA) and processed using Olis GlobalWorks software. These measurements were all performed in the split-beam mode, whose optical path is schematically represented in fig. 2.7. Broad-spectrum ultraviolet and visible light is provided by two distinct lamps within the device. Their output is guided to a diffraction grating, where it is spectrally dispersed, after which a narrow wavelength range is selected by a slit. The resulting monochromatic light is then alternated between a reference and a sample holder, containing liquid filled cuvettes. The light transmitted by the materials in either holder is collected and converted to an electrical signal by a photomultiplier tube. The device consequently measures transmission only and cannot discriminate between the various ways light can be subtracted from the incoming beam by the sample, being scattering, reflection or absorption.

Absorbance is defined by the Beer-Lambert law and is a function of the optical path length traveled through a material as well as its optical properties [5]. In the absence of significant reflection and scattering, the absorption (quantified by the extinction coefficient) dominates. This assumption is satisfied by all samples studied in this thesis as these are pure, homogeneous solutions. Mathematically, the spectrometer reports the absorbance (A) as defined by eq. (2.1).

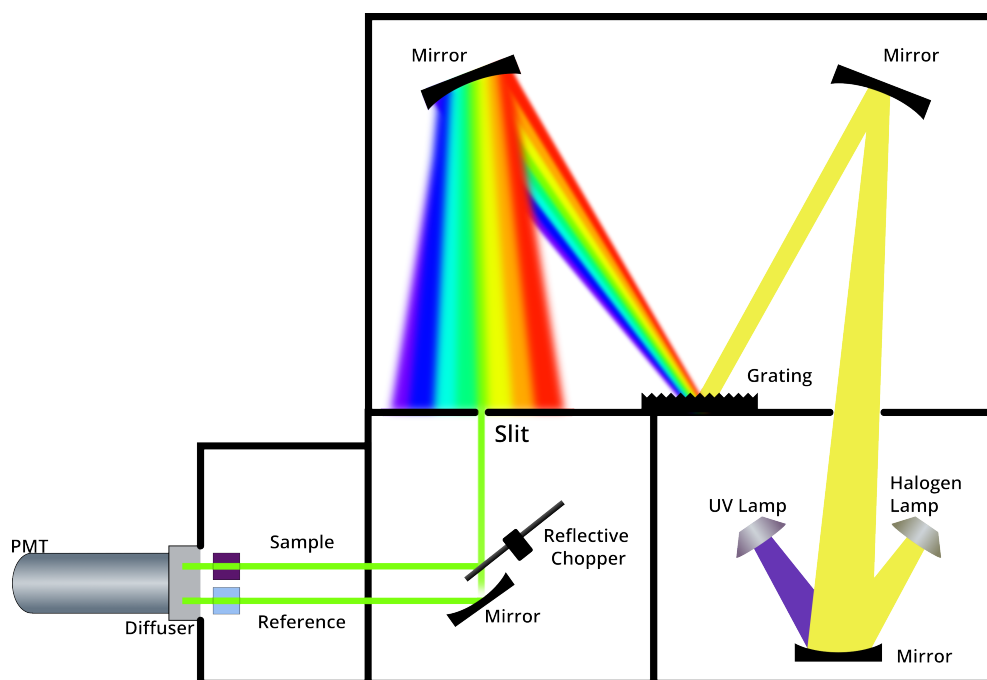


Figure 2.7: Schematic representation of the main components in the DW2000 optical beam path.

$$A_{\lambda} = \log_{10} \left(\frac{I_{ref}(\lambda)}{I_{sample}(\lambda)} \right) = -\log_{10} (T_{\lambda}) \quad (2.1)$$

Where $I_{ref}(\lambda)$ and $I_{sample}(\lambda)$ are the wavelength (λ) dependent intensities of the beam transmitted through the reference holder and the sample holder respectively.

Unless otherwise specified, typical measurements vary the probe wavelength from 200 nm to 800 nm in 1 nm increments. The DW2000 spectrometer switches between the lamps for the UV and visible regions of the spectrum between 339 nm and 340 nm. This transition can be seen as a discontinuity in time-resolved spectra where relative changes were under consideration. Other spectra were all baseline corrected to remove this discontinuity. Baseline correction is done by measuring two identically prepared references against each other. Any spectral variation in the absorbance spectrum is then a consequence of the measurement setup and the spectrum can then be set in the software as a baseline to be subtracted from all spectra.

To improve the signal-to-noise ratio each measurement point is the result of the averaging of five sequential reads of the photomultiplier tube. All measurements were done using identical 3 mL poly(methyl methacrylate) (PMMA) cuvettes as it is transparent above 350 nm [6].

Verification of the measurements was achieved by comparing absorbance spectra from an available Holmium calibration sample before and after every experiment.

2.2.2 Current-voltage characterisation

Characterising solar cells is typically done by measuring their current-voltage (IV) curves. An example of such curves is shown by the solid line in fig. 2.8. Measurements are performed by applying and stepping the voltage in fixed increments while current is measured for each step, resulting in the solid dots. Two important observables that can be derived from such curves are the short-circuit current (I_{sc}) and the open-circuit voltage (V_{oc}), defined in eqs. (2.2) and (2.3).

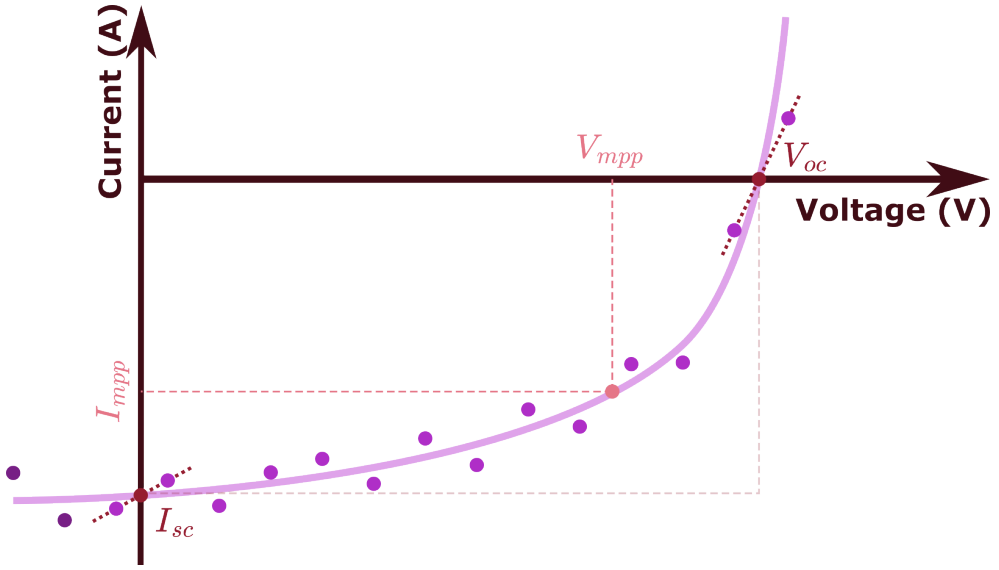


Figure 2.8: Schematic representation of the experimental measurement of an illuminated solar cell (SC) current-voltage curve (solid line). The dots represent measured data, while the dashes connect derived quantities.

$$I_{sc} = I(V = 0) \quad (2.2)$$

$$V_{oc} = V(I = 0) \quad (2.3)$$

$$FF = \frac{P_{max}}{V_{oc}I_{sc}} \quad (2.4)$$

$$\eta = \frac{P_{max}}{P_{in}} \quad (2.5)$$

Where P_{in} is the incident solar power, typically around 1000 W m^{-2} for AM1.5G solar radiation. These must be numerically determined by detecting which points are just before and just after any axis and interpolating between each pair. The intersection between such an interpolated line and the corresponding axis yields the desired observable. By examining the maximum among the products of current and voltage for each point, the so-called maximum power point (P_{max}) can be determined. Fill factor (FF) and efficiency (η) can then be determined using eqs. (2.4) and (2.5).

The IV measurements performed in this thesis were done using a custom setup controlling a Keithley 2450 source measure unit (SMU), schematically represented in fig. 2.9. Solar cells can be connected electrically to the measurement setup by applying crocodile clips to their electrodes. When using test cells, printed circuit board (PCB)-based holders, developed in this work and described in section 2.2.3, can be used instead. In both cases, the corresponding leads are connected to a multiplexing unit consisting of electromechanical relays, controlled by an Arduino Mega 2560 Rev3. The solar cells' anodes are connected to the relays' common terminal, while the normally open (NO) terminals are interconnected between all relays and connected to the positive front terminal of the SMU. Their cathodes are connected to the SMU negative front terminal, which is common to all solar cells. This configuration ensures that solar cells can be individually be connected to the SMU by switching its corresponding relay to connect the common terminal to the NO terminal. As both the SMU and the Arduino can be remotely controlled via LabVIEW, these measurements can be readily automated.

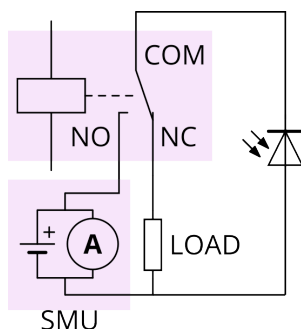


Figure 2.9: Simplified electronic schema representing the IV measurement setup. The relay (with NO, normally closed (NC), and common (COM) terminals shown), a single solar cell and resistive load (LOAD), and the SMU are depicted schematically. The open terminals of the relay are connected to an Arduino controlled power source.

IV measurements sweep from a slightly negative applied voltage to above the expected open-circuit voltage (V_{oc}), this maximum value depends on the chosen dye and electrolyte. Curves are measured by stepping the voltage in discrete increments, typically 10 mV, 20 mV, 50 mV or 100 mV. At each step the current is measured, and a delay time (0.1 s-0.5 s) is ob-

served before stepping the voltage again. These measurements are always performed both in the forward and the reverse directions to account for hysteresis common in DSSC.

Additionally, the NO terminal of each relay is connected to resistor board PCBs, designed in accordance with existing prototypes. Consequently, the LabVIEW program is responsible for switching the connection of the solar cells' anode between the SMU and the resistor boards. These boards were upgraded from prototype boards to fabricated PCBs and each consist of rows shown in fig. 2.10. The PCBs connect to the SMU negative front terminal as well as the solar cell cathodes at the other end. The rows place four resistors in a series connection of two sets of two resistors in parallel, allowing for a wide variety of resistance values to be obtained from commercially available standard values. Consequently, each solar cell can be connected to a dedicated resistive load for continuous operation.

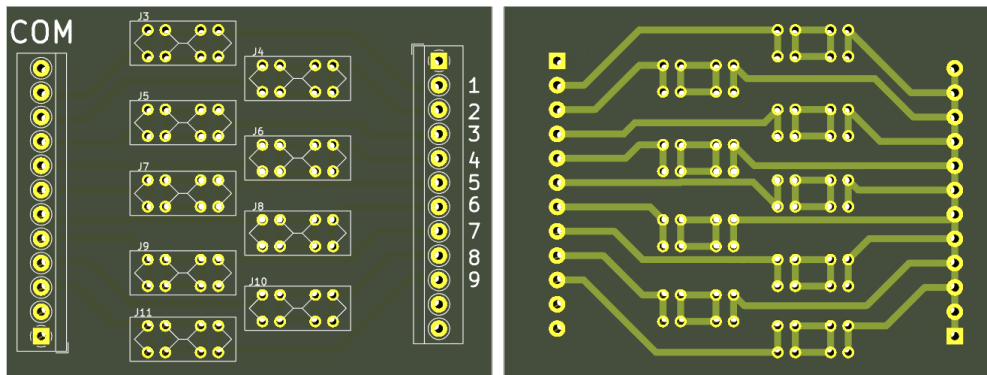


Figure 2.10: Rendered image of the new resistor PCB showing the top (left) and bottom view (right, mirrored). Note that four resistors can be placed per row, bridging the gaps. The numbered silkscreen aids in connecting the individual terminals to the corresponding relay.

Originally designed to characterise up to 16 solar cells sequentially, the system was expanded in this work to accommodate a maximum of 40 devices. A practical upper limit of 36 cells is currently imposed by the available illuminated area under the solar simulator rather than by electrical or software constraints.

2.2.3 Solar simulator setup

The ability to perform IV measurements must be complemented by the ability to illuminate each solar cell in a repeatable and standardised manner. All IV characterisation measurements performed under illumination were done using a class AAA+ large area LED Solar Simulator (Sunbrick Base-UV model, purchased in 2020) from G2V Optics (Canada). The lamp spans a spectral range from 350 nm to 1100 nm, with a spectral mismatch and spatial non-uniformity reported by the manufacturer are below 5 % and 2 %, respectively. The device can be remotely controlled through the same LabVIEW virtual instrument responsible for performing IV sweeps.

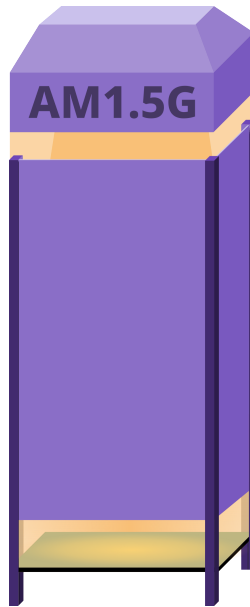


Figure 2.11: Schematic representation of the solar simulator lamp and stand.

The solar simulator is mounted atop a mirrored stand, about 1 m above a black, actively cooled, sample holding table measuring 25 cm by 25 cm, illustrated in fig. 2.11. This sample holding table was built from two thick sheets of aluminium which were machined with a watertight internal channel, connected via tubing to a Minichiller-NR (Huber, Germany) water-cooling stage. A solenoid valve, controlled by a Pt100 platinum resistance thermometer, ensures water is circulated through the holding

table to maintain a constant operating temperature of 25°C. The top of this table was additionally machined with an array of M3 threaded blind holes to allow samples to be rigidly held in place.

New, PCB-based, holders were designed and ordered to increase the maximum number of test cells that can be simultaneously placed in the device from 12 to 36. The small, 20 mm × 20 mm, cells can be fitted between two such PCB holders and are aligned using lasercut PMMA spacers. This stack, shown in fig. 2.12, can rigidly hold solar cells while monitoring their temperature, cooling them when needed, while reliably providing electrical contact to both electrodes. Both PCBs were manufactured by JLCPCB® in China. The bottom PCB was made from 1.6 mm aluminium to ensure good thermal contact with the cooling plate. The top PCB was manufactured from 0.8 mm fiberglass material with matte black silkscreen. Electrical contact between these and the solar cells is achieved by using five surface-mount technology (SMT) spring-loaded pins (Mill-Max part 0965-0-15-20-80-14-11-0, purchased from Mouser Electronics, Netherlands) per electrode. Both PMMA spacers are lasercut from 1.6 mm sheets, with an additional cutout in the bottom spacer allowing the Pt100 sensor to be placed under one of the solar cells.

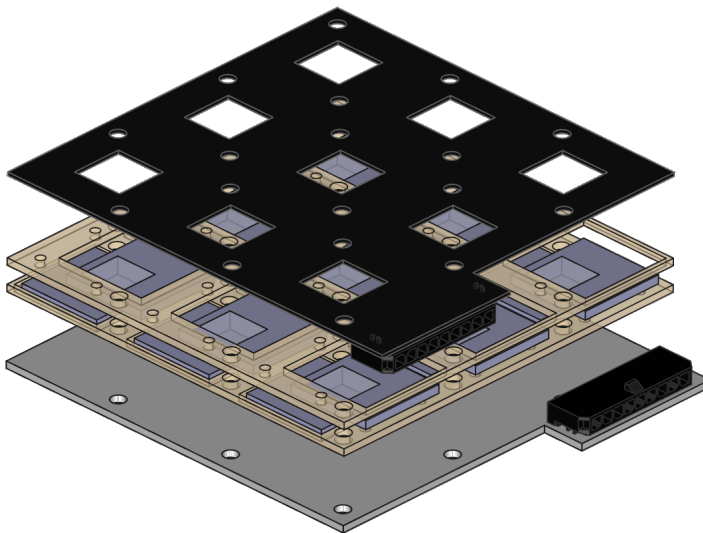


Figure 2.12: Exploded schematic render of the new PCB holders (top: black; bottom: gray) and spacers (yellow) designed for 9 small cells (20 mm × 20 mm, blue).

2.3 New Instruments and Tools

The particular requirements of this work, including a significant amount of data analysis and the unique combinations of traditional SC research meant that specific instruments and tools were required. This section is dedicated to an overview of each of these tools, starting with a brief summary of a laser-beam-induced current (LBIC) measurement device (more thoroughly discussed in chapter 4), an imaging cabinet built in collaboration with dr. Vrancken (artist and photography expert at LUCA School of Arts) and prof. dr. Halme (lecturer at Aalto University, Finland), and ending with an open-sourced data management and x-labpm framework.

2.3.1 Laser-beam induced current measurement device

For this work a new instrument, capable of spatially mapping the current produced by a solar cell when locally illuminated was constructed.

This device was constructed from open source hardware specifications and utilises common off-the-shelf mechanical, optical, and electronic components, as well as a Keithley 2450 SMU for the current measurements. A digital rendering of the device is shown in fig. 2.13 and the details of its construction and operation are the subject of chapter 4. The main advantage of this design lies in the use of standard off-the-shelf components as well as in the use of equipment commonly available in most solar cell research laboratories. In doing so, the device can be constructed with a limited budget (comparable in price to some secondhand devices [7, 8])

2.3.2 Digital photography for scientific colourimetry

Aesthetic appeal is a central concept in this thesis but is complex to quantify as it is a highly subjective experience. In order to discuss these aspects as introduced in the previous chapter they must ideally be measured and quantified in a reproducible manner. This was achieved by building a digital photography cabinet, schematically shown in fig. 2.14, which can be

calibrated for colour. Using a digital camera allows complete images to be captured and analysed, as opposed to colour only.

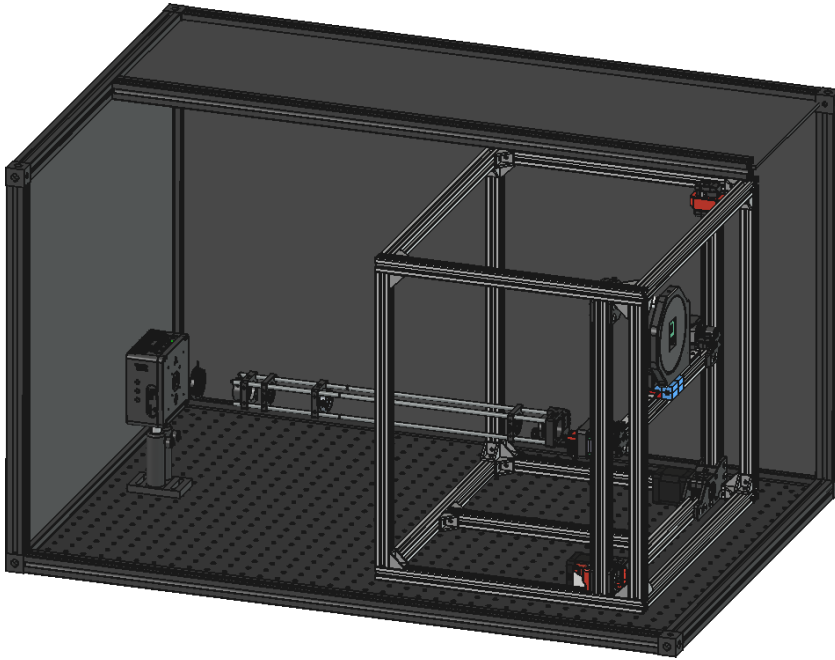


Figure 2.13: CAD render of the custom-built instrument for LBIC measurements.

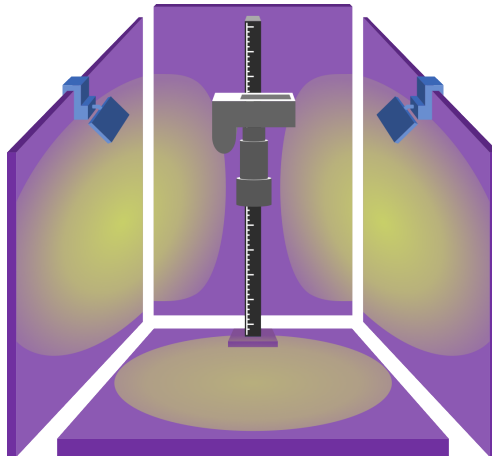


Figure 2.14: Schematic representation of the imaging cabinet showing the digitization stand, camera, walls and lamps.

After a consultation with photography expert and artist Kristof Vrancken (LUCA School of Arts, Belgium), a Nikon Z 7 II camera was chosen for its 45 megapixel full frame sensor and ability to be remotely controlled via a USB connection. It was equipped with a Laowa 100 mm, f2.8, CA-Dreamer 2x macro lens to manually achieve high magnification. The combination was mounted on a Kaiser photography stand to control the height of the camera. This setup is surrounded by white cloth to provide as much diffuse light as possible.

Two Bresser PT 158 II LED lamps are fitted next to the objective to illuminate the imaging area indirectly. Their placement and initial angle are verified by placing a mirror in the imaging area, ensuring they are not directly visible. Their light is reflected by the surrounding white cloth and the mounting angle is adjusted to achieve approximately uniform illumination. A non-reflective glass panel is placed on the stand base to reduce direct reflections of the lamps into the camera lens. Achieving uniformity is paramount, as it is possible that various areas of an otherwise uniformly coloured sample might be detected as being different. However, it proves to be one of the most difficult aspects of building such a setup as small differences are easily detected by a digital camera. The limitations of the setup and optical properties of the lens resulted in less than ideal uniformity of the illumination as perceived by the camera. The best case scenarios still suffered from a phenomenon called vignetting, where a central bright spot is present and the edges appear darker. Ideally this vignetting would be compensated during post-processing of the images through the use of a well calibrated lens profile but such a profile could not be found for our lens. Alternatively, given the well controlled lighting environment, a flat-field correction can be used to correct any non-uniformity in the image. Doing so requires the use of a gray card, which can be imaged before and after a series of images. Correcting several gray-card images with an initial photograph resulted in excellent, albeit artificial, uniformity results.

Images taken in such an imaging cabinet can increase reproducibility by capturing and systematically correcting colours with a prepared correction profile. This was made possible by an international collaboration with the Energy Materials & Interfaces (EMI) group at Aalto University (Finland), who are similarly working on the accurate and precise determination of colour in PV cells [9, 10]. This calibration is achieved by taking images

of objects whose colour is known or well defined. In photography this is typically done by using a colourchecker passport, however more extensive calibration tools exist, such as the American National Standards Institute (ANSI) IT8.7/2 reflective target. Such a target was purchased online with the corresponding colour coordinates [11]. This target can be photographed and the flat-field correction can be applied to the RAW image during post-processing while also selecting an appropriate colour space, here ProPhoto as it is widely used in photography. Open-source software, originally built and provided by Aalto University (Finland) to achieve reproducible colourimetry using digital photography, can then be used to quantify the difference between the measured and known values of the target's colours [10]. The shifts needed to map each measured colour to its true coordinates can then be interpolated as well as extrapolated to the full colour spectrum. The final result is a lookup table capable of mapping every detected colour to a best matching *true* colour. This table can be saved and used to correct colours from images taken in the same illumination at the same distance from the object and with identical camera and lens settings.

The setup was used to examine possible differences in PV photographs before and after a 1000 h illumination period. The details of the analysis as well as the results are the subject of chapter 5.

2.3.3 Data management and analysis

When performing experiments, a significant amount of data, potentially complex or large in size, will be generated. Many tools already exist to analyse such datasets but most are associated with significant drawbacks such as control or cost. While capable, widely available proprietary and open-source spreadsheet programs are typically useful mostly for light analysis and visualisation tasks. More powerful proprietary programs and ecosystems are partially or completely hidden behind costly licenses. For this reason, many scientists turn to programming languages to perform their own analyses and create visualisations. Scientific libraries are often made freely available by the community for various programming languages [12, 13, 14]. Due to its focus on rapid prototyping, Python stands out as a frequently used programming language with users across many

disparate fields [15]. However, many Python users have limited experience, with JetBrains™ reporting that half of their respondents in their 2024 survey have less than 3 years of programming experience [16].

In this work, I developed a graphical tool, named X-LAB Plotting Manager (X-LAB PM) shown in fig. 2.15, for researchers proficient with the Python programming language but not familiar in managing research software. This tool aims to aid in structured data management and analysis while providing examples on programming best-practices such as single-responsibility [17]. This section will provide a high-level description of this tool and its principles [18]. More extensive documentation for this tool is outside the scope of this section and has been made available online given the open publication of the source code [19].

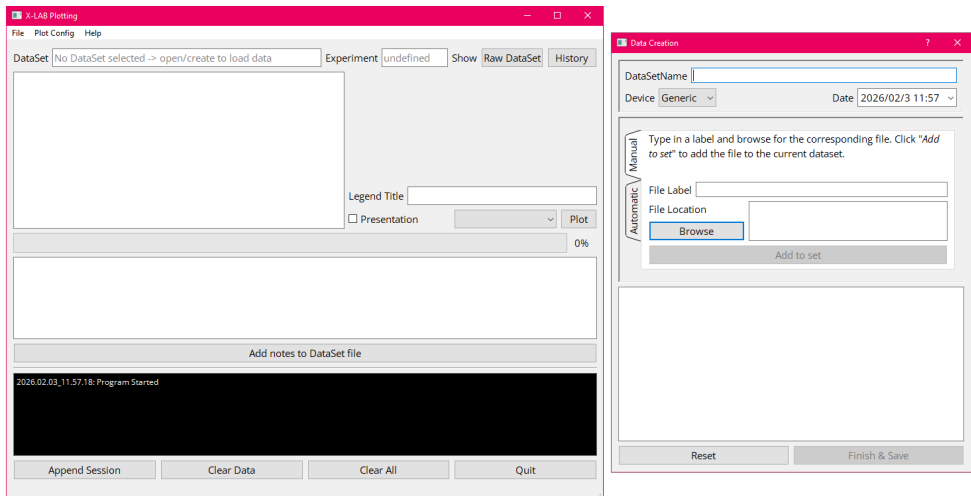


Figure 2.15: Screenshot of the X-LAB Plotting Manager (X-LAB PM) graphical user interface (GUI)

This tool was developed to leverage two strengths: structure and re-usability. These concepts are powerful programming tools and can be achieved in many ways but are often underutilized, or even unknown, by junior researchers. Most researchers have a well structured system enabling them to quickly retrieve a particular dataset. However, this structure is often lost at the analysis and visualisation stage. To help solve this issue the X-LAB PM is built around a GUI and JavaScript Object Notation (JSON)-based *datasets*. These datasets are h files assigning labels to

filepaths so that data can be assembled and retrieved from their original location. These contain important experimental metadata, such as the type of device used for the measurement, and the experiment date and time. Consequently, users can save these datasets in a central location, without needing to copy files or manually edit lists of file locations. Datasets of this type can be easily constructed, saved, and reloaded using the X-LAB PM.

The strength of this tool lies in the definitions it provides, enforcing a specific code structure. In doing so, it encourages researchers to segment different aspects of the data analysis pipeline in a reusable manner. Reading data files, processing derived quantities, and choosing and configuring specific visualisations are all cleanly separated. This simplifies a complex task and organises it in a way that can be easily managed, updated, and extended. This structure is visualised in the diagram of fig. 2.16, showing how various classes interconnect. An example implementation of this specification is provided to use and extend as needed [18].

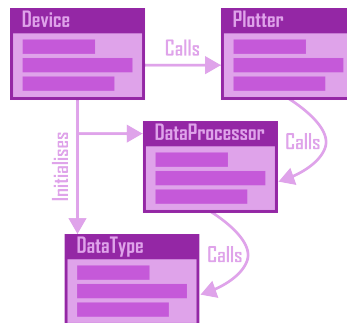


Figure 2.16: Class diagram of the specifications defined for the X-LAB PM.

A significant amount of data analysis was required for this work, from the numerical analysis of measured IV-curves, to the automated extraction of short-circuit current (I_{sc}), V_{oc} , FF, and P_{max} time series from these individual curves (often requiring the analysis of over 25 000 individual measurement files), as well as x-labpm UV-vis and Fourier-transform infrared spectroscopy (FTIR) data and showing and analysing LBIC photocurrent maps. Most of the code used for this analysis is implemented according to the contracts shown in fig. 2.16 and these implementations are provided under an open source license to be used and examined [20].

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Chapter 3

On the Underlying Mechanism of Light-Induced Patterning of N719-Stained Photoanodes for “Photovoltaic Photographs”



On the underlying mechanism of light-induced patterning of N719-stained photoanodes for “photovoltaic photographs”

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Data Availability

Raw data for all figures shown in this publication, and source code used for figs. 3.3 and 3.4 are made available through publicly accessible Zonodo data repositories [1, 2].

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3.1 Abstract

Recently, “photovoltaic photographs” were proposed as a creative application of photovoltaic technologies, relevant in fields such as architecture. A high-resolution image is created in solar cells by light-induced patterning of the photoactive layer, causing a local change in the appearance of the solar cell. Here, we investigate the physico-chemical changes induced by this process in the photoactive layer of proof-of-concept N719 photovoltaic photographs, to better understand the underlying mechanisms and further develop the concept. By combining a variety of techniques, we show a previously unreported multi-step degradation of the isothiocyanate ligand of the dye, correlated to visual colour changes. Time-resolved UV-VIS spectroscopy revealed the catalytic role played by TiO_2 , causing a blueshift (35 nm) in the dye’s 495 nm metal-to-ligand charge-transfer peaks within 10 hours. This is confirmed through infrared spectroscopy showing a 24 cm^{-1} shift to smaller wavenumbers of the CN-stretching vibration. Finally, time-of-flight secondary ion mass spectrometry (ToF-SIMS) reveals the multi-step nature of the degradation, through the transient increase of an NCO^- signal. These insights are of importance for a better understanding of the photo-induced degradation of N719, a more substantiated control of the patterning process, and to design appropriate light-induced patterning techniques for other classes of solar cells.

3.2 Introduction

The fundamental study of light-matter interaction mechanisms has enabled the development of several classes of photovoltaic (PV) solar cells, whereby the interaction between light and semiconductor materials is leveraged in the generation and subsequent collection of electron-hole pairs, converting sunlight into electricity [3]. In recent decades, the rapid expansion of PV energy research and production has been motivated in part by the challenges posed by climate change, the growing population, and global economic growth [4, 5, 6, 7]. During this period, scientists have kept advancing the technology at an impressive pace by offering new and exciting opportunities. Some of these new opportunities address

the integration of solar installations in contexts such as architecture [8], agriculture [9] and even the Internet of Things [10]. Such applications require careful consideration of materials and aesthetics throughout the entire design process. Freedom of design and aesthetics therefore must be included as key features of solar cell technologies in this context. Consequently, researchers have been focusing on properties other than efficiency, such as semi-transparency [11], flexibility [12], and colour [13]. Installations showcasing some of these applications already exist, such as the International School in Copenhagen [14] or the EPFL's SwissTech Convention Center [15].

Recently, our group introduced the concept of "photovoltaic photographs" [16]. This innovation allows for spatial control over the visual appearance of solar cells, offering greater flexibility in module design. The key to this control lies in patterning the photoactive layer using a dedicated light-induced patterning step in the preparation process. Light-matter interactions therefore have a dual role in this application, first, the earlier mentioned photon-semiconductor interactions yield the desired photovoltaic power output during operation, second, still unknown light-matter interaction mechanisms are responsible for the patterning observed in photovoltaic photograph (PV photograph) devices. By integrating design elements directly into energy-producing components, this approach opens new opportunities for applications where both aesthetics and energy generation are essential.

A proof-of-principle of this approach is showcased in fig. 3.1 (left), where an image is embedded into the photoactive layer of a dye-sensitized solar cell (DSSC). This class of solar cells is often researched for their low production cost [17] and advantages in indoor applications [18]. Their main working principle is the injection of electrons from a photo-excited dye into the conduction band of titanium oxide (TiO_2), after which the dye is reduced by a redox-couple. A typical DSSC photoanode is made up of a glass substrate coated with a transparent conductive oxide layer, onto which anatase TiO_2 nanoparticles are deposited. These are then sintered to form a mesoporous structure ensuring conductivity throughout the volume [19]. Embedding a photograph within these cells is achieved by exposing stained photoanodes to light, transmitted selectively through a mask, before applying the counter-electrode. Other techniques have

previously been explored for the potential design advantages that they offer. Printing technologies are already commonly explored in the production of solution-processable types of solar cells, like organic or perovskite solar cells for their production advantages in addition to its potential for patterning [20]. Hashmi et al. [21] took inspiration from these and drop casting, proposing a method for ink-jet printing multiple dyes to achieve single-cell multicolour, patterned dye-sensitized solar cells. An entirely different approach has been explored by Mittag et al. [22] who introduced a module concept featuring sub-cells, enabling easy implementation of mosaic design at the module level. However, PV photographs differ from such patterning approaches by combining design freedom, scalability, and ease of integration into existing production lines.

Despite these advantages, the demonstrated concept of photovoltaic photographs faces a crucial research gap related to the nature of the underlying mechanism of light-induced patterning. Although the added step in the preparation methodology enabled us to obtain successfully patterned transparent solar cell demonstrators with sizes of 9 cm by 9 cm and with photographic resolution, a thorough understanding of how this process works is lacking. More specifically, it remained unclear how this photo-induced patterning method causes the visual properties to change and how this is related to the molecular structure of the dye. Thorough understanding of the patterning mechanism in this proof-of-principle device is crucial to further develop the technique and transfer it to other emerging photovoltaic technologies. In the initial publication on “photovoltaic photographs”, Hustings et al. [16] hypothesised oxygenic photobleaching as an underlying reaction mechanism in the preparation of photovoltaic photographs. However, the role of the TiO_2 substrate and its effect on the sensitizing dye remained to be investigated explicitly. An additional research question relates to the illumination times required to achieve patterning. According to Hustings et al. visual contrast achievable with the technique is dependent on the illumination time, they specifically mention needing longer bleaching times for dyes with superior photo-stability.

The main contribution of this work is to obtain a better understanding of light-induced patterning of solar cells by examining the specific case of DSSC PV photographs made using the synthetic ruthenium dye di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-

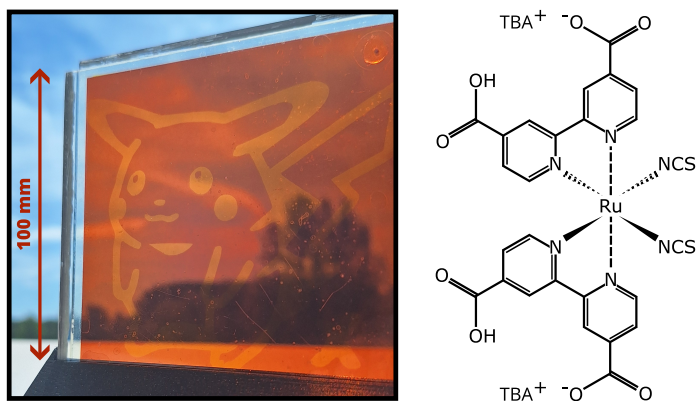


Figure 3.1: Left: Photograph of a 100 mm x 100 mm “photovoltaic photograph”, prepared using N719 and containing an image of a popular Japanese cartoon figure. Right: Chemical structure of the N719 dye

dicarboxylato)ruthenium(II), commonly known in the literature as N719 and whose structure is shown in fig. 3.1 (right).

The novelty of the approach discussed in the following sections lies in the use of UV-VIS and infrared spectroscopic techniques in combination with state-of-the-art ToF-SIMS to disclose the mechanisms underlying the photo-induced patterning. More specifically, we discuss the role of the substrate, and short and long illumination times in affecting the visual properties of N719 in photovoltaic photographs. In doing so, we reveal previously unreported insights on the photo-stability of N719 in the presence of TiO_2 . Additionally, the findings inspire the design of light-induced patterning strategies applicable to other classes of solar cells.

3.3 Materials and experimental methods

3.3.1 Materials

All experiments described here used TechniSolv® ethanol euro denatured (96%, CE Emb 28007A), purchased from VWR International, as solvent. Ruthenizer 535-bisTBA synthetic dye powder, known in the literature as

N719, and Ti-Nanoxide T/SP paste (product codes: 21613 and 14451, respectively) were purchased from Solaronix (Switzerland). Pre-sintered test cell titania anodes (product code 74111) were also purchased from Solaronix (Switzerland). These transparent anodes consist of a glass substrate (20 mm x 20 mm) coated with fluorine-doped tin oxide (FTO) onto which an anatase Ti-Nanoxide layer (6 mm x 6 mm) is homogeneously screen-printed. Sodium hydroxide (NaOH), used to detach N719 dye from TiO₂ nanoparticles, was purchased from Emplura (pellets, B1835162 131). Finally, custom anode holders were 3D printed from neutral BASF Ultrafuse polyamide (PA) filament using a Prusa MK4 machine.

3.3.2 Time resolved UV-VIS spectroscopy

To disentangle the effects of TiO₂ and illumination time on the dye degradation kinetics, time-resolved UV-vis spectroscopy measurements were performed. For these measurements, two types of samples are required, a negative control consisting only of N719, as well as N719 attached to anatase TiO₂. Comparing UV-VIS spectra on deposited films can be challenging due to differences in scattering, reflection and even layer thickness/composition. In order to ensure comparable results, two distinct mixtures were therefore prepared. The first mixture, a *pure solution*, was a 0.3 mmol L⁻¹ solution of powdered N719 in ethanol, acted as a negative control sample. The second mixture, a titanium suspension, was prepared by weighing Ti-Nanoxide T/SP paste and N719 powder to obtain concentrations of 60 mmol L⁻¹ and 0.3 mmol L⁻¹ respectively. The Ti-Nanoxide T/SP paste was chosen as it is used in the preparation of photoanodes, ensuring sufficient similarity between the mixture and photoanode composition. This second mixture thus serves as an analogue for DSSC photoanodes.

Both mixtures were stirred overnight in the dark, ensuring no exposure to light. These mixtures were kept in identical glass bottles, sealed by a plastic cap. Immediately after preparation, the mixtures were illuminated concurrently using a Xenon short arc lamp (Thermo Oriel instruments, model 66902, USA), powered by a 150 W power supply (Oriel instruments, model 6890, USA), at a distance of 30 cm from the lamp opening. This illumination setup was chosen to resemble the light-induced patterning step in the preparation of PV photograph as closely as possible. The two mixtures

were therefore both simultaneously exposed to the same light as well as atmospheric oxygen. Consequently, the two master mixtures only differ in the use of Ti-Nanoxide T/SP paste.

Samples were taken by pipetting 500 μL from each master mixture every 15 minutes during the first two hours of illumination, then every half hour for a total illumination time of 10 hours. Pure solution samples were diluted 10-fold before measuring to remain within the Beer-Lambert linear range. However, to isolate the altered dye from the TiO_2 nanoparticles (shown in figure S1) a post-processing step was needed for the suspension. Extraction was achieved through centrifugation (8 minutes at 13000 rpm) using an Eppendorf MiniSpin centrifuge equipped with the F-45-12-11 rotor. Subsequent removal of the supernatant, addition of 0.1 mol L^{-1} NaOH, and a final centrifugation cycle [23, 24] yielded samples used for time-resolved UV-vis spectroscopy (TR UV-vis) measurements. Consequently, the *extracted* solution samples consisted of N719 dissolved in NaOH rather than ethanol. The resulting solution was dark red, leaving behind a white sediment, indicating a successful extraction procedure. A 5-fold dilution of the extracted solution was used for the UV-VIS measurements. These were performed using a DW2000 spectrophotometer from SLM Instruments Inc. (USA) and Olis GlobalWorks software. The DW2000 spectrometer utilises two distinct lamps for the UV and visible regions of the spectrum and must switch between these. This transition is seen as a discontinuity in all spectra. In addition, to improve the signal-to-noise ratio each measurement point is the result of the averaging of five sequential reads. All measurements were done using identical 3 mL poly(methyl methacrylate) (PMMA) cuvettes and performed against a pure ethanol reference (for comparison with pure solutions) or NaOH reference (for comparison with extracted solutions).

3.3.3 Preparation of “photovoltaic photograph” anodes

PV photograph anodes were prepared according to the procedure described by Hustings et al. [16]. Briefly, the purchased TiO_2 anodes were re-fired at 450°C for 30 minutes to remove possible pollutants before being allowed to cool slowly to 60°C . Subsequently, these anodes were placed in a 3D-printed PA holder, with the TiO_2 side facing-down to avoid potential

precipitation onto the substrate, fully submerged in an N719 solution prepared freshly as before, and left to stain overnight in the dark. The next morning, these anodes were removed from the dye solution and rinsed with ethanol to remove residual dye not adsorbed onto the anode and left to air-dry. After drying, light-induced patterning was achieved by placing the anodes on a glass support in front of a Xenon short arc lamp (Thermo Oriel Instruments, model 66902, USA), which was powered by a 150 W power supply (Oriel Instruments, model 6890, USA). The anodes were illuminated as shown in the diagram of fig. 3.2 under ambient atmosphere. The TiO₂ layer of the anodes was placed facing the lamp, ensuring a direct path between the light source and the surface of the sample.

Short (4h) and long (22h) illumination times were chosen to investigate their effect on completed PV photograph anodes. The longer illumination time of 22 hours was chosen for consistency with previous work whereas the 4 hour illumination time ensured a perceptible change while remaining significantly shorter than the reported 22 hour illumination.

In order to simplify the experiments and data analysis, a simple mask was used instead of more intricate, patterned masks. These “simplified masks” consisted of a metal plate placed over a portion of each anode. Consequently, the prepared photovoltaic photographs (figure S4) contained a binary pattern composed of two distinct regions: areas of the anode surface that were masked during illumination, and areas that were directly exposed to light. These areas of interest will be referred to as *covered* and *illuminated* respectively and are depicted in fig. 3.2.

3.3.4 Fourier-transform infrared spectroscopy and gas chromatography - mass spectrometry

To elucidate the chemical changes underlying the light-induced degradation mechanism in N719, six semi-transparent DSSC photoanodes, prepared as described in section 3.3.3, were analysed with FTIR. One anode was kept in the dark, another was fully exposed to light for 22 hours, two were patterned as shown in fig. 3.2 for 4 hours, while the last two were patterned for 22 hours. Measurements were taken of the covered and the illuminated areas of all patterned anodes, leading to a total of ten areas.

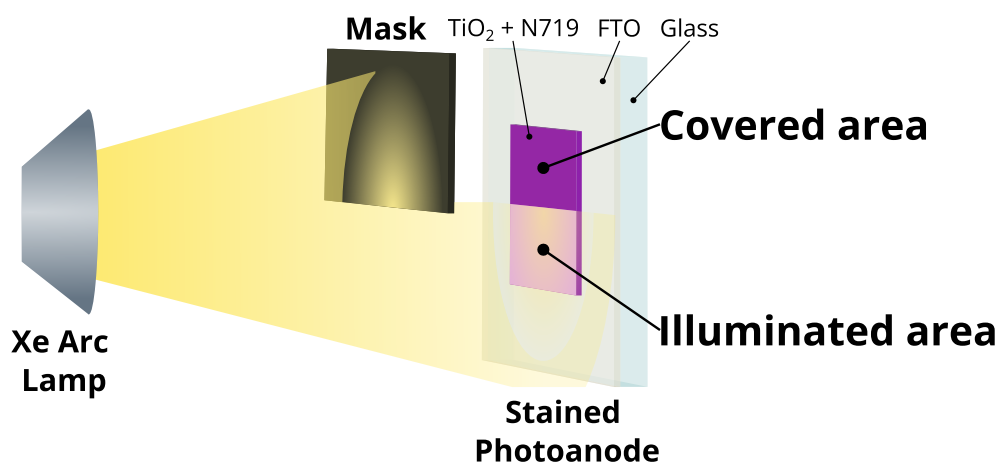


Figure 3.2: Schematic representation showing the illumination step in the preparation of test PV photograph anodes for analysis. Light from a Xe short arc lamp was shone onto stained DSSC photoanodes (consisting of anatase TiO₂ nanoparticles, screenprinted onto FTO covered glass) that were partially covered by a mask. The masked area (covered) was minimally exposed to light while the unmasked area (illuminated) showed strong discolouration.

For each area two separate spectra were taken in different locations. One spectrum was qualitatively identical to its duplicate but uniformly shifted towards lower transmittance values. One measurement of the illuminated area on a 4 hour anode was nearly flat and thus excluded. In total, 19 measurements were considered for analysis. All samples were prepared fresh and kept in the dark until they could be measured. All spectra were collected between 4000 cm^{-1} and 600 cm^{-1} , with a spectral resolution of 4 cm^{-1} , where every spectrum presents the sum of 32 scans to improve the signal-to-noise ratio. These measurements were done using a Bruker INVENIO-S spectrometer equipped with a mercury cadmium telluride (MCT) detector and an attenuated total reflectance (ATR) setup equipped with a Germanium crystal and peaks were identified in the OPUS 8 software (Bruker).

A pure N719 sample was analyzed by ultraviolet (UV) pyrolysis gas chromatography–mass spectrometry (PY-GC/MS) using an EGA/3030-D Multi-Shot Pyrolyzer with a UV-1047Xe Micro-UV Irradiator (Frontier Laboratories, Japan) coupled to a Trace 1300 GC system (Thermo Scientific, USA) equipped with a DB-5MS capillary column (30 m length, 0.25 mm I.D. 0.25 μm film thickness, Agilent, USA) and an ISQ 7000 quadrupole MS (Thermo Scientific, USA). This sample was irradiated for 1 h at 35°C under a 10 mL min^{-1} air flow. Vapors were introduced into the column with a 1:10 split. Gas chromatography (GC) analysis followed with He as carrier gas (1 mL min^{-1}), temperature ramped from 35°C (1 min) to 320°C at $12^\circ\text{C min}^{-1}$, held 9 min. Injector and transfer line temperatures were 300°C and 280°C , respectively. Following irradiation, residues were analyzed by flash pyrolysis at 550°C for 0.2 min in Eco-Cup SF crucibles (PY1-EC50F) under He. Pyrolyzates were introduced with a 1:80 split and analyzed under identical GC conditions. Data were processed using Chromeleon 7.3 (Thermo Scientific, USA).

3.3.5 Time-of-flight secondary ion mass spectrometry

The effect of the light-induced patterning process on the local chemical composition of the photoanode was further analyzed using time-of-flight secondary ion mass spectrometry (ToF-SIMS) with a TOF.SIMS 5 instrument (IONTOF GmbH, Münster, Germany) at Imec (Leuven, Belgium). Two semi-transparent N719-dyed TiO_2 anodes were prepared under identical

conditions as detailed in section 3.3.3 with a light exposure time of either 4 hours or 22 hours. For each area, three repeated measurements were performed, sufficiently spatially separated to ensure independent measurements. Since ToF-SIMS results from the covered areas were nearly identical, they were combined into a single group. Therefore, three groups of areas were analyzed: covered, illuminated for 4 hours, and illuminated for 22 hours. Measurements using the so-called high-current bunched mode, which maximizes the mass resolution, were performed with a 30 keV Bi_3^+ primary ion beam transmitting a current of approximately 0.2 pA at a cycle time of 200 μs . Areas of $100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$ were analyzed by randomly scanning over 64×64 pixels until reaching a primary ion dose density of 3×10^{12} ions/ cm^2 . A more extensive description of the technical procedure and the data processing strategy have recently been detailed by Fransaert et al. [25]. The fast-imaging mode, optimized for maximum spatial resolution, was additionally employed for the current work. A $250\text{ }\mu\text{m} \times 250\text{ }\mu\text{m}$ area was scanned at 512×512 pixels using a 30 keV Bi_3^+ primary ion beam, transmitting 0.13 pA at a cycle time of 65 μs . The total dose density for imaging was 5×10^{11} ions/ cm^2 .

3.4 Results and Discussion

Each experimental technique described in section 3.3 was chosen to address a specific research question related to the changes caused by the added photo-induced patterning step in the preparation of photovoltaic photographs. In the following sections we show a strong correlation between the observed visual changes in the PV photograph after the light-induced patterning step and the chemical degradation of the dye's isothiocyanate ligand. TR UV-vis measurements demonstrate the role of TiO_2 in facilitating degradation of the isothiocyanate ligand leading to the observed discolouration. Furthermore, FTIR and PY-GC/MS support the proposed hypothesis of degradation of the isothiocyanate ligand, and indicate additional changes to the dye structure. The combination of these techniques therefore reveals a more pronounced description of the various aspects of the underlying light-matter interactions occurring during the light-induced patterning of N719-stained TiO_2 photoanodes. Finally, ToF-SIMS reveals the multi-step nature of this degradation by uncovering transient products

with maximum intensities at intermediate illumination times.

3.4.1 TiO_2 plays a crucial role in the light-induced patterning process

To elucidate the role of TiO_2 , as used in DSSCs, in the observed visual changes, TR UV-vis spectroscopy was employed. Spectral changes over time (i.e., during illumination) for pure and surface-bound N719 were compared. As justified in section 3.3.2, two master mixtures were prepared, one consisting only of pure N719, and the second incorporating Ti-Nanoxide T/SP paste to ensure compositional similarity to DSSCs photoanodes. Both mixtures were prepared and subsequently illuminated concurrently for 10 hours. Figure 3.3 shows the absorbance spectra over time for both the pure (top) and extracted (bottom) solutions, normalised to the height of their 305 nm-310 nm peak to eliminate uniform changes not dependent on wavelength.

Four prominent peaks are visible in all results and identified by their (local) maximum. In the pure solution results these are found around 260 nm, 310 nm, 380 nm, and 520 nm. The first two peaks in the UV region are associated with intraligand charge transfer (ILCT) involving the bipyridine ligands, while the two peaks in the visible region correspond to a metal-to-ligand charge transfer (MLCT) associated with the isothiocyanate ligands [26, 27].

Comparing pure and extracted solutions before illumination reveals differences in these peak locations. Specifically, the MLCT peaks are shifted by about 10 nm to 25 nm in the extracted solution results compared to the pure solution spectra. This initial difference is attributed to the different environments (ethanol vs NaOH) used for the UV-VIS measurements (see figure S2). Over time, both MLCT peaks of the extracted solution exhibit a drop in intensity as well as significant broadening. Over the 10 hour measurement period, the peak in the blue-green region, around 495 nm, experiences an additional 35 nm blue-shift on top of this general broadening. In the pure solution and over the same measurement period this peak only minimally shifted by 5 nm. The observed shift indicates that illumination causes chemical changes to the isothiocyanate ligands coordinated to

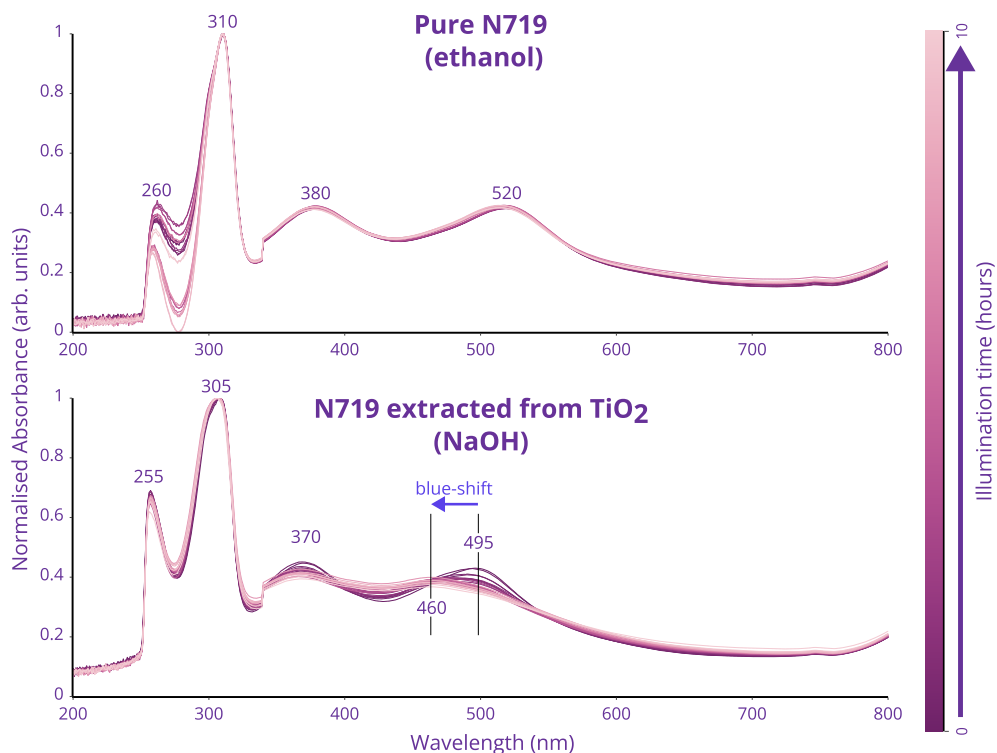


Figure 3.3: Normalised time resolved UV-VIS spectra for N719 in ethanol (top) and N719 extracted from a suspension of stained TiO₂ nanoparticles (bottom). The colour gradient represents illumination time, with a lighter colour corresponding to longer times. The highlighted blue-shift is perceptible as a change of colour of the solution.

the ruthenium metal atom, which is greatly accelerated by the presence of TiO_2 . Specifically, the blue-shift potentially shows a degradation of these ligands to cyanide [26].

3.4.2 Chemical degradation of the dye on TiO_2 anodes revealed by FTIR and py-gc-ms

Further insights into the chemical changes induced in the dye were obtained by performing Fourier-transform infrared spectroscopy measurements on covered and illuminated anodes, prepared as described in section 3.3.4. The 19 spectra unambiguously separated into three distinct groups corresponding to covered areas, areas illuminated for 4 hours, and areas illuminated for 22 hours. Figure 3.4 shows representative spectra for each of these groups alongside the chemical structure of the N719 dye.

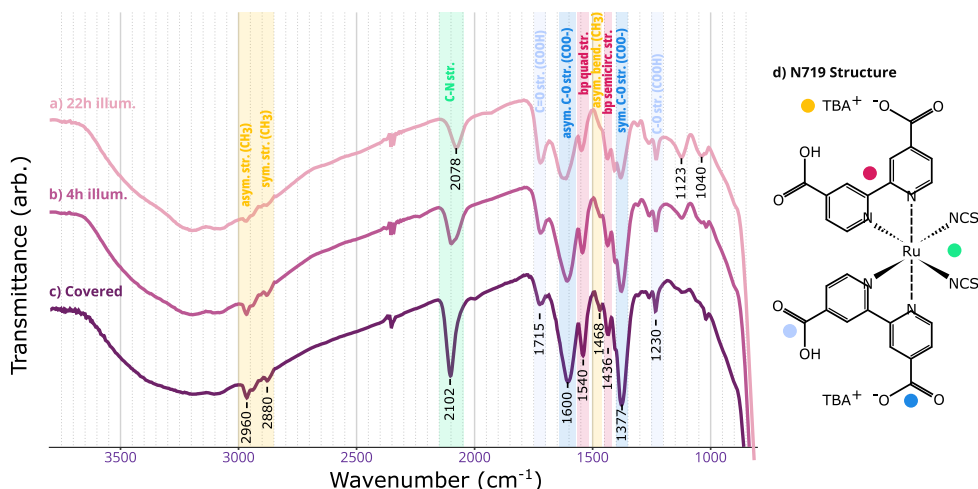


Figure 3.4: Left: Representative FTIR spectrum of the illuminated (a and b) and covered (c) areas of anodes prepared according to section 3.3.4. The spectrum for the covered area is identical to that of a dark area sample (figure S3). The coloured regions highlight vibrational bands that were identified using the covered area. Right: Chemical structure of the N719 dye, colour coded to link ligands and functional groups to features in the FTIR spectrum.

Characteristic vibrational bands were assigned based on the FTIR spectrum

of the negative control anode that was stored in the dark, whose spectra are identical to the covered areas. These vibrational bands were assigned in accordance with the literature [28, 29].

The NCS ligand is probed by the CN stretching vibration, initially present at 2102 cm^{-1} but decreasing over time. Meanwhile, a nearby peak appears under illumination at 2078 cm^{-1} . These changes indicate time dependent changes to the NCS ligands in the illuminated area, consistent with conclusions found in the literature regarding N719 degradation [23, 29].

The carboxylic acid vibrational bands (1715 cm^{-1} , 1234 cm^{-1}), as well as carboxylate stretching bands (1376 cm^{-1} , 1600 cm^{-1}) all showed proportional changes relative to each other. In the illuminated area, the carboxylate vibrational bands decreased in intensity relative to the carboxylic acid band with negligible changes in wave number (less than 5 cm^{-1}) detected for these peaks. These observations can be associated with protonation of the dye in the illuminated samples. The bands in the high wavenumber region (2960 cm^{-1} , 2880 cm^{-1}) as well as the 1470 cm^{-1} peak are typically associated with CH_2 and CH_3 vibrations and have been associated with the tetrabutylammonium (TBA) counter-ion [30]. These peaks steadily decrease with illumination time. Together with the protonation of the dye it can be concluded that this counterion is affected and replaced by hydrogen in the molecule.

The vibrational bands assigned to the quadrant stretching and semi-ring deformation of the bipyridine rings (1540 cm^{-1} , 1436 cm^{-1}), were almost identical in the covered and illuminated areas, suggesting that the bipyridine rings remained unchanged.

These findings are further supported by PY-GC/MS measurements performed on powdered N719 (see tables S1 and S2). Upon UV illumination, tributylamine was detected as the most prominent volatile degradation product. Additional compounds identified in this stage include N,N-dibutylformamide, dibutyl disulfide, N,N-dibutylacetamide, as well as butyl (iso)-thiocyanate. These results confirm the vulnerability of NCS, even in pure conditions, while suggesting that the TBA counter-ion is not only replaced during illumination but also dissociates and readily reacts with the dye's NCS ligands, leading to the formation of various TBA-derived products.

No fragments related to the bipyridine ligands were detected in this first measurement. However, a second PY-GC/MS analysis was conducted after pyrolysis of the remaining sample, in which bipyridine-derived fragments were observed, along with additional tributylamine. This confirms the resistance of the bipyridine rings to direct photodegradation and indicates that the NCS ligands were eliminated during the initial UV treatment.

While the frail nature of NCS as ligand in the N719 molecule has been reported previously [31], the fate of the sulfur atom during degradation remains unknown. The very strong peak centered at 1126 cm^{-1} , with a shoulder at 1069 cm^{-1} , appearing in the FTIR data of the illuminated area could provide an additional reaction path, as it has been associated with sulfur oxides in the past [32]. However, peaks related to isocyanate or nitrile groups would be expected in the 2150 cm^{-1} - 2400 cm^{-1} range and are not present in these results. While FTIR analysis confirms that patterning primarily involves the changes in the NCS ligand, insights into the specific degradation pathway and reaction products involved required additional chemical investigation, which were performed with time-of-flight secondary ion mass spectrometry.

3.4.3 TOF-SIMS analysis shows a multi-step degradation pathway for NCS

ToF-SIMS is a surface-sensitive chemical analysis technique and was used to further examine the process leading to patterning in photovoltaic photographs. By locally bombarding the sample's surface with a pulsed primary ion beam, secondary ions are ejected and subsequently detected based on their time of flight, allowing for the construction of mass spectra. ToF-SIMS is often used in DSSC research to study the distribution of dye throughout the TiO_2 layer [33], both in single dye as in co-sensitized solar cells [34]. It has also been applied previously in aging tests, analysing dye adsorption on the counter electrode [35]. Here, the chemical analysis potential of ToF-SIMS was further leveraged to analyze the degradation mechanism locally. This was achieved by comparing three areas of N719-dyed TiO_2 anodes in two distinct photoanodes: a covered area, an area illuminated for 4 hours, and another illuminated for 22 hours.

Figure 3.5 (a) shows a steady decrease in NCS ligand intensity during illumination, with near-complete disappearance after 22 hours. This irrefutably confirms the substantial photodegradation of the NCS ligand, as supported by FTIR and discussed in previous sections. Additionally, ToF-SIMS detected sulfur oxide signals, including SO_4^- , as shown in fig. 3.5 (b), along with other derivatives like SO_3^- and SO_4H^- (not shown here). These findings indicate that the primary degradation pathway involves photooxidation of the isothiocyanate sulfur atom, emphasizing oxygen's role in this process.

Furthermore, ToF-SIMS results suggest that substitution of the NCS ligand's sulfur atom by oxygen may occur. Figure 3.5 (c) shows an initial increase in NCO^- concentration after 4 hours of illumination, followed by a decrease after 22 hours. This transient increase suggests that substituted compounds also degrade over time, while highlighting the photosensitivity of isothiocyanate's sulfur atom. This time-dependent behavior offers crucial insights into the N719 photodegradation mechanism, characterized using a recently proposed ToF-SIMS data analysis strategy [25]. This approach identifies compounds that behave differently over the two illumination timescales (4 h and 22 h), and highlights variations in the $\text{Ru}(\text{NCS})(\text{NCS})$ metal ligand's sulfur content. Closer examination of peak intensities in fig. 3.5 (d) reveals that, although the absolute intensities of $\text{Ru}(\text{NCS})(\text{NCS})^-$ and its derivatives decrease, the relative intensities of $\text{Ru}(\text{NCS})(\text{NC})^-$ and $\text{Ru}(\text{NC})(\text{NC})^-$ increase after 4 hours and then decrease after 22 hours. These results suggest that sulfur loss occurs rapidly, relative to the overall degradation of the isothiocyanate ligand. In combination with previous observations, these time-dependent ToF-SIMS results suggest an oxygen-catalyzed, multi-step photodegradation pathway, beginning with sulfur substitution or loss within the NCS ligand and culminating in the removal of the ligand.

Finally, ToF-SIMS was used to chemically image the surface composition of a N719-dyed TiO_2 anode after 22 hours of illumination. A $250 \times 250 \mu\text{m}^2$ region centered around the illumination interface was scanned, producing mass spectra for each pixel. Figure 3.6 presents intensity images of NCS^- (blue), SO_4^- (red), and NCO^- (green), both separately and as an RGB overlay. As expected, the NCS^- and SO_4^- images are anticorrelated, reflecting the degradation of the isothiocyanate ligand and the formation of sulfur ox-

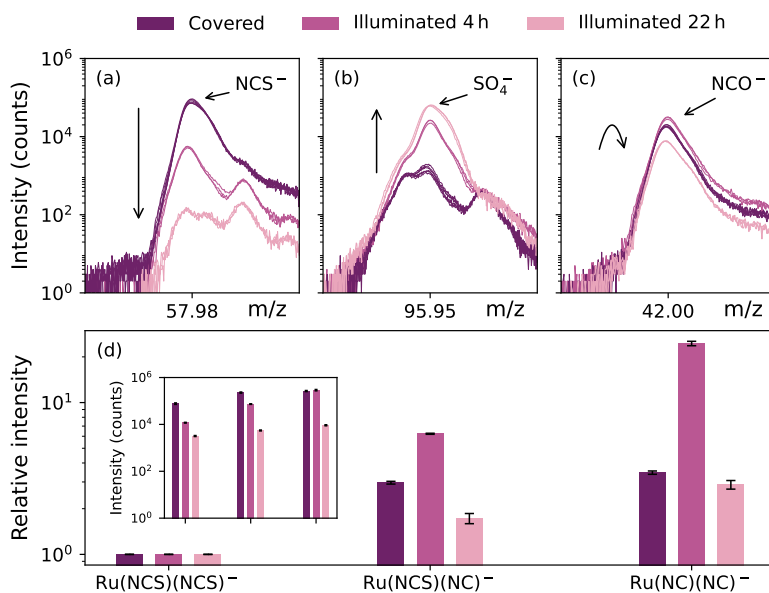


Figure 3.5: ToF-SIMS comparison of three areas from N719-dyed TiO_2 anodes: a covered area, an area illuminated for 4 hours, and another illuminated for 22 hours. Spectral intensities are shown for (a) NCS^- , (b) SO_4^- , and (c) NCO^- . The time-dependent nature of the photodegradation is highlighted in (d). The inset shows the absolute peak intensities of Ru(NCS)(NCS)^- , Ru(NCS)(NC)^- , and Ru(NC)(NC)^- , while the main plot presents their relative intensities, calculated as the absolute intensity of each species divided by the absolute intensity of Ru(NCS)(NCS)^- in the corresponding area. Error bars indicate 95 % confidence intervals of the means.

ides. The NCO^- signal is most intense at the illumination interface, likely due to edge effects that partially expose this region to light, resulting in substantial degradation over the 22 hour period. This increase in NCO^- intensity at the interface mirrors the effect observed in the fully exposed area after 4 hours of illumination, translating the time-dependent degradation process into a spatial variation and reconfirming the multi-step nature of N719 photodegradation during patterning of photovoltaic photographs.

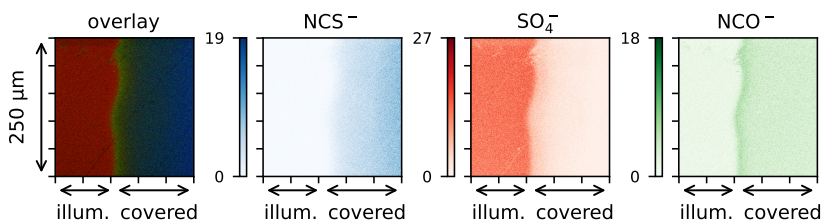


Figure 3.6: ToF-SIMS images of the illumination interface in a N719-dyed TiO_2 anode. The area to the left of the interface was illuminated for 22 hours while the area to the right remained covered. The intensity images for NCS^- (blue), SO_4^- (red), and NCO^- (green) show distinct spatial variations corresponding to the illuminated and covered areas. These images are combined in an RGB overlay to emphasize spatial relationships.

3.5 Conclusions

The recently proposed photovoltaic photographs add to the growing field of aesthetically oriented photovoltaic technologies by combining patterning, colour and semi-transparency in the photoanode. Yet, the physical and chemical origins of these light-induced visual changes remained unclear. In this work, we investigate in detail how the patterning originates from the intentional and selective degradation of the N719 dye during illumination in ambient conditions. Time-resolved UV-vis spectroscopy showed a

strong catalytic effect of TiO_2 on the dye degradation by showing a seven-fold increase in the blue shift of the 495 nm metal-to-ligand charge transfer peak. This is confirmed by the 24 cm^{-1} shift and intensity drop of the CN-stretching vibration in the FTIR spectra. These findings are in line with previously reported FTIR and UV-VIS studies on the degradation of N719 [29, 23]. A partial replacement of the TBA counter ion is also concluded from these spectra and from the identification of tributylamine and dibutyl disulfide in pyrolysis gas chromatography–mass spectrometry measurements. This may also suggest an influence on the anchoring strength of the dye to the TiO_2 surface [30]. ToF-SIMS analysis showed a decreasing NCS^- signal with illumination time, while sulfate (SO_4^-) intensities increased. The transient NCO^- ions, however, peaked after 4 h before declining again at 22 h. These trends show that sulfur is rapidly lost from the ligand, partially replaced by oxygen to form short-lived NCO^- intermediates before the ligand is ultimately removed from the dye-complex under patterning conditions.

Collectively, the results establish a multi-stage photodegradation sequence catalysed by TiO_2 under illumination and atmospheric oxygen. To the best of our knowledge, this is the first report of the multi-step nature of N719 photodegradation on TiO_2 . The changes in the visual absorption correlate with the increased transparency and colour contrast between illuminated and covered regions observed in photovoltaic photographs. These mechanistic insights are consistent with the efficiency decrease previously reported for complete devices by Hustings *et al.* [16].

This improved understanding of the light-induced patterning step offers guidance for future research. It illustrates how apparent weaknesses in dye stability can be repurposed as functional features when properly understood. Additionally, the results emphasize the importance of effective encapsulation to limit oxygen ingress, preserving both aesthetic integrity and photovoltaic performance. Future research should validate these mechanisms for a broader category of sensitising dyes, while also examining the long-term stability of these photovoltaic photographs, both in terms of their electrical output and the durability of the colour and contrast in the image, verifying their viability as an application.

The insights gained in this research open opportunities for intentional and

controlled photo-bleaching in other solar-cell architectures, expanding the potential use of spatially tuned optical properties for both aesthetic and functional purposes.

CRedit authorship contribution statement

Allyson Robert: Data curation, Formal analysis, Investigation, Methodology, Visualization, Writing – original draft. **Nico Fransaert:** Data curation, Formal analysis, Investigation, Methodology, Visualization, Writing – original draft. **Willem Awouters:** Data curation, Formal analysis, Investigation, Methodology, Writing – review & editing. **Wouter Marchal:** Validation, Writing – review & editing. **Peter Adriaenssens:** Validation, Writing – review & editing. **Roland Valcke:** Writing – review & editing. **Jean V. Manca:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing – original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work the author(s) used OpenAI's ChatGPT (GPT-4-turbo, April 2025) in order to rephrase specific sentences of the draft for clarity and readability. After using this tool/service, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the published article.

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Chapter 4

2D Spatial Current Mapping on Patterned Solar Cells using a Custom-Built Laser-Beam Induced Current Device



2D Spatial Current Mapping on Patterned Solar Cells using a Custom-Built Laser-Beam Induced Current Device

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MANUSCRIPT IN PREPARATION

Data Availability

All raw data and source code will be made available upon submission of this manuscript. The manuscript will be made available as a pre-print before submission [1, 2].

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4.1 Abstract

Laser-beam-induced current (LBIC) is traditionally used to spatially map light-induced currents in solar cells, thereby obtaining information on local defects and inhomogeneities. Here, we present LBIC as a powerful tool for studying visually patterned solar cells, an upcoming trend in various emerging PV technologies to enhance their aesthetic properties and broaden their creative application possibilities. In this work, we demonstrate the benefits of a custom-built LBIC measurement system for so-called 'photovoltaic photograph' demonstrators. These are semi-transparent solar cells including an image, integrated in the photoactive layer, obtained via a photo-induced process in dye-sensitized solar cell. On the one hand, we provide technical details and guidelines towards the realisation of a custom LBIC system using off-the-shelf components and common photovoltaic (PV) research equipment, and on the other, we describe the results obtained for 'photovoltaic photograph'. More broadly, this work shows that LBIC is a powerful technique for obtaining a 2D spatial photocurrent map in patterned solar cells.

4.2 Introduction

The global climate crisis has highlighted the necessity of sustainable and renewable energy sources. One such source, researched since the discovery of the photoelectric effect, is the conversion of sunlight to electricity [3]. Understanding the physics behind this effect in relation to material properties has allowed solar cell efficiency to increase over time, bringing single-junction devices closer to their Shockley-Quisser limit [4]. These advances were possible only through the use of various characterisation techniques to examine the detailed physics of candidate devices. Among the tools available to researchers, spatially resolved and/or scanning techniques are particularly powerful, as they enable scientists to consider material properties, such as morphological features or energetic defects, locally [5, 6, 7, 8].

Nowadays we have access to many scanning techniques, such as electron-beam induced current scanning, photoluminescence imaging, conductive atomic force microscopy (C-AFM) and laser-beam-induced current (LBIC) scanning. LBIC stands out for its simple mode of operation, the spatially resolved photocurrent generation in PV devices, non-destructive measurement regimes and the ability to scan completed devices rather than individual components. In its simplest form, an LBIC device consists of a tightly focused laser beam impinging onto a photoelectrically active sample. Changing the relative position of the beam relative to the sample is achieved by placing the PV devices in a movable holding stage. A current measurement device, typically a picoammeter, is then used to measure the photocurrent produced by the beam for each position. This current is directly determined by the local photoelectrical conversion physics and global electron transport properties of the device. This technique can therefore reveal crucial design and operational insights. Consequently, LBIC devices are available commercially [9, 10, 11] and have been used at scale to find micro-cracks in Si-solar cells [12], as well as in a research context to study device properties in thin-film [13, 14, 15] and perovskite solar cells [16, 17, 18].

Beyond efficiency-driven optimisations, more pragmatic constraints, such as production cost [19] and the potential for complementary integration [20, 21] continue to inspire researchers to consider new types of solar cells. Among these is the upcoming trend to broaden the creative application possibilities of solar cell (SC), e.g. for integration in architecture (e.g. building-integrated photovoltaics (BIPV)). Societal acceptance of BIPV still remains limited ; conventional panels are often perceived as visually intrusive and architecturally restrictive. Commercial silicon solar panels are typically only offered in limited colors and fixed sizes. The class of emerging photovoltaics (i.e. dye-sensitized solar cell (DSSC), organic photovoltaic (OPV), perovskite solar cell (PSC)) address this limitation by offering vast aesthetic potential. These solar cell technologies provide additional degrees of design freedom, as they can be processed by printing and allow the realization of semi-transparent solar cells and the use of various colors . Over the last decade, extensive research has sought to harmonize PV technology with architectural design, leading to various approaches, concepts and techniques to obtain solar cells with different colors or patterns . Recently, so-called "Photovoltaic Photographs", shown

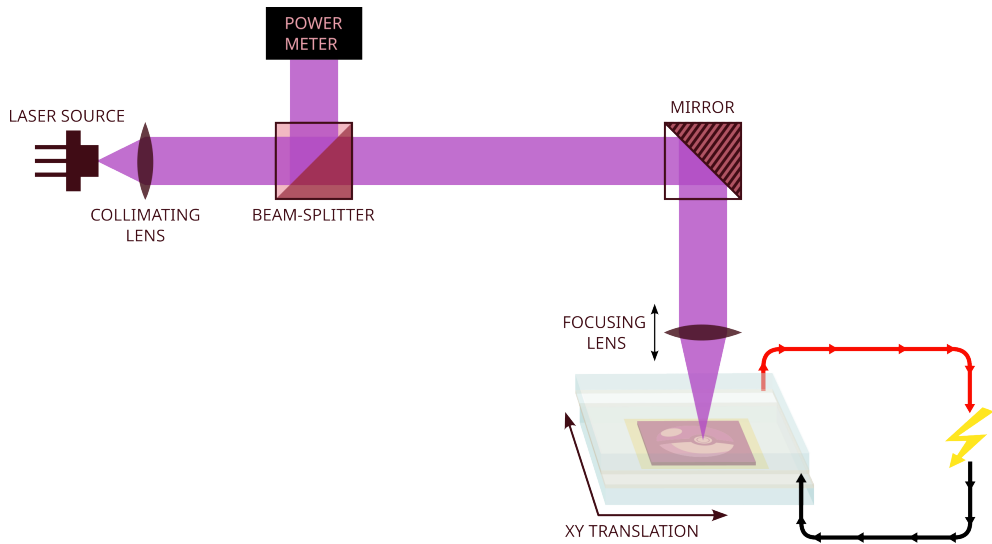


Figure 4.1: Schematic representation of common LBIC measurement set-up, adapted from [13]. Light is produced by a (laser) source and collimated before being sampled for intensity monitoring. The remaining light is directed and focused onto a sample. The focused beam is able to be moved relative to the surface of sample which is electrically connected to a current measurement device.

in fig. 4.2, were introduced as a new approach towards patterned PV [22]. These consists of (semi-transparent) solar cells with an image integrated in the photoactive layer, allowing creative applications such as photovoltaic photographs, paintings, or posters, with additional aesthetic benefits. The approach introduced by Hustings et al. involves using a direct photo-induced patterning process, i.e. one-step photolithography (with mask / without resist), and was demonstrated in proof-of-principle devices based on DSSC using biological and synthetic dyes [22]. The concept of photovoltaic photographs is not restricted to DSSC, but has the potential to be transferred to other emerging solar cell technologies.

DSSC have been studied since the early 1990s, first for their potential cost-benefits in terms of fabrication [23, 24], then for their remarkable performance under indoor light conditions [25, 26]. Their main working principle relies on the sensitization of a semiconductor whose band gap lies in the ultraviolet or above. This sensitization is achieved using a light-absorbing pigment with chemical properties allowing efficient adsorption onto the semiconductor as well as efficient charge-transfer to its conduction band. Crucial in this application are: the photoelectrical conversion by the dye, efficient charge transfer to the supporting semiconductor, and the subsequent reduction of oxidized dye molecules. Dye reduction is typically achieved by a liquid redox-couple capable of shuttling charges from the cathode. Time-dependent short-circuit current measurements usually exhibit a rapid initial rise followed by a slow decay toward a steady-state value. This effect is well known and impacts the measurement parameters when performing IV characterisation on these cells. The physics of these devices is known [27] and their potential still drives research, optimising their performance [28].

Recently, the underlying mechanism behind the colour change observed in photovoltaic photographs (PV photographs) prepared using the commercial N719 dye was shown to follow from a chemical degradation of the dye's isothiocyanate ligand [29]. The presence of intact and degraded versions of the dye on one anode can be considered a form of de-facto co-sensitized DSSC. However, the effects of this chemical change on the photo-electrochemical properties of completed devices remained to be examined locally.

Unfortunately, the clear trade-off between resolution and measurement time, is exacerbated in DSSC. Long equilibration times, on the order of seconds, would either lead to low-resolution (1 mm beam diameter) [30], prohibitively long measurement times for relatively small areas [31] or non-quantitative results due to the lack of steady-state measurement conditions [32]. Previous uses of this technique for DSSC research involve electron diffusion length determination [33] or true photoactive area measurements and uniformity measurements [34]. The resolutions reported in these studies typically range from $1\text{ }\mu\text{m}$ to $100\text{ }\mu\text{m}$ [32, 33, 35, 36, 37].

In this work we make the case that this technique can yield valuable insights for patterned DSSC research, in spite of the known limitations, achieving decent resolutions and acceptable scan times with readily available equipment and off-the-shelf components. Its successful application on patterned PV photograph DSSC can therefore be considered a demonstration of LBIC as a crucial technique in the investigation of patterned solar cells of any class. Figure 4.2 shows an example of a PV photograph, depicting *The Church at Auvers* from the renowned Dutch artist Van Gogh [38], as well as an LBIC scan of a similarly prepared cell. A first example of an LBIC scan of a PV photograph demonstrator is shown in fig. 4.2 (right) to illustrate the typical 2-dimensional photocurrent maps that can be obtained on patterned solar cells.

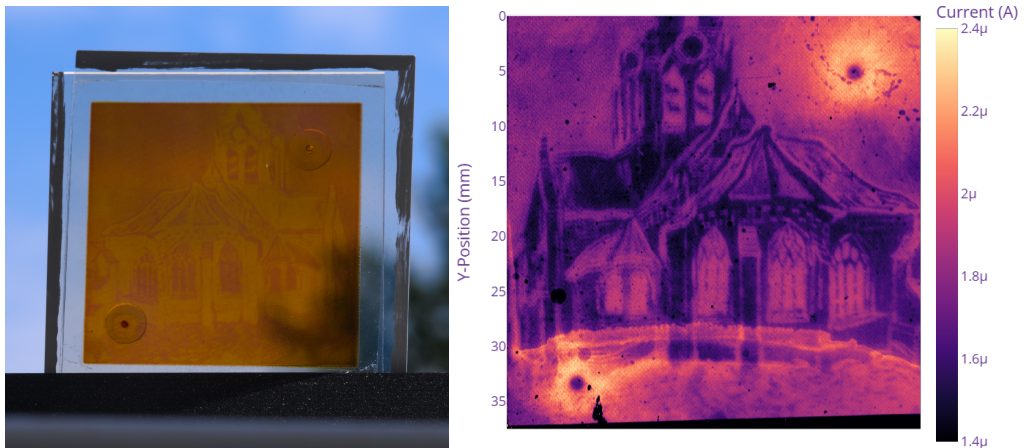


Figure 4.2: Left: Example a PV photograph depicting Van Gogh's *Church at Auvers*. [38]. Right: LBIC scan of a similarly prepared PV photograph.

This article contains two main parts: we first describe in detail the technical aspects involved in the construction of an affordable LBIC system using common PV-research equipment, as well as the approach taken to validate measurements, before subsequently detailing the preparation of example PV photographs and discussing resulting measurements.

4.3 Building a Custom-Built LBIC Device

While laser-beam-induced current devices are commercially available, they can carry a significant cost. For this reason, the version represented in fig. 4.3 was built using off-the-shelf hardware and available measurement devices for approximately 5 000 EUR, comparable in price to some secondhand devices [39, 40]. The bill of material for this particular build as well as some rudimentary instructions can be found in the supplementary material and on GitHub. There are three main aspects to the device, a mechanical stage carrying and moving the sample, an optical stage consisting of a laser and focusing optics, and finally device control and data acquisition.

4.3.1 Mechanical Stage

An open-source 3D printer, the Voron Trident r1 (2022) [41], was chosen as a base for the mechanical stage as it allowed to shorten the design phase of the device. The frame was simplified for this application as no z-axis movement is required and additional parts were designed and 3D-printed to fit the altered application. The hardware was purchased from European vendors, following the Voron Design bill of materials for a blind-joint stock size build of the Trident model. The 2020 aluminium extrusions and linear rails were cut to size, allowing a scanning area of over 100 mm × 100 mm.

Motion is achieved using two 200 steps/revolution NEMA 17 stepper motors controlled by: an Arduino Uno Rev 3, a computer numerical control (CNC) Shield, and microstepping capable DRV8825 stepper drivers, all purchased from 123-3D (Netherlands). The motors are powered by a

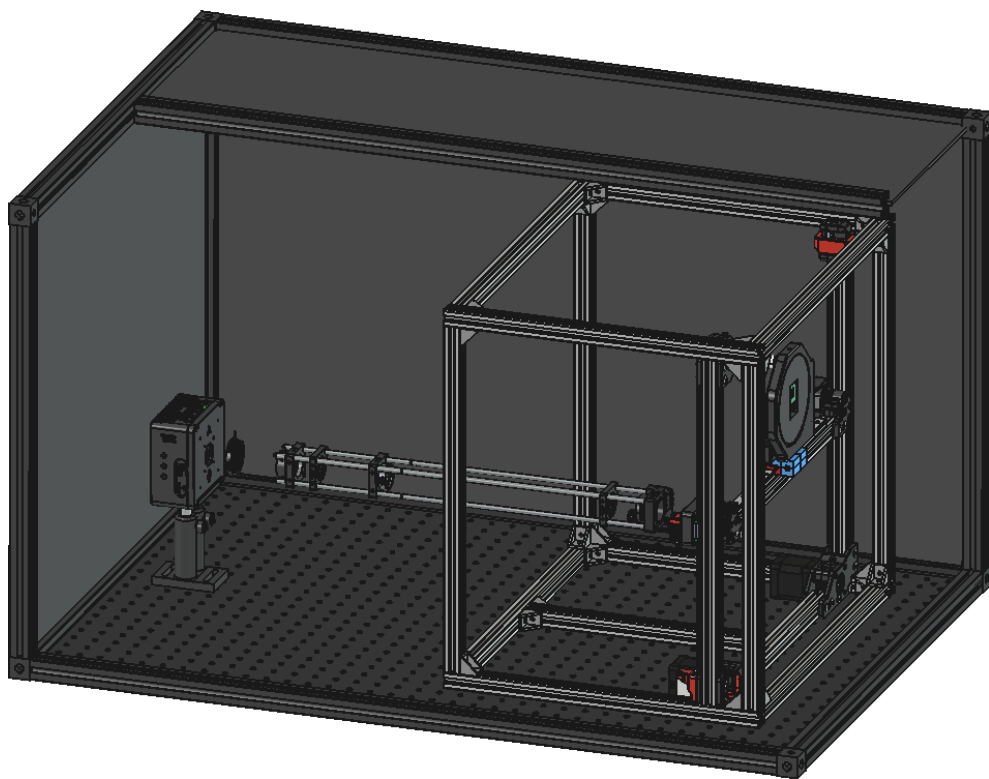


Figure 4.3: Simplified computer-aided design (CAD) render of a custom, home-built, laser-beam-induced current device.

lab-bench power supply, set to provide 12V, through the drivers and CNC shield. Nominally, each motor step corresponds to 200 μm , a distance determined by the 6 mm wide GT2 timing belts with 2 mm pitch teeth and the 20-tooth pulley, also purchased from 123-3D. By utilising 1/8th microstepping, a common method of sub-division of stepper motor increments, the step size can be reduced to a nominal 25 μm /microstep. The motors and belts are arranged in the modern coreXY kinematic configuration, minimizing vibrations by keeping both motors stationary, as opposed to the more common cartesian configuration which requires one motor to move with the sample stage [42].

The sample holding stage consists of a Thorlabs KS4 precision kinematic mount, coupled to the motors through CNC machined clamps holding onto the belts and guided by linear rails. Solar cells are sandwiched by two PCB electrodes and 3D-printed spacers, screwed into a fitting holder and held in the kinematic mount by a setscrew.

The mechanical stage was attached to a 90 cm by 60 cm Thorlabs breadboard using 3D-printed fixtures in such a way that the x-axis is horizontal and y-axis is vertical. Single pole, double throw microswitches (D2F-01L3, Omron) were used as limit switches at either end of both axes to ensure that the sample stage cannot move out of bounds and damage the frame.

An enclosure built from black Thorlabs aluminium rails, Thorlabs black hardboard and connecting hardware shields the samples from ambient lighting. Easy access to the device internals is ensured by the inclusion of two doors in the enclosure.

4.3.2 Optics

The optics of the device consist mainly of components purchased from Thorlabs (Germany) with a L405P20 405 nm TO-can laser diode powered and temperature controlled by a LDM56(M) mount. This mount is powered, monitored, and controlled by power (LDC205C) and temperature (TED200C) controllers. The optical output from the diode is immediately collimated using a 9.6 mm focal length aspheric lens (C060TMD). Collimation within the device bounds was verified using a Spiricon SP620U beam

profiler, ensuring equal beam diameters near the laser output and near the measurement plane. The initially elliptical profile of the beam is immediately passed through an iris to shape the profile into an approximately Gaussian shape. A Keplerian beam expander, consisting of two plano-convex lenses of 25.4 mm (LA1951-A-ML), and 74.8 mm (LA1608-A-ML) focal lengths 100.2 mm apart, is placed behind the iris to magnify the beam to three times its size to improve divergence properties [43, 44]. A final LA1951-A-ML lens, focusing the enlarged beam into the measurement plane, is held by a SM1ZA Z-Axis Translation Mount enabling fine control. Alignment between the focusing lens and beam expander is ensured by cage mounting both elements together. By temporarily replacing the KS4 mount with the beam profiler the size of the beam could be minimized by adjusting the Z-Axis Translation Mount. All elements are rigidly secured to the optical breadboard by appropriate posts, post mounts and hardware.

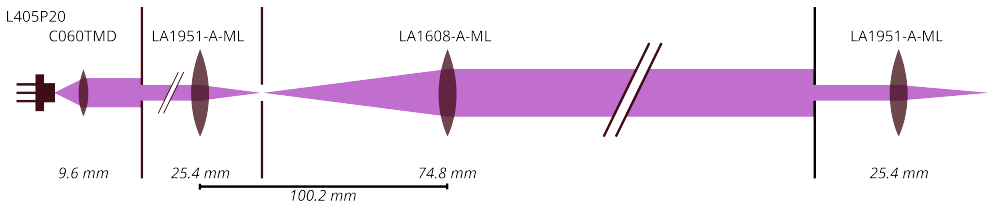


Figure 4.4: Diagram showing the optical components and beam path.

4.3.3 Device control and data acquisition

Device control is achieved using a two-tier host-controller architecture with custom Arduino firmware providing low level motor control and a custom LabVIEW-based user interface handling experiment sequencing. This LabVIEW virtual instrument (VI) is responsible for communication with the Arduino motor controller and the source-meter. The stepping sequence is a bare-bones single step routine without software defined acceleration curves. Scanning is performed in horizontal lines from top to bottom, starting at the top right of the sample and ending at the bottom left. The scanning direction is identical for every line to avoid artifacts from direction changes. Each line consists of a series of discrete steps, whose size is a user-definable multiple of the nominal 25 μm , with a current measurement taken before each step. Typical measurements are currently limited by

the source-meter measurement speed, area of interest and pixel size. A manual waiting time per pixel can be specified if needed but is usually undesired for high-resolution scans. These measurements are saved in a JavaScript Object Notation (JSON) format after each line to ensure device or power failures do not cause significant loss of data. Current measurements are performed using a Keithley 2450 source-measure unit and the provided proprietary LabVIEW drivers. Before any experiment the Keithley 2450 is automatically initialised. During measurement a sequence of commands is sent to read the photocurrent for each pixel. No independent control of the laser diode is possible with this setup, meaning the laser is continuously shining onto the samples.

4.4 Validation of Device Operation

Both the mechanical and optical stage have a significant impact on the resolution that can be achieved when scanning samples. As such, determining the resolution requires a two-tiered approach. First, the mechanical motion and beam characteristics are examined in isolation using a 543-575 Mitutoyo Metric plunge/dial indicator (purchased from RS Components, Brussels) and Spiricon SP620U Beam Profiler. Then, the combination of these can be characterised using a negative version of the well-known 1951 USAF resolution target (purchased from Thorlabs, Germany). Finally, DSSC samples will be imaged under short-circuit conditions to show the effectiveness of the technique in patterned solar cells. These measurements will compare photovoltaic photograph with stained DSSC covered by the masks used in the light-induced patterning step.

4.4.1 Mechanical characterisation

The accuracy, precision, and repeatability of the mechanical motion were all analysed by recording the relative position of the sample holding stage. Motion was verified when travelling over a distance of 6 mm, both in individual steps (nominally 25 μm in size) and in 'continuous' sequences. Figure 4.5 shows that the average step has a size of 25(3) μm , deviating from

this expected size only within the accuracy of the Mitutuyo indicator. However, a small systematic error is also clear from these results over the course of the 6 mm travel distance, first ahead of the motion by approximately one full step but then slowly drifting to lag about two steps behind the expected position. It can therefore be concluded that, over the tested range, the relative error on the position is below 2 %.

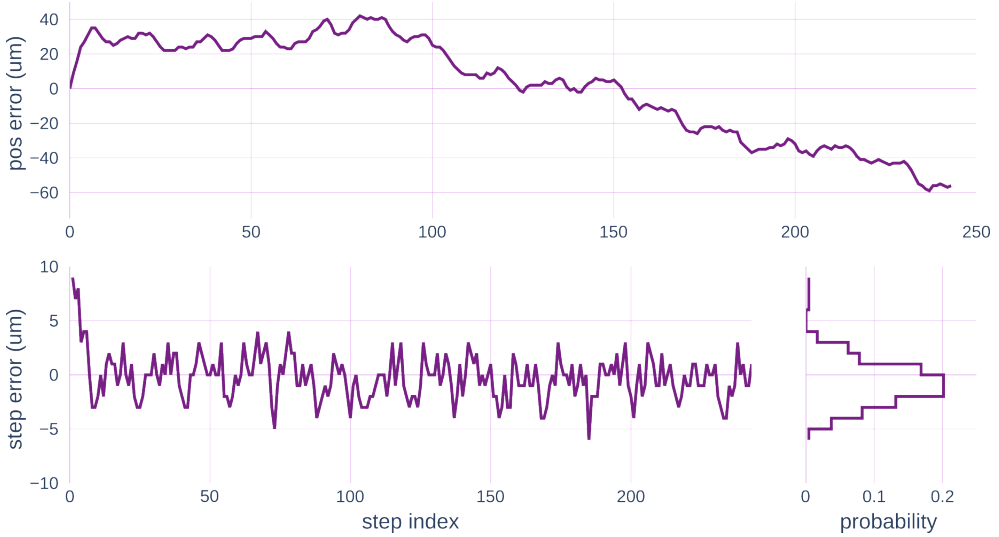


Figure 4.5: Position (top) and step (bottom, right) error as measured by a 3 μm accuracy plunge indicator. The bottom left panel shows the distributions of the step errors lie within the plunge indicator accuracy.

Finally, a periodicity in the positional error can be identified in fig. 4.6. This periodicity leads to peaks at spatial frequencies of $2.5(2) \text{ mm}^{-1}$ and $5.0(2) \text{ mm}^{-1}$ on both axes and additional harmonics at $10.0(2) \text{ mm}^{-1}$ and $15.0(2) \text{ mm}^{-1}$ for the horizontal axis. The second peak, at $5.0(2) \text{ mm}^{-1}$, as well as its harmonics are directly attributable to the 200 μm period. This period is determined by the 2 mm belt pitch, 20 tooth pulley and 200 revolutions/step of the NEMA 17 motors and clearly translate directly in a strong periodicity in the mechanical stage showing up every 8 microsteps. The half-frequency subharmonic is also very likely tied to these mechanics in an alternating fashion, repeating every 16 microsteps.

These results are consistent for both axes in both travel directions, with the notable exception that the harmonics seem to be suppressed on return

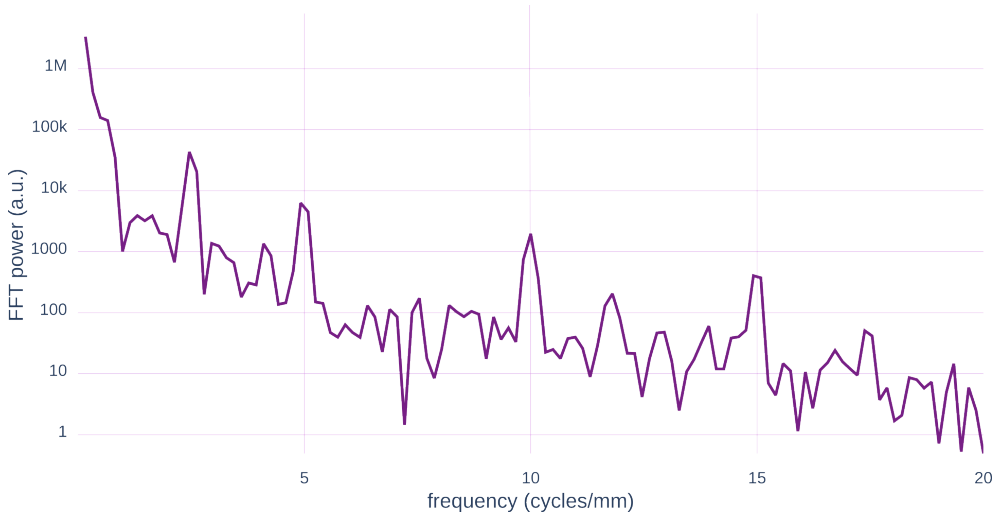


Figure 4.6: Position error periodicity obtained by plotting the position error graph in its Fourier domain on a logarithmic scale.

trips. Interestingly, the return travel on the horizontal axis took 20 additional steps due to an initially lower average step size. The origin of this error is unknown and was not reproduced by the subsequent ‘continuous’ sequence measurements.

4.4.2 Beam geometry at the measurement plane

The profile of the probe beam is shown in fig. 4.7, with some key metrics listed in table 4.1. The colour axis is shown on a logarithmic scale to emphasize the wings of the beam with respect to the dominating central peak. The beam diameter was measured to be $30.0(44) \mu\text{m}$, according to all metrics, with a slight ellipticity in favour of the horizontal scanning direction. These results are similar to the step size obtained for the mechanical motion and were deemed sufficient to move to the next test.

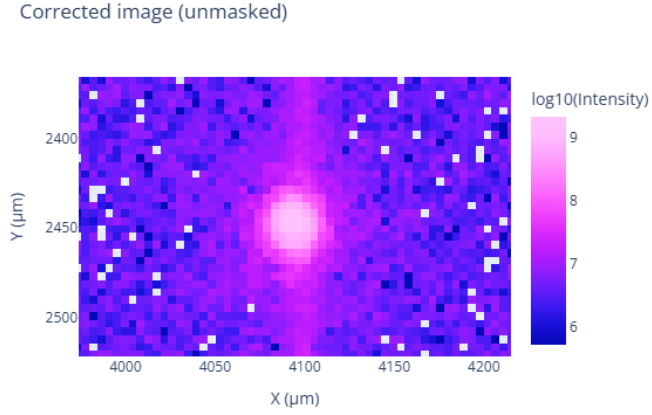


Figure 4.7: Image of the focused probe beam taken using the Ophir Spiricon SP620U beam profiler. The figure shows a cropped area of the complete sensor image. The colour axis is shown on a logarithmic scale as the beam drops off sharply outside the centroid.

Table 4.1: Beam profile parameters extracted from fig. 4.7. All beam width measures give a width of less than $30\text{ }\mu\text{m}$.

Parameter	x	y	Units
Peak location	930	556	pixel
Peak value	2×10^9		counts
$D4\sigma$	25.4	30.2	μm
FWHM	15.0	15.8	μm
$1/e^2$	27.4	29.9	μm

4.4.3 Effective resolving power

A test image was produced to verify the overall machine properties, using a USAF resolution mask as target and a DSSC photodetector. After ensuring that a photocurrent could reliably be obtained in this configuration, the resolution target was placed in the sample holding stage and scanned over an area of $20\text{ mm} \times 20\text{ mm}$ in $25(3)\mu\text{m}$ steps. Figure 4.8 shows that the smallest resolvable groups and element combinations are indexed 3-6 for the horizontal scanning direction and 3-5 in the vertical direction. This corresponds to box widths of $40\mu\text{m}$ and $35\mu\text{m}$ respectively and is slightly higher than the beam size.

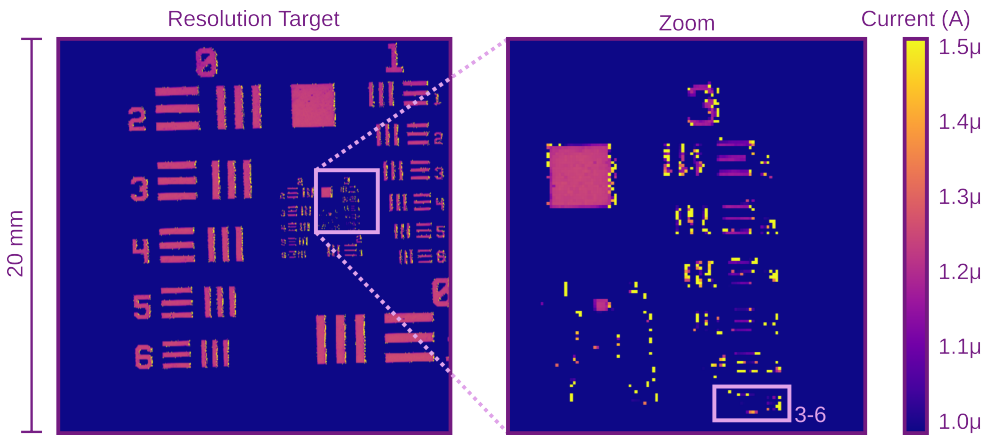


Figure 4.8: Scan of a USAF 1951 resolution target, measuring the photocurrent from a DSSC placed as beamstop/photodiode behind the target. The first non-resolvable group/element combinations are indexed 3-6 for the horizontal scanning direction and 3-5 in the vertical direction. This corresponds to box widths of $40\mu\text{m}$ and $35\mu\text{m}$ respectively.

As established, the current microstepping regime limits the machine to $25\mu\text{m}$ increments. This leads to a Nyquist cutoff at 20 periods/mm under theoretically perfect conditions. However, this optimal frequency consists of only two measurements per period which is very sensitive to the initial alignment (phase). Even under those ideal conditions element 4-3 would be the first to become ineligible. In all subsequent measurements the pixel size will consequently be kept at $25\mu\text{m}$ to not limit the resolution further by reducing this optimum.

4.5 DSSC and Photovoltaic Photographs

In the second part of this work we focus on DSSC and PV photograph, first detailing the materials used to prepare these. Then, DSSC samples will be imaged under short-circuit conditions to show additional features of the technique in controlled conditions. Finally, measurements of example PV photograph are shown and discussed, comparing photovoltaic photograph with stained DSSC covered by the masks used in the light-induced patterning step.

4.5.1 Materials and sample preparation

Ruthenizer 535-bisTBA synthetic dye powder (product code: 21613), known in the literature as N719, was purchased from Solaronix (Switzerland). TechniSolv® ethanol euro denatured (96%, CE Emb 28007A), purchased from VWR International, was used as solvent in dye-solutions. Pre-sintered test cell titania anodes and platinum covered cathodes (product codes 74101 and 74201) were purchased from Solaronix (Switzerland) as well. The electrodes consist of a glass substrate (20 mm × 20 mm) coated with fluorine-doped tin oxide (FTO). Anodes have two additional Ti-Nanoxide layers (6 mm × 6 mm), one consisting of 15 nm-20 nm anatase TiO₂ nanoparticles, while the second is composed of larger (>100 nm) diffusing TiO₂ nanoparticles. The cathodes are additionally coated with Pt, used as catalyst. A heat-meltable plastic gasket is used to join both electrodes while leaving space for the Mosalyte TDE-S125 liquid electrolyte (also purchased from Solaronix). Finally, the cells are sealed using a two-part epoxy and glass cover.

The preparation protocol follows to the one used in [22, 29]. A dye solution was prepared by weighing dye powder and diluting with ethanol to obtain a concentration of 0.3 mmol L⁻¹. This was stirred for 8 hours in the dark before submerging refired anodes in the solutions overnight. Refiring was done at 450 °C for 30 minutes after which the anodes were left to naturally cool. They were placed in dye-solutions after reaching 60 °C. The anodes were kept face-down by a polyamide (PA) holder to protect the TiO₂ surface from potential precipitation. These holders were 3D printed from neutral

BASF Ultrafuse PA filament using a Prusa MK4 machine. The next day they were rinsed with ethanol and dried using a nitrogen gun before either being stored in the dark (*stained controls, St.*) or placed in front of a Xenon short arc lamp (Thermo Oriel Instruments, model 66902, USA), powered by a 150 W power supply (Oriel Instruments, model 6890, USA). Two masks were used, one consisting of a metal plate covering approximately half of the photoactive area (*half-half, HH.*), another consisting of a cartoon image printed on a transparency (*patterned, PB.*). After an exposure of 22 hours all cells (stained, half-half, and patterned) were completed by placing a gasket around the TiO_2 and heat pressing a counter-electrode on top. The cells were then filled with electrolyte and the counterelectrode sealed with a two-part epoxy and glass cap. Silver electrodes were painted to lower contact resistance with the measurement holders.

4.5.2 Uniformly stained dye-sensitized solar cells

Figure 4.9 shows typical LBIC images performed on uniformly stained reference DSSCs, immediately showing important features.

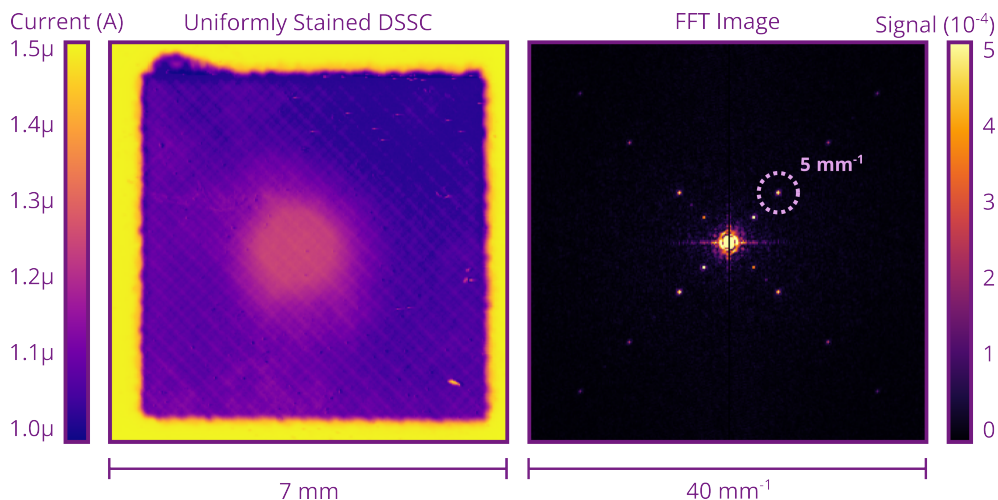


Figure 4.9: Left: Photocurrent scan of a $6\text{ mm} \times 6\text{ mm}$ N719 DSSC. Right: Fourier transform image

First, the photoactive area can clearly be distinguished from the surrounding area. Second, the produced photocurrent is non-uniform, despite the assumed uniformity of the dye-loading. This made evident by three distinct features:

1. A 'bright' low current region behind the pre-drilled hole in the cathode
2. A slight gradient from the bottom left to the top right
3. A relatively sharp diagonal lattice

The first feature overlaps with a visually distinct region in the solar cell, opposite the pre-drilled hole used to fill the cell with electrolyte. The exact origin of this discolouration is unclear but is likely a complex combination of various effects, including the manufacture of the cell. For example, studies have indicated that the TiO_2 -layer can act as a molecular filter, affecting all PV-parameters, including a reduction of the short-circuit current near the filling hole [45, 46]. The second is most likely a small tilt of the sample combining with a non-linear response to illumination of the sample.

To elucidate the third artifact some additional analysis is required. Examining the image in its Fourier domain reveals very sharp and symmetric peaks on the diagonals at $5.0(2) \text{ mm}^{-1}$ as well as harmonics at $10.0(2) \text{ mm}^{-1}$ and $15.0(2) \text{ mm}^{-1}$ and a subharmonic at $2.5(2) \text{ mm}^{-1}$. The measured frequencies are identical to the periodicity described in section 4.4.1. The diagonal orientation of these peaks is consistent with the core XY kinematics, as this configuration strongly couples the two motors in a 1:1 ratio. These peaks in frequency-space were identical across all measurements, regardless of sample and sample orientation. It must therefore be concluded that the lattice is not a feature of the samples but a machine dependent artifact.

4.5.3 Photovoltaic photographs

Four cells were prepared according to section 4.5.1, two DSSC were kept as controls and are labelled *stained*, one PV photograph was prepared with a metal mask and labelled *half-half*, and the last sample was prepared as

PV photograph of cartoon object containing a few discrete transparency values, and labelled *patterned*. After finishing the preparation of these solar cells they were photographed, these are shown in the first row of fig. 4.10.

Each cell was imaged using our custom-built LBIC device, using a laser power of $250\text{ }\mu\text{W}$ and $25(3)\text{ }\mu\text{m}$ step size over an area of $7\text{ mm} \times 7\text{ mm}$, leading to images 280×280 pixels. This resulted in images with currents ranging from $-11\text{ }\mu\text{A}$ to $0\text{ }\mu\text{A}$, shown using the same blue to yellow scale for all measurements. The bottom row in fig. 4.10 shows these results. From this figure we can see that the colour change observed when preparing the samples correlates to a local drop in short-circuit current production. Importantly, a general decrease in current production, clear from “brighter” values, can be concluded by comparing the LBIC images of the PV photograph and the stained sampled, consistent with the global reduced efficiency observed by Hustings et al..

Furthermore, while the half-half sample shows that the exposed half of the cell produces less photocurrent than the covered half, it is still above the background current by an order of magnitude. The stage of degradation reached by the dye in that region is therefore shown to remain photoactive, confirming that all parts of the cell still contribute to the overall photocurrent.

Areas of reduced photocurrent production correlate directly with the degree of discolouration, reproducing with striking similarity, the image from the mask. From this it can be deduced that the chemical changes, described by Robert et al. [29], not only affect the optical properties of the dye but also the photo-electrical conversion efficiency of the device at the local level.

A second test was performed to compare the local photocurrent production of aesthetically similar devices. This was scanning the two regularly stained DSSC again, this time covered by a mask to emulate an additional sticker layer. This allows a direct comparison with the recently proposed PV photograph. The half-half pattern was replicated using black tape, while the exact patterned mask used to prepare the *patterned* PV photograph was used in the last measurement. LBIC scans using each of these masks are shown in fig. 4.11.

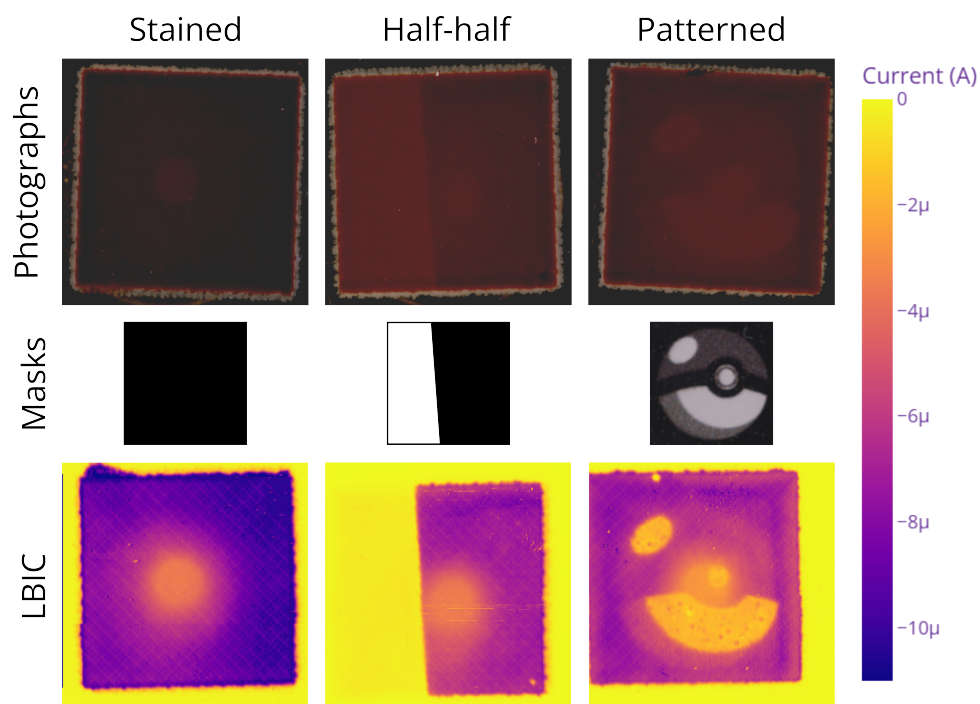


Figure 4.10: Photographs (top) and LBIC images (bottom) of DSSC and PV photograph samples made using three different masks (middle). All LBIC colour axes are identical, ranging from no ($0 \mu\text{A}$) to high ($-11 \mu\text{A}$) currents.

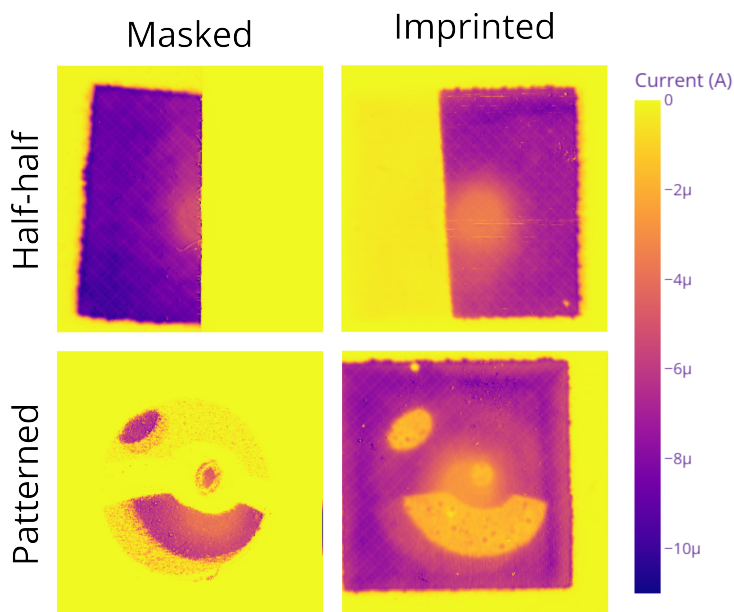


Figure 4.11: LBIC measurements of masked DSSC (left) and PV photograph (right) for a binary (top) and patterned (bottom) mask.

The results from the half-half masked sampled are qualitatively similar to the corresponding PV photograph. However, while the background currents are similar, the high current area (darker colours in the image) was measured to be significantly higher in the masked DSSC compared to the PV photograph. Consequently, in this particular case an additional mask is preferable to light-induced patterning. This is likely to be the case for most masks which are sufficiently transparent, and thus lead to large areas with degraded dye.

The most interesting results come from looking at the samples prepared/measured using the patterned mask. In the imprinted cell, the photocurrent is still around $-2\mu\text{A}$, which is $40\times$ higher than the background produced from the measured background current. Additionally, while the imperfect opacity of the mask in its darkest areas still lead to some discolouration, the currents are only affected by at most a factor of two. Finally, comparing this PV photograph to the masked DSSC measurement shows the most striking result so far. For these cells, using the mask as additional layer leads to negligible current production. The opaque areas

of the mask were sufficient to completely block the incoming light and are now indistinguishable from the surrounding background. While the pattern is still recognisable, it is clear that the overall current production at each pixel is dramatically affected by the presence of the mask. From these local photocurrent measurements, we can conclude that these masks are inadequate for direct deployment as added layers, while PV photograph prepared with them still perform appreciably.

4.6 Conclusions

We have shown that it is straightforward to build a moderate setup using components that most photovoltaic research laboratories are already likely to possess. Such a device can achieve resolutions below $50\text{ }\mu\text{m}$ per pixel, with relative errors below 2% over travel ranges of 6 mm. Our device can trivially measure locally produced currents from photoactive materials down to dark currents. Tests show easily recognised systematic artifacts in measured images consistent in frequency and placement with the chosen characteristics of the device, not significantly affecting the benefits from performing this type of measurement. The resolution could be pushed further by selecting a higher microstepping ratio as the chosen drivers can go down to 1/32nd microstepping. The alignment of the optical beam should then be tuned to drop the beam diameter by at least the same factor of four compared to its current configuration.

While the newly proposed PV photographs were shown to be a promising addition to the arsenal of aesthetically focused energy production devices, their viability as an application must be examined from multiple angles. It was already clear from the initial publication of Hustings et al. that preparing PV photograph requires an initial sacrifice in the overall device efficiency. Our group additionally showed that the N719 dye degrades chemically, in a complex fashion, under the preparation conditions. It remained to be explored explicitly whether this chemical degradation can directly explain the drop in efficiency by studying the local photoelectrical conversion properties of the cell. LBIC was chosen as a technique of choice as it is capable of directly probing the energy production of a complete device by illuminating the cell locally.

This device was used to examine the difference between PV photograph and masked DSSC, showing that the slow kinetics of DSSC do not preclude the use of this particular scanning technique. Furthermore, remaining dye colour does not guarantee a significant photocurrent in patterned areas. It is therefore crucial to verify the properties of neat and light-exposed dye in completed devices before attempting further tests. From these measurements we additionally conclude that an optimum in mask design, regarding its opacity, is possible. This lends more credibility to the ability of this application to find a niche where it can contribute meaningfully to our battle against the climate crisis. In a more general context, this work shows that LBIC is a powerful technique for obtaining a 2D spatial photocurrent map in patterned solar cells and can contribute to the diverse R&D approaches to develop solar cells with enhanced aesthetic properties, opening novel avenues for creative PV applications.

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Chapter 5

**Combining digital
photography,
photocurrent mapping
and in-situ
IV-measurements to
study patterned solar cell
stability.**



Combining digital photography, photocurrent mapping and in-situ IV-measurements to study patterned solar cell stability.

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MANUSCRIPT IN PREPARATION

Data Availability

All raw data and source code will be made available upon submission of this manuscript. The manuscript will be made available as a pre-print before submission [1, 2].

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5.1 Abstract

To increase photovoltaic (PV) adoption, new properties beyond efficiency are regularly being proposed and demonstrated, such as semi-transparency and colour. However, many of these new applications rely on PV technologies that have yet to reach commercial maturity. A common issue for all new generation PV involves their long term stability, which is often studied independently. In this article we propose methodology to study the stability of patterned solar cells. Specifically, the long term behaviour of so-called photovoltaic photographs (PV photographs), solar cell (SC) with an image imprinted in the photoactive layer, is compared against regularly stained dye-sensitized solar cell (DSSC), on which they are based. Here we introduce, next to the well-known in-situ current-voltage (IV) characterisation, spatially resolved scientific colourimetry using digital photography and local photocurrent mapping through laser-beam-induced current (LBIC) measurements. By combining these methods, optical and electrical properties can be correlated locally, leading to more precise understanding of long-term device operation. A better understanding of the specific application is therefore enabled, potentially enabling new insights in the underlying PV technology as an added benefit.

5.2 Introduction

The global challenges imposed by a growing energy demand and the climate crisis keep emphasising the need for a transition to clean and renewable sources of energy. Over the past half century silicon PV panels have become a common sight in cities across the world owing to their excellent commercial stability and performance. Efficiency, however, is no longer the only metric of interest as additional considerations such as material cost and availability [3], ease of manufacturing [4] and integration into buildings [5] are becoming more and more relevant. As such, researchers have kept searching for novel technologies capable of harnessing the large amount of energy received by our planet every hour. This search has led to device architectures that have the possibility to be tailored to include freedom of design and aesthetics. For example, solar cells have been in-

vented which can be made flexible [6], semi-transparent [7], colourful [8] and even visually patterned [9].

Discussing such advantages requires careful consideration of the methods used to quantify these, sometimes subjective, properties. For example, the transmission properties of semi-transparent panels [10], the mechanical properties of flexible PV [11], or even the overall optical properties of coloured solar cells [12]. Researchers quantify and study these aspects by relying on known methods and on standards utilised in other industries. For example, digital photography for scientific colourimetry is often applied to describe the colours of solar cells, using metrics defined by the International Commission on Illumination (CIE) [13]. Digital photography is particularly powerful for studying patterned solar cells as it is a widely available, easy to use, and a relatively low cost imaging method with the potential for high spatial resolution.

The types of PV technologies enabling aesthetic applications vary wildly, from thin-film solar cells [14], to photosynthesis inspired DSSC [15], or the newly discovered perovskite solar cell (PSC) [12]. For the latter two, it still remains crucial to show that energy can be harvested reliably for a significant period of time. Accelerated ageing tests are the weapon of choice to study this particular research question. While standards exist to perform such tests with Si-based PV, such as the IEC61215 specification [16] or the ISOS-3 consensus for organic photovoltaic (OPV), newer generations PV are more challenging owing to their complexity. For example, the degradation of DSSC and PSC in particular, can be attributed simultaneously to multiple pathways. Both intrinsic effects relating to device properties as well as extrinsic factors, such as preventing water and oxygen ingress, are known to affect DSSC stability. These thus need to be disentangled and understood [17]. While a consensus has been reported for PSC [18], incorporating methodology well suited for the underlying physics and chemistry of these cells, no such consensus could be found for DSSC.

Additionally, the aesthetic properties often highlighted are rarely explicitly discussed or included in aging tests. Many studies are limited to demonstrations of proof-of-principle devices or to outstanding new properties [11, 19, 20, 21, 22]. Including this added dimension in aging studies, with

carefully considered metrics, has a dual advantage. First, it discusses advantageous properties (e.g. flexibility or colour) explicitly while yielding additional information that can be used in correlation to standard physical and chemical analyses. Quantification methods which are non-destructive can be added to ageing studies by performing comparative tests before and after exposing samples to aging conditions.

In this article we wish to illustrate this power by proposing a methodology for patterned PV devices. This is achieved by combining in-situ ageing tests with ex-situ colour photography and 2D photocurrent mapping. Specifically, we focus on the newly proposed PV photographs, as a demonstration. In these, a light-induced patterning step, similar to a photolithographic process, is used to imprint an image into the active layer of a DSSC through local discolouration [19].

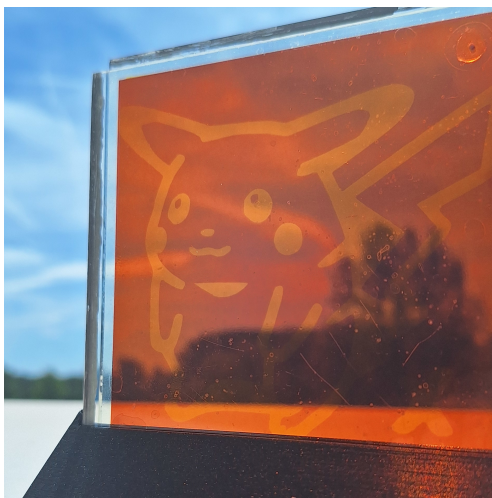


Figure 5.1: Example of a 10 cm, semi-transparent, N719 PV photograph containing the image of a popular Japanese cartoon character.

In the following sections we illustrate a suggested protocol to test the stability of reference and patterned solar cells when exposed to light for an extended period. We show this by describing how we prepared example PV photographs and leveraged spatially resolved scientific colourimetry using a digital camera in addition to the typical hourly in-situ current-voltage characterization. This combination allows the changes induced in the aesthetic and physical properties of our samples to be compared. We fur-

ther connect these two aspects by correlating colour changes with local photoelectrical properties through the use of laser-beam-induced current (LBIC) mapping. The methodology described here for the case-study of PV photographs is transferrable to any other type of patterned solar cell, highlighting its general applicability in the field.

5.3 Materials and Experimental Methods

The stability experiments in this work were performed on so-called PV photographs, described in more detail in the next section. A total of 36 solar cells were prepared in two batches as described in section 5.3.1 from the measurement matrix shown in fig. 5.2. All cells were imaged using a photography cabinet described in section 5.3.3, before being mounted on a temperature-controlled stage held at 25 °C for a light-soaking aging test. Cells were operated under load, illuminated with 1 Sun AM1.5G, and their PV properties were regularly measured as described in section 5.3.2. All samples were imaged again after the aging test to determine any potential changes in colour and contrast. The local photoelectric properties of a subset of samples was mapped using a custom in-house built LBIC, described in section 5.3.4 before and after light-soaking.



Figure 5.2: Schematic representation of the types of photo-anodes prepared for this work. From left to right: unstained control cells (C.), half-half PV photographs (HH.), and stained references (St.). The top row (in red) represents transparent SC, while the bottom row (in purple) represents opaque samples.

5.3.1 Photovoltaic photograph preparation

The PV photographs investigated in this work are based on the DSSC architecture. All DSSC in this work were prepared according to previously published protocols [19, 23], using TechniSolv® ethanol euro denatured (96%, CE Emb 28007A), purchased from VWR International, as solvent. Opaque and transparent test-cell kits, containing prepared photo-anodes, cathodes, and sealing materials, were purchased from Solaronix (Switzerland) as well.

A dye solution was prepared by weighing dye powder and diluting with ethanol to obtain a concentration of 0.3 mmol L^{-1} , and stirring overnight in the dark. Samples were split roughly evenly in two batches, separated by a day and prepared as follows. Anodes were refired at 450°C for 30 minutes to reactivate the TiO_2 before being submerged in the dye solution overnight. They were placed face-down in holders and submerged overnight in dye-solutions after naturally reaching 60°C . After rinsing with ethanol and drying using a nitrogen gun they were either stored in the dark (*stained references, St.*) or placed in front of a Xenon short arc lamp (Thermo Oriel Instruments, model 66902, USA), powered by a 150 W power supply (Oriel Instruments, model 6890, USA). *Unstained controls (C.)* were treated identically to these stained samples but were submerged in pure ethanol rather than in a dye solution.

The masks used for the photo-induced patterning step consisted of a metal plate covering approximately half of the photoactive area (*half-half, HH.*) After exposing PV photograph anodes for 17 hours, all cells were completed by placing a meltable gasket around the TiO_2 and heat pressing a counter-electrode on top. The cells were then filled with electrolyte and the counterelectrode was sealed with a two-part epoxy and glass cap. Silver electrodes were painted to lower contact resistance with the measurement holders. The complete set of prepared samples is schematically summarized in fig. 5.2.

5.3.2 Light-soaking aging test and photovoltaic characterisation

Light soaking, i.e. long-term light exposure of solar cells, was done using a class AAA+ large area light-emitting diode (LED) Solar Simulator (Sunbrick Base-UV model, purchased in 2020) from G2V Optics (Canada). The simulator spans a spectral range from 350 nm to 1100 nm, with a spectral mismatch and spatial non-uniformity reported by the manufacturer below 5 % and 2 %, respectively. The temperature of one of the cells was monitored using a Pt100 platinum resistance thermometer and held at 25 °C by thermal coupling to the cooling plate [24]. The cells were connected to a constant resistive load, selected to operate each cell near its maximum power point, while being illuminated under 1 Sun AM1.5G illumination, for a duration of over 1000 h. The value of this resistance is chosen by finding a local maximum in the cell's initial power-voltage curve and determining the ratio of the voltage and current at that point.

PV characterisation was achieved through in-situ IV measurements at regular intervals by electronically switching cells individually from their load to a Keithley 2450 source measure unit (SMU) and back. Current was measured while the voltage varied in 20 mV steps from -0.1 V to 0.8 V and back to -0.1 , with a 0.5 s delay between each step/measurement. Each IV-curve was saved to a dedicated file for analysis. The complete setup ran automatically through a custom LabVIEW virtual instrument (VI), controlling measurement as well as switching using an Arduino® Mega 2560 Rev 3 and electromechanical relays.

5.3.3 Spatially resolved colourimetric measurements

In order to study spatially resolved colour changes in PV samples, images were taken in a controlled environment, ensuring interpretability of the measurements. A custom-built imaging cabinet was constructed, carefully controlling the lighting conditions between measurement sessions. Images were taken with a digital camera, and were then processed and colour corrected before being prepared for numerical analysis. The details for each of these three steps are described in this section.

Imaging setup

In order to capture colour from images of our samples in a reproducible manner, we built an imaging cabinet with controlled and repeatable illumination, identical environment and adjustable camera position. The setup is shown schematically in fig. 5.3.

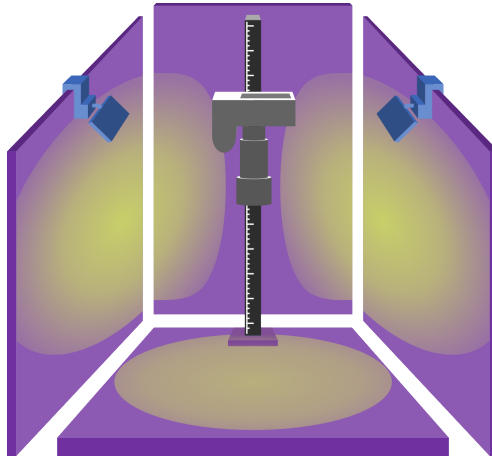


Figure 5.3: Schematic representation of the imaging cabinet showing the digitization stand, camera, walls and lamps.

We used a Nikon z 7 II camera with Laowa 100 mm, f2.8, CA-Dreamer 2x macro lens attached to a height adjustable digitization stand. The height of the lens above the samples was set to 30 cm resulting in a resolution of $4\mu\text{m}/\text{pixel}$. The samples were illuminated by two rigidly mounted Bresser LED lamps, pointed towards cloth covered walls, whose intensity and angle was adjusted to provide even and diffuse lighting from both sides. Critically, the conditions were kept identical for both imaging sessions. Each measurement session started by imaging the same gray card and American National Standards Institute (ANSI) IT8.7/2 colour target for colour correction purposes. This colour target, including calibrated colour coordinates for each patch, was obtained from Faust [25], allowing a custom colour profile to be prepared using software developed and provided open-source by Aalto University [26, 27]. The camera lens is adjusted once before imaging all solar cells such that the active area is in the focal plane of the system. The gray card is then imaged again before imaging all solar cells sequentially in the center of the camera's field of view. White printer

paper was used as a matte background for transparent samples, reflecting light from the back similarly to opaque samples where this is intrinsically achieved by the reflecting TiO_2 layer.

Image processing and correction

All images were captured in Nikon's proprietary RAW format and processed identically using the open source RawTherapee photo processing package [28]. Remaining non-uniformities in lighting conditions, not eliminated by the aforementioned adjustments of the lamp position and angle, as well as by the optical properties of the lens, were corrected by using the grey card as a flat-field reference. This divides image pixel values by the corresponding region in the gray card image, essentially normalising them. A processing profile was prepared and applied to all images, differing only in the image chosen for flat-field correction, reflecting the two separate imaging sessions. In this profile, white balance was manually set to 5600 K to match the lamp settings, the flat-field radius was set to 8 pixels to reduce the impact of noise while retaining some smoothing, the output colour domain was set to the ProPhoto industry standard with absolute colourimetric rendering intent. Each image was finally manually straightened and cropped to an area of 575 px by 575 px, encompassing the cells' photoactive layer, to isolate the coloured area from its surroundings. After exporting these images to an uncompressed 16 bit TIFF format they are colour corrected with a look-up table (LUT) prepared using the aforementioned colour target and custom software available on GitHub [26].

Data extraction and analysis

After processing the images additional steps are necessary to meaningfully describe and quantify the colour information in the samples. Given the patterned nature of HH. PV photographs samples, their measurements were separated into distinct sub-images with the use of digital masks representing those used in the light-induced patterning step. Consequently, this procedure produced a collection of (sub)images ready for numerical analysis, demonstrating the spatially resolved nature of the measurement. In this

article the PV photographs consist of two simple regions: illuminated and covered. This methodology can be extended to more complex images but might require adaptation for PV photographs containing smooth gradients as defining regions in these cases is more challenging.

Numerical analysis is performed in the CIELAB colour-space for interpretability as the colour-space is widely used in industrial and photographic applications. This colour space is device independent and approximately perceptually uniform to a standard observer under standard illumination conditions [29]. The three axes in this space correspond to lightness (L^*) and two opponent colour axes, green-red (a^*) and blue-yellow (b^*). Initial visualisation of the samples is performed by projecting all coordinates in the a^*b^* -subspace by discarding the L^* value. There, average and spread in colours within a (sub) image was represented by computing the mean and the average Euclidian distance from this mean. Each image is represented by a disc on a colour diagram whose radius represents the spread of colours. A perfectly uniform sample would be a point at the image colour on such a diagram.

While this projection is informative, proper quantitative analysis requires all three channels. Consequently, we analyse these coordinates in two complimentary ways. First, colours are examined through an aggregate histogram produced from all the images in the group. These are used to compute before and after difference in each L^*, a^*, b^* channel and plotted for analysis. Second, we determine the average colour of a group and compute the distances of all pixels to this average according to eq. (5.1) [30].

$$\Delta E_{00} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T \left(\frac{\Delta C'}{k_C S_C}\right) \left(\frac{\Delta H'}{k_H S_H}\right)} \quad (5.1)$$

Where $\Delta L'$, $\Delta H'$, and $\Delta C'$ are the differences in lightness, hue, and chroma, computed from the CIELAB coordinates as defined by [31]. Lightness corresponds to light intensity while hue and chroma are polar coordinates computed from a^* and b^* . The constants k_{α} , S_{α} , and the cross-term are included to ensure perceptual uniformity of the distance metric. The cross term in eq. (5.1) specifically reflects and includes perceptual coupling of

hue and chroma in human vision. A detailed description of this formula can be found in the original CIE publication and subsequent analysis thereof [32]. The average and standard deviation of these distances is then determined and plotted, allowing colour shifts to be determined.

5.3.4 Laser-beam induced current mapping

To spatially resolve the local photo-electrical properties of example photovoltaic photographs samples, connecting optical and IV-properties, an in-house custom LBIC-setup was used [33]. Briefly, the setup consists of a temperature and power controlled 405 nm laser diode set to 250 mW and 25 °C. The optical beam is collimated, passed through a Keplerian beam expander, before finally being focused onto the measurement plane. The beam width was measured at the measurement plane to be 30 μm , using a Spiricon SP620U beam profiler. The sample was mechanically stepped in the x and y directions using Arduino® controlled stepper motors in 25 μm steps, coupled in a core XY kinematic configuration [34]. Pixels are consequently 25 $\mu\text{m} \times 25 \mu\text{m}$. However, the combined optical resolving power of the setup, determined using a USAF 1951 resolution target, was 40 μm . A computer controlled Keithley 2450 SMU recorded the current produced by the cells in short-circuit condition for each pixel. The selected example cells were measured before and after submitting them to the aging test for comparison.

5.4 Results and Discussion

In this section we discuss how the traditional in-situ IV characterisation is complemented by using digital photography to determine colour and contrast within example PV photographs before and after a light-soaking aging test. Finally, LBIC mapping is applied to further connect and enrich these conclusions by visualising local photocurrent production.

5.4.1 In-situ IV characterisation shows photovoltaic photograph weaknesses compared to reference dye solar cells.

The in-situ IV measurements are shown in figs. 5.4 and 5.5. The group average values for each PV parameter is shown as a function of illumination time in both figures. Figure 5.4 showing the short-circuit current values for both batches while fig. 5.5 shows the relative change in all four parameters over time. Individual time series for all parameters of all cells can be found in the supplementary material.

The unstained controls (TrC and OpC) have very low initial short-circuit current density (2 nA cm^{-2}) and open-circuit voltages (40 mV). Both steadily increased by more than an order of magnitude over the total experiment time. Half of these samples reached a maximum before dropping sharply to zero, indicating failure.

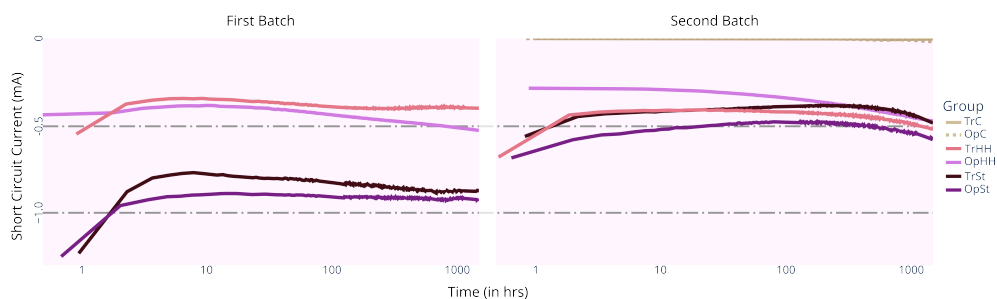


Figure 5.4: Short-circuit current (I_{sc} , in mA) for all cells prepared, averaged per group for each batch of samples (left: first batch; right: second batch).

The PV-parameters of the first batch (fig. 5.4, left) are well separated according to sample type: stained (St), PV photograph (HH), or unstained controls (C). Initially, the stained DSSCs (TrSt and OpSt) produce stronger (more negative) currents than PV photographs (TrHH and OpHH). Other PV-parameters are similarly well separated at the start of the light-soaking test. A lower I_{sc} for the PV photographs leading to correspondingly lower efficiencies is expected and is consistent with reports from Hustings et al. [19]. This separation between PV photographs and stained DSSC remains present for the entire duration of the experiment. Interestingly, the transparent and opaque samples seem to differ qualitatively.

No clear separation can be observed between stained DSSC and PV photographs for the second batch samples (fig. 5.4, right). Strictly from a current-voltage perspective, the groups cannot be distinguished in this batch. This mixing is maintained over the entire experiment duration with no additional separation occurring over time. From this qualitative difference, we conclude an unknown treatment difference between both batches. The following analysis will continue by considering the first batch only, as the PV-parameter results for these samples at the start of the experiment are consistent with previously reported IV-characteristics. Note that the unstained samples were only prepared in the second batch and must therefore still be included.

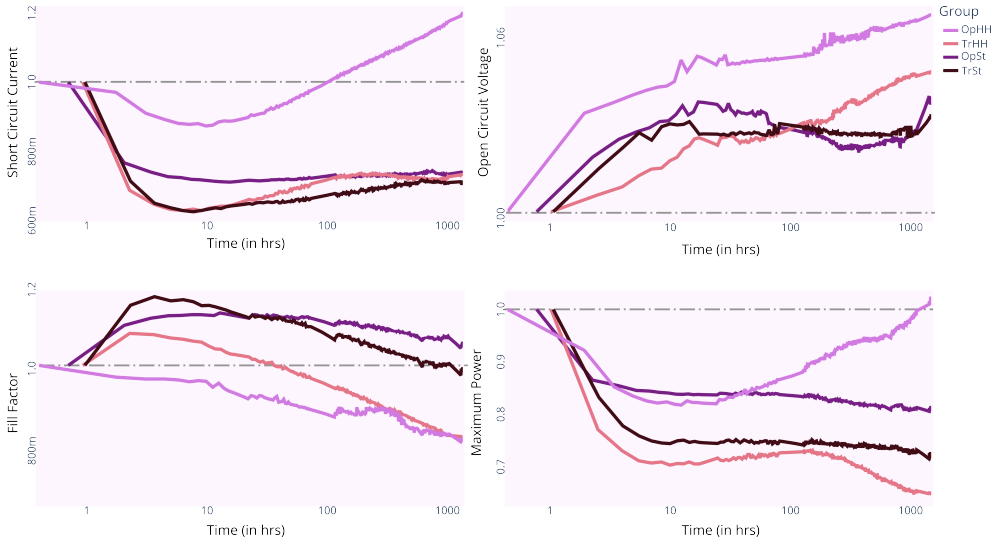


Figure 5.5: Ratio of all PV parameters (top left: $I_{sc}/I_{sc,0}$; top right: $V_{oc}/V_{oc,0}$; bottom left: FF/FF_0 ; bottom right: $P_{max}/P_{max,0}$) relative to their first measured value for cells prepared in the first batch, averaged per group, as function of illumination time.

Figure 5.5 shows the PV parameters for the first batch of samples. Parameter by parameter we observe a few features of interest. The short-circuit current of OpHH seems to diverge drastically in behaviour. All groups experience a fast drop within the first hours of illumination. TrSt samples appear to equilibrate past this point, steadily producing 70% of their initial current production for the complete experiment duration. Both TrHH and OpSt recover slightly from a minimal current production but still re-

maintaining at the same 70% production threshold. However, OpHH samples reach a surprisingly high minimal current, not dropping below about 85% and then steadily increasing over time.

All groups show a moderate increase of V_{oc} , notably, PV photographs keep steadily increases towards 105 percent of their starting value while stained DSSC reach a maximum within hours. Only the TrSt V_{oc} remains near this maximum value, with OpSt showing a much more complex time evolution.

Discussing the fill-factor, St and HH groups show clearly diverging behaviour. Relative to their initial value the FF for St groups reach a higher maximum value within before steadily reducing over time. The OpHH group never reaches a maximum but decreases steadily over time. Transparent PV photographs (TrHH) similarly reach a maximum but reduce faster, 'catching up' to the OpHH group by the end of the experiment.

The maximum power output of all groups show a similar fast decrease in the first hours with stained samples (TrSt and OpSt) continuing to decrease slowly over time. Both PV photographs groups diverged in behaviour from each other and from the stained DSSC, with faster degradation of the TrSt samples and an increase in power output for the OpHH group, matching the increase in I_{sc} .

In summary, a fast initial change is observed for all samples in the first batch. This is attributed to the light-soaking effect described in the literature [35, 36, 37]. After this initial phase OpHH seem to most drastically differ in behaviour from other groups. The steady increase of all parameters (except fill-factor) is peculiar and unexpected in this context. The stained reference samples for transparent and opaque anodes seem relatively well behaved after this initial soaking period. TrHH PV photographs show complex behaviour over time with their I_{sc} stabilising after 100 hours and the V_{oc} destabilising after this point. Overall these striking differences between stained references and PV photographs may indicate additional weaknesses compared to reference stained DSSC.

5.4.2 Slight colour changes primarily indicate various degrees of iodide depletion

The pattern present in PV photographs is their main defining feature and originates from nearby contrasting colours. As such, digital photography was used to spatially resolve colour differences before and after subjecting the samples to aging conditions. Example images are shown in fig. 5.6.

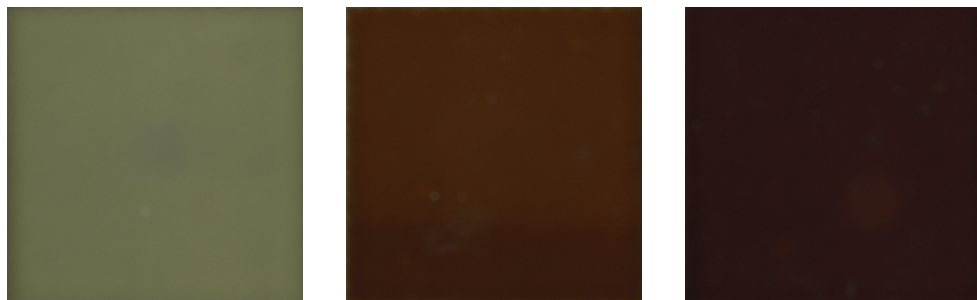


Figure 5.6: Example of colour corrected images of opaque samples. Left: an unstained DSSC; middle: a binary N719 PV photographs, note that the bottom third is slightly darker than the top part; right: a regularly prepared N719 DSSC. While these images were colour corrected the controlled environment and fixed imaging conditions yielded images with much lower contrast than expected from visual inspection.

The pattern in the PV photograph (fig. 5.6, middle) can be difficult to discern. This is influenced in part by significant variations in colour accuracy of printers and screens. However, the constrained conditions under which the images were taken play a significant role. The subjective colour in such SC depends on many factors, such as illumination intensity and direction, as well as on the viewing angle. These were all tightly controlled for reproducibility and precision of the colour measurements rather than accuracy.

Figure 5.7 shows the average a^* and b^* coordinates for all groups. The coordinates of the stained transparent samples (left, dark circle) appear not to have changed after 1000 h of illumination. A minimal change is observed for stained opaque cells (right, dark circle). Furthermore, smaller colour spreads for transparent samples seem to indicate a higher degree of visual uniformity.

For all PV photographs images a similar behaviour in the a^* and b^* co-ordinates can be observed, both in direction and in magnitude. A move towards lower b^* values corresponds to a loss of yellow colour, which is significantly smaller in magnitude than for the control sample images (fig. 5.7, yellow circles). In addition, a minimal move towards lower a^* -values indicates a slight loss of red in these images. While these shifts are readily seen in these diagrams the spread of colour is rather subtle in all samples, except for the unstained control samples. These controls seem to gain slightly in the a^* -channel, which is opposed to all other samples.

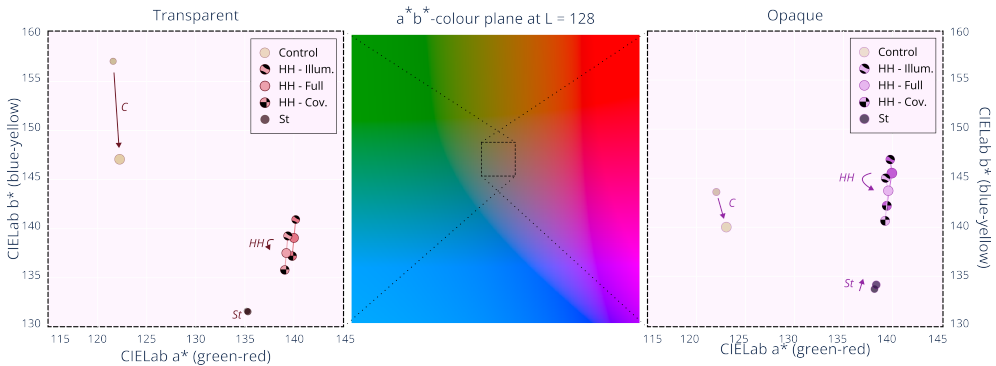


Figure 5.7: Colour diagram of transparent (left) and opaque (right) samples, before and after aging. The middle figure illustrates the plotted region in the full a^*b^* -plane at $L^* = 50$.

The relatively small change in colour of the stained reference samples for both types of anodes shows that discolouration is minimal in our completed DSSC. The loss of yellow in unstained controls is a direct indication that the electrolyte tri-iodide concentration has decreased in these samples, as established by Tiihonen [38]. Figure 5.7 shows that all prepared samples show this shift to lower b^* -values, indicating that all samples likely suffer from a similar loss of tri-iodide in the electrolyte. While changes in the dye cannot be ruled out from this observation alone, a previous study shows a blueshift in the absorption spectrum of N719 upon light-induced degradation [23]. This blueshift would simultaneously correspond to a gain in the b^* -channel and a loss in the a^* -channel, which is inconsistent with these results. The application of a ultraviolet (UV) filter might therefore be insufficient to protect the electrolyte from degradation.

Figure 5.7 showed consistent changes in the a^*b^* space for PV photographs. The overall changes across all PV photographs are significantly larger than typical DSSC, and indicate a more pronounced colour shift in PV photographs. The distance between sub-image average colors remains for both types of anodes, before and after illumination, indicating that contrast might be maintained despite the a^*b^* -shifts.

To complete the colour analysis the L^* -channel behavior must also be examined. Histograms were computed for each channel and image. The L^* -channel histograms are plotted in fig. 5.8 while the a^* and b^* channels are deferred to the supplementary material as they yield no additional insights. Overall the lightness of all samples seems to decrease by about 5 %, meaning that the samples get darker between the two imaging sessions. This is counter intuitive as N719 DSSC typically becomes less absorbing when exposed to the light-patterning step. Consequently, the white background should become more visible, leading to increasing L^* -values. An overall shift to lower L^* values is therefore very surprising and is more likely the result of effects not yet accounted for in the colour correction process.

While the $L^*a^*b^*$ colour analysis yields interesting insights, showing likely tri-iodide depletion in all samples, it is important to determine whether these changes are sufficiently large to be perceived by a standard observer. Consequently, eq. (5.1) is used to determine mean colour changes between the two sets of images (before and after treatment) shown in fig. 5.9. The spread in colour in these images, determined from the average ΔE_{00} from the mean, is represented by the error bars. The shaded area represents colour differences which are defined as imperceptible by the CIE, while the dashed lines show the threshold beyond which the change is considered perceptible for inexperienced observers.

From this graph it can be concluded that the colour changes described above are perceptible only to the experienced observer, except for the unstained controls (TrC and OpC). For the stained DSSC (TrSt, OpSt), used as reference samples, the changes are considered imperceptible to a standard observer. Error bars in fig. 5.9, quantifying colour spread within an image, indicate that the images are perceptibly non-uniform. The larger error bars combined with the histograms suggest that the L^* axis has a

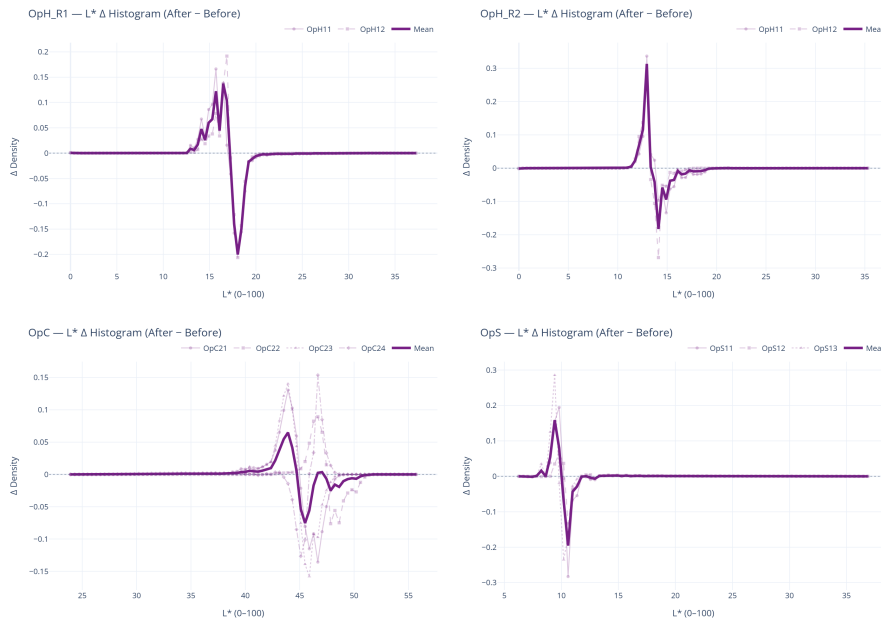


Figure 5.8: Lightness distribution in opaque sample (sub)images. The top images represent the illuminated (top left) and covered (top right) halves of the binary samples. The bottom row are the unstained (bottom left) and stained (bottom right) control samples.

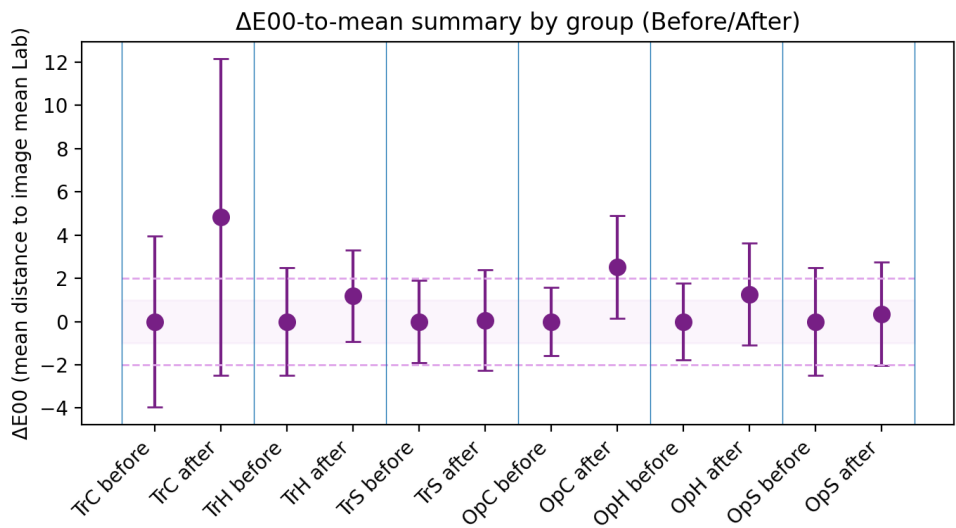


Figure 5.9: ΔE_{00} between the average colour of group samples before and after illumination. The error bars represent the mean ΔE_{00} value within the group at both times, representing the spread of colours in the images.

greater impact on perception for the transparent cells than for opaque cells. Additionally, while the mean colour shifted noticeably for most, the spread of colours does not seem considerably affected. This spread is slightly larger for PV photographs samples, reflecting the presence of an imprinted image.

To verify contrast, the sub-images for the HH PV photographs were further examined. The ΔE_{00} between the region's average colours was computed, both before and after the light-soaking test. These results are tabulated in table 5.1, showing imperceptible contrast for second batch opaque group, highlighting differences in this group. Contrast values for all other groups show that, on average, the difference between the two regions in HH samples is apparent to most observers. This colour difference changes by less than 10% after light-soaking. Given the numerical ΔE_{00} values we conclude that this contrast did not meaningfully change during this experiment.

Table 5.1: ΔE_{00} between HH image region average colours (μ_1 and μ_2) before and after the light soaking test.

Batch	Sample type	$\Delta E_{00}(\mu_1, \mu_2)$	
		Before	After
1	Transparent	2.81	2.70
	Opaque	3.67	3.50
2	Transparent	2.43	2.28
	Opaque	0.46	0.55

Finally, it should be emphasised that these conclusions are based on a simple before and after comparison. It is therefore unknown whether these changes are gradual and ongoing or whether some equilibration happened over times. To distinguish between these scenarios, and thus properly determine the colour fastness, requires additional imaging sessions throughout the aging test. For such tests we would recommend the use of holders designed to be compatible between the solar simulator setup and the imaging cabinet.

5.4.3 Locally dependent changes in photocurrent production shown using laser-beam induced current mapping

Finally, photocurrent maps were taken using a custom-built LBIC to connect these global IV trends to the locally resolved optical properties. All maps shown in fig. 5.10 show a similar diagonal grid across the complete photoactive area. This is a known artifact of the machine determined to be strongly linked to the mechanical motion of the sample [33]. Furthermore, it is clear that all photoactive areas, regardless of sample type, are distinguishable from the surrounding glass. Figure 5.11 shows the current distribution for each map, highlighting that the exact magnitude of these differences depends on the type of sample, with most having a background below 100 nA.

The opaque unstained control sample showed currents in the tens of nA, significantly higher than their dark current measured at 100 pA but $20\times$ lower than stained samples. Currents after 1000 hours of illumination are more broadly distributed and have increased ten-fold.

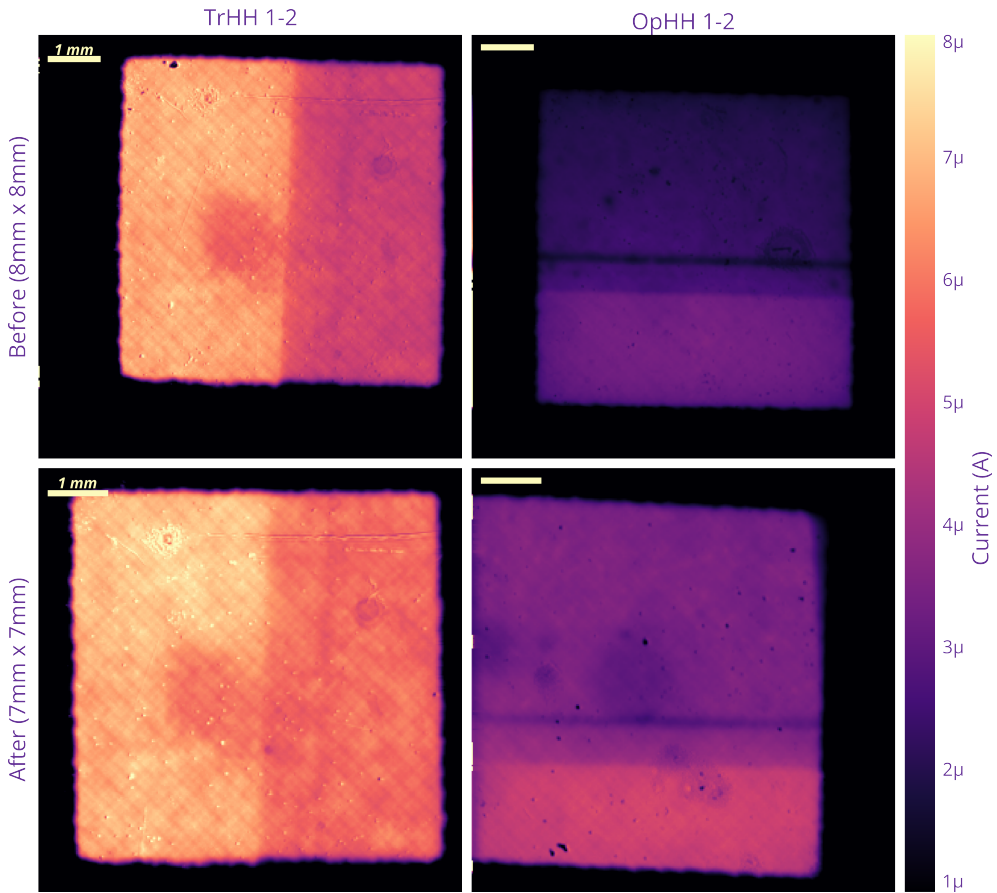


Figure 5.10: LBIC photocurrent maps for three selected sampled (left: transparent HH; right: opaque HH) before (top) and after (bottom) a light-soaking stress test. The scale bars indicate 1 mm on the images. All images are scaled to the same minimum and maximum current values shown in the gradient.

Both HH samples (one opaque and one transparent) show two well-defined region separated by a sharp boundary. The high current regions in these images correspond to the areas which were covered during illumination. While some variation can be seen within each region these are initially minimal, becoming more pronounced after the light-soaking test. This is accompanied by a less sharply defined transition between both regions in the cells. Figure 5.11 shows the distribution of currents in each image. Two cleanly separated peaks can be seen for each image, roughly corresponding to the illuminated and covered areas of the solar cell. It is also interesting to see that, while currents increased everywhere, the contrast between both regions seems to have changed, as evidenced by the distance between both peaks in each current distribution. Slight changes can be seen in their separation, with a decrease for the transparent cell and increases for the opaque one.

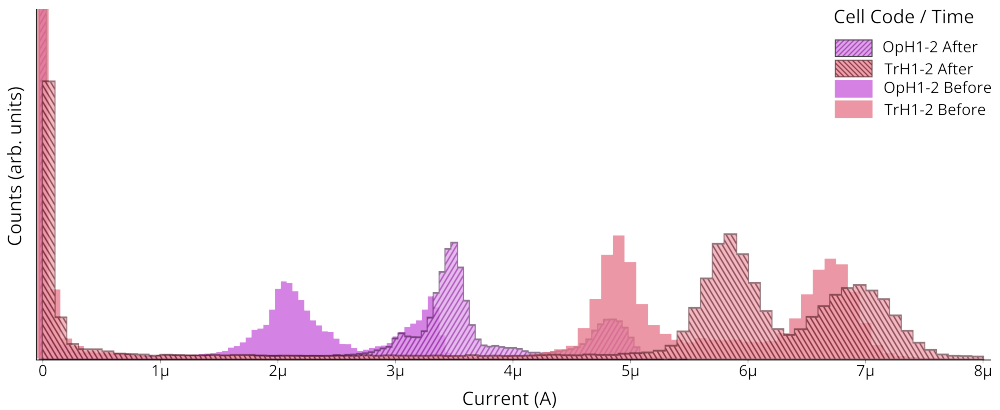


Figure 5.11: Current distribution for two HH sample (coral: transparent; purple: opaque) photocurrent maps, taken with a custom-built LBIC. Counts are arbitrarily normalised for clarity. Plain areas represent the distribution of currents in the map taken before light-soaking, while the hatched area represents currents from the map taken after the test.

Given the identical power setting of the laser beam in both measurements it is unlikely to be able to explain the tenfold increase in the opaque control. The shift in currents observed additionally depends on the area of the image, increasing more for illuminated areas, indicating a loss of contrast in photocurrent. Consequently, it should be expected that the imprinted image has an impact on the SC performance and degradation mechanisms.

5.5 Conclusions and Outlook

The advances made in PV technologies in recent decades have unlocked more varied and creative applications of SC. However, the technologies on which these new applications rely have yet to reach research and commercial maturity. Publication of accelerated aging and other stress tests are common, attempting to understand and control degradation mechanisms, are common,. However, the alternate properties allowing new applications are rarely discussed in such tests. Here we focused on a specific property with artistic value: visual patterning.

We propose a methodology to examine the long term behaviour in these visually patterned SC. A three-pronged analysis combining global IV characterisation, local optical properties, and local photoelectrical properties, was demonstrated on newly introduced PV photographs. While in-situ IV characterisation are a necessary part of any aging test, the properties that can be derived from them are global in nature, making them insufficient for solar cells with additional properties, such as patterned SC which are non-uniform by design. Digital photography and photocurrent mapping can complement these global measurements by resolving optical and electrical properties locally. The resilience of applied visible patterns required the use of spatially resolved qualitative and quantitative colour measurements. An added strength of their inclusion is the potential diagnostic power with respect to specific degradation mechanisms, such as iodide loss or dye desorption, adding to or strengthening electrical results. By adding photocurrent mapping the correlation between optical variations and photoelectrical properties can be probed directly. When combining these techniques it is therefore possible to reach more nuanced and robust conclusions on the exact mechanisms leading (or not) to unstable samples. While the prepared samples required only limited analysis complexity, the methodology is straightforward to extend to more complex images. This can be achieved with more advanced image and data processing workflows, mirroring the requirements of the prepared samples.

This methodology is demonstrated by comparing the long term stability of PV photographs to reference stained DSSC. This application is particularly challenging as known degradation methods for DSSC involve oxygen and

water ingress, requiring excellent encapsulation methods [17]. Oxygen in particular is linked to the mechanism underlying the change of colour observed during patterning [19, 33]. Additionally, the often yellow-tinted electrolyte is known to be sensitive to UV [39]. Here we showed that the prepared PV photographs did not match the reference DSSC in long term performance. IV measurements show an initially surprising increase in efficiency in some samples, which optical measurements strongly link, through the detection of a loss of yellow colour, to a decrease in iodide concentration in the electrolyte. However, the optical measurements show that this loss is a feature even in samples whose short-circuit current (I_{sc}) did not increase past the initial equilibration. Furthermore, LBIC maps show a slight increase in current non-uniformity and a slight change in current contrast between covered and illuminated regions of two PV photographs. The photocurrent production changes are accompanied by the same decrease in the b^* -channel values. The change in contrast is inconsistent with either an increase in current caused by higher transparency of the electrolyte.

Future work should repeat these tests with sufficiently large sample groups and low preparation variance, mitigating known difficulties related to lab-scale preparation of DSSC. While the results currently suggest a potential long-term weakness of PV photographs related to the electrolyte, they remain inconclusive due to batch-variations. A replication addressing this variation is thus required to confirm the changes observed in our measurements. To further strengthen conclusions, these replications should include optical and photocurrent measurements at various point during illumination, providing time-resolved results.

These results nonetheless show the value in combining these three techniques when studying the stability of coloured or patterned SC. Combining all three types of measurements allows the detection of nuances in device behaviour which might be missed otherwise. In understanding these nuances new insights can be obtained, potentially applicable to technology as a whole.

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Chapter 6

Conclusions and Future Work

I started my introduction by arguing that the inherent value that humanity places in art and aesthetics can be used as a driving force towards societal change. This is only one particular example of the power that is held by a fundamentally cross-disciplinary approach, with collaboration across seemingly drastically different fields. I now hold the firm belief that artistic questions can and often do lead to relevant scientific questions. This collaborative path not only led directly to photovoltaic photographs but a lot of my scientific work involving colourimetry and dye-sensitized solar cell (DSSC) were enabled or accelerated through art-science collaborations.

Moreover, I have been fortunate to explore my own conception of beauty through the many photovoltaic photograph (PV photograph) prototypes that I have made throughout the years. This highlighted the possibilities and limitations associated with a laboratory meant for exploration, compounded by the fact that I inherited the newly built OptiX lab still in its infancy. I was frequently reminded that preparation of DSSC and PV photographs in non-commercial contexts requires a significant amount of manual work and places strong constraints when approaching certain research questions. Despite these limitations, I am happy to observe that very first PV photograph I made, similar to fig. 1.5, still sits proudly on my

desk as a testament to the application and to my own work. Limitations also proved to be an opportunity as I was able to expand the capabilities of the OptiX lab by upgrading existing equipment and building additional measurement devices.

These developments were crucial in answering the research questions stated at the end of chapter 1. In this final chapter I wish to formulate direct answers to these research questions before providing an overview of potential future avenues of research.

6.1 Answers to the Research Questions

In 2022, Hustings et al. [1] demonstrated a low-cost and scalable protocol to imprint high-resolution images into the photo-active layer of DSSC. They showed a resulting decrease in efficiency for these functional devices, mainly induced by a lower short-circuit current (I_{sc}). While oxygen seemed to play a role in this patterning, the chemistry involved still remained to be examined explicitly. Furthermore, it was not clear whether subsequent encapsulation would be sufficient to protect the PV photographs from further physical and chemical degradation. It was also unclear whether the imprinted image would fade over time after encapsulation.

6.1.1 Which mechanisms underlie the visual changes enabling patterning in photovoltaic photographs?

While the proof-of-principle devices developed through exploratory research were successfully produced, proper understanding of the mechanisms underlying their preparation was still required. In this particular case the role of oxygen had already been strongly suggested by Hustings et al. [1], but it was unclear which pathways were involved. Given the working principles of DSSC, both an in-situ chemical change of the dye and a physical desorption from the mesoporous substrate are likely explanations for a perceived change in colour. The question of the underlying mechanism was investigated for N719-dye stained and patterned photoanodes. Focusing on this work-horse dye enabled increased experimental

control over the preparation procedure while at the same time ensuring sufficiently interpretable results.

Several techniques were employed to understand the exact changes occurring in this N719-dye under the preparation conditions. Through the use of time-resolved UV-vis spectroscopy we showed a strong effect of TiO_2 on the dye degradation with a significant shift of the 495 nm metal-to-ligand charge transfer peak. The chemical change of this ligand is confirmed by the a shift and intensity drop of the CN-stretching vibration in the Fourier-transform infrared spectroscopy (FTIR) spectra. Both findings are in line with previously reported results on the degradation of N719 [2, 3]. In addition, these spectra show a partial replacement of the TBA counter ion, which is confirmed by the identification of tributylamine and dibutyl disulfide in pyrolysis gas chromatography–mass spectrometry measurements. An influence on the anchoring strength of the dye to the TiO_2 surface is therefore deemed possible [4].

New time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements and analysis showed that the NCS^- signal decreased with illumination time, while sulfate (SO_4^-) intensities increased, indicating oxidation of the ligand. Unexpectedly, transient NCO^- ions peaked at 4 h of illumination before declining again by 22 h. Showing that, under patterning conditions, sulfur is rapidly lost and partially replaced by oxygen to form short-lived NCO^- intermediates before the ligand is ultimately removed from the dye-complex. Collectively, the results establish a multi-stage photodegradation sequence catalysed by TiO_2 under illumination and atmospheric oxygen. To the best of our knowledge, this is the first report of the multi-step nature of N719 photodegradation on TiO_2 .

These experiments uncovered previously unreported findings regarding N719 dye degradation kinetics while reinforcing the role played by oxygen in the preparation of PV photographs.

6.1.2 Can photocurrent mapping be used to study visually patterned dye-sensitized solar cells, and thus photovoltaic photographs?

The visible discolouration seen under PV photograph preparation conditions naturally leads to questions relating to the local photoelectric properties of the system. Which exact mechanisms underlie these visible and chemical changes? By probing the induced photocurrent under localised illumination it is possible to determine to which extent the chemically altered dye can contribute to the current produced by the complete device.

In chapter 4 we have given a description of the approach following to build an instrument capable of focusing laser light onto a movable target device while measuring its I_{sc} to answer this research question. Our device was built using components that most photovoltaic research laboratories are already likely to have purchased in the past. We show overall resolving powers below $50\mu\text{m}$, using simple optical elements, mechanical steps of $25\mu\text{m}$ per pixel, and mechanical errors below 2% over travel ranges of 6 mm. A additional grid-pattern, seen in most images, was determined to be consistent in frequency and placement with the chosen mechanical characteristics of the laser-beam-induced current (LBIC) measurement device. While outside the scope of this work, the nature of these artifacts is such that they could be filtered from the data, improving image quality.

We used this custom-built LBIC-equipment to examine the difference between PV photographs and masked DSSC. In doing so we demonstrated the surprising effectiveness of this method considering the slow kinetics of DSSC. Despite this limitation it is apparent that the image present in PV photographs has a significant effect on the local production of free charges, showing strongly reduced photocurrents in discoloured areas. We also show that PV photograph energy production can be competitive when compared to additionally applied aesthetic layers as discoloured areas still produce an appreciable photocurrent when compared to masked areas. More generally, with this LBIC-work on photovoltaic photographs we have demonstrated that the technique is a powerful tool to investigate patterned solar cells and can therefore be more broadly used for other types of patterned solar cell technologies.

6.1.3 How should potential for stable operation of photovoltaic photographs be compared to similarly prepared dye-sensitized solar cells?

When discussing the preparation of PV photographs with other solar cell (SC) researchers one aspect systematically surprised them. Given that SC are intended to be placed under (sun)light during operation one question is immediate to most. Are these devices not going to continue discolouring and thus degrading during operation? To answer this question it is necessary but insufficient to perform a traditional light-soaking test with in-situ current-voltage (IV) monitoring. The aesthetic nature of this application requires quantification of this new dimension. Consequently we explored a new methodology to measure the stability of PV photographs, applicable to any (coloured) patterned SC. This proposed methodology consists of combining the well known IV characterisation with local photocurrent mapping (e.g. using LBIC) and digital photography. This method not only explicitly includes the aesthetic dimension but correlation between measurements lead to more precise and robust conclusions.

A full demonstration and validation of this methodology for the long-term stability of photovoltaic photographs is beyond the scope of this thesis. An illustration of the methodology is however provided on some introductory experiments on PV photographs and reference stained DSSCs. The batch-1 IV measurements show an initial increase in efficiency in some samples, which optical measurements strongly link, through the detection of a loss of yellow colour, to a decrease in iodide concentration in the electrolyte. However, the optical measurements show that this loss is a feature even in samples whose I_{sc} did not increase past the initial equilibration. LBIC maps may suggest a slight increase in current non-uniformity and a slight change in current contrast between covered and illuminated regions of two PV photographs, not consistent with a simple increase in current caused by higher transparency of the electrolyte.

It must be noted that significant difficulties in the preparation of DSSC and PV photographs were highlighted by this study. The initially large number of samples required preparation in two separate batches, leading to the inclusion of a confounding variable. However, the results from the first batch possibly suggest an increased long-term weakness of our prepared PV pho-

tographs under AM1.5G illumination conditions and at constant temperature. More significantly, the value in combining all three measurements when studying the stability of coloured or patterned SC is highlighted as new insights can be gained from the detected correlations.

6.1.4 General conclusion

In this thesis we have first gained additional insights in the physico-chemical mechanisms underlying the light-induced patterning in photovoltaic photographs. Additionally, the future study of PV photograph, as well as patterned solar cells of any kind, has been furthered, experimentally speaking, in two aspects: the in-house build of a custom-LBIC system for 2D-mapping of photocurrent production and the development of a correlative measurement methodology of the ageing of patterned SC where in-situ photovoltaic (PV) characterisation is combined with the aforementioned photocurrent mapping and with scientific colourimetry based on digital photography.

6.2 Future Work

As is typical, the research performed in this thesis, leading to the conclusions in the first part of this chapter, has also led to additional research questions which may be explored in the future. In these last sections I seek to contextualise and offer a starting point for some of the questions that remain open and which my curiosity has a hard time letting go of.

6.2.1 Spectrally resolved LBIC

It is well known that dyes with different colours have correspondingly different absorption spectra. Furthermore, the use of these dyes in solar energy conversion system leads to unequal spectral properties. In DSSC, different devices can have very different external quantum efficiency (EQE) characteristics. Consequently, the use of a single wavelength of light in LBIC

thus leads to limited information. While the chosen 405 nm wavelength initially selected for this study leads to significant absorption and qualitative results, even in unstained devices it is expected that the spectrum influences the absorption to some extent. It is therefore interesting to compare LBIC results which are generated by different pump wavelengths. Red (670 nm) and green (532 nm) laser diodes have been purchased and inserted in the device, leading to test measurements shown in fig. 6.1.

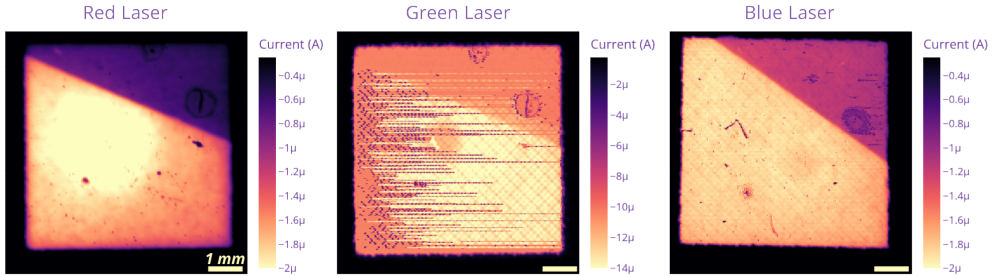


Figure 6.1: LBIC scans taken of 6 mm × 6 mm binary-patterned PV photograph using three different wavelengths: Left: Red (670 nm); Middle: green (532 nm); Right: blue (405 nm).

During alignment and optical fine-tuning it was clear that the optical properties are sensitive to the exact diode used and the utilised cage system is too mechanically restrictive for optimal focusing. In addition, the very first lens, collimating the laser output, is ill-matched for the red and green laser diodes. A lens with a larger opening may improve the beam characteristics, aiding in improving the resolution.

6.2.2 Expanding the applicability of photovoltaic photographs

PV photographs are currently monochromatic in nature. The use of a single dye leads a gradient along a single axis in colour space. It is therefore interesting to look at utilising more than one dye in a single device. To do so two additional dyes were purchased and used in patterning tests: RK1 (bright-red) and SQ2 (blue).

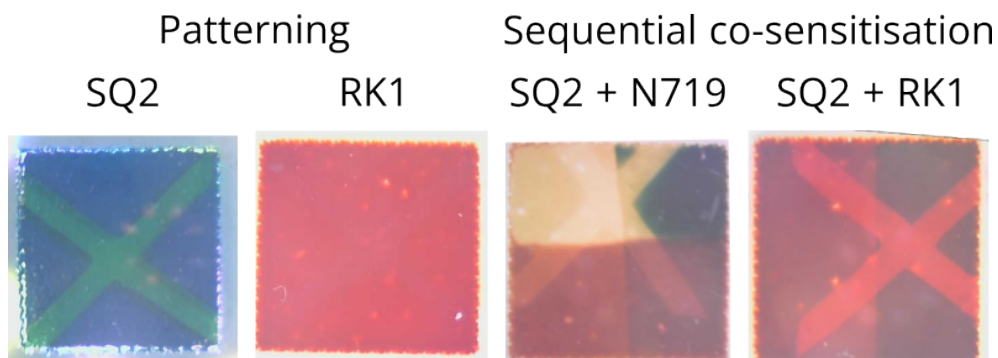


Figure 6.2: Images of DSSC-anodes prepared for initial multi-colour co-sensitisation experiments. An initial bleaching result is shown for the blue SQ2 (leftmost) and RK1 (middle left). On the right are anodes initially 'X'-patterned using SQ2 before submerging the anode in N719 (middle right, incomplete submersion) and RK1 (rightmost) and exposing only half of the anode vertically.

The images on the left of fig. 6.2 show clearly that the blue dye can easily be used for PV photographs as it changes drastically in colour to a dark green in a few hours. The bright red dye is less suited as it only discoloured slightly, even after more than 30 hours of illumination.

The images on the right of fig. 6.2 show the results of a two-step process. Both anodes were initially stained using SQ2 (blue) and patterned with an **X**. A subsequent immersion step was then applied with N719 (middle right) and RK1 (rightmost) before illuminating the right half of the anode. Note that the N719 was only partially stained due to incomplete submersion. The difference in pattern was chosen to clearly identify preparation steps from final visual features. Both patterns are clearly visible for both anodes with some interesting differences. Concentrating on the SQ2 + N719 cell already reveals an interesting feature: the top right colour only contains SQ2 and is dark blue, the bottom was exposed to N719 as well and shows a combined colour in the bottom right, and finally the bottom left corner contained SQ2 as well as N719 and only colours red. Together these results show that, following a patterning step, SQ2 can be (partially) replaced by N719 and will be preferentially bleached in subsequent patterning steps. Interestingly, the top left corner on that same anode is tainted by two different shades, showing that the remaining SQ2 continued bleaching past

green while maintaining meaningful contrast. Furthermore, the right-most image confirms that SQ2 seems replaced when bleached as the **X** has taken on a bright red colour there. The vertical bleaching interface here also likely shows a combined presence of SQ2 and the new dye (RK1) and preferential bleaching of the blue dye. Together, these results offer a very promising start towards sequential co-sensitisation and patterning towards multi-colour photovoltaic photographs.

6.2.3 Dye desorption and photovoltaic photograph stability

Current measurements show that the cells I prepared might not stand the test of time as their output seems to deviate from reference DSSC. Their change in colour, while slight, is numerically more pronounced than the reference DSSC. While it is entirely possible that this is strongly linked to our preparation methodology and the permeability of the gasket to oxygen I believe this can be explored further with respect to the underlying mechanisms of the patterning step.

The LBIC results from chapter 5, combined with the FTIR and pyrolysis gas chromatography–mass spectrometry (PY-GC/MS) may indicate that dye-desorption plays a role in PV photographs, and might do so even in perfectly encapsulated devices. First, FTIR shows that the protonation of the anchoring groups changes under illumination conditions. It is thus possible that dye molecules are bound less strongly to the substrate.

Furthermore, LBIC measurements showed a somewhat greater degree of non-uniform current production after illumination, which could be a result of some equilibration of the cells in the first few hours of illumination. However, it is also possible that the dye could locally desorb from the TiO_2 over time, exposing the electrolyte to photocatalytic degradation. This is consistent with the strong discolouration seen in unstained controls and the overall loss of yellow colour.

Together, these measurements indicate that the multi-step degradation of the dye, observed and described in chapter 3, might be accompanied by a physical desorption of the dye.

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