Unravelling the Charge Generation Pathways in Hybrid Perovskites for Solar Cell Applications

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Unravelling the Charge Generation Pathways in Hybrid Perovskites for Solar Cell Applications

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Dedicated to God Almighty

My Family and Friends

I am grateful for everyone's blessings and presence in my life. It has shaped me into the person that I am.

Supervisor Certification

This is to certify that the thesis entitled "**Unravelling the Charge Generation Pathways in Hybrid Perovskites for Solar Cell Applications**" being submitted by **Ms. Satakshi Gupta** to the Indian Institute of Technology Delhi and The University of Queensland for the award of degree of **Doctor of Philosophy** is a record of *bonafide* research work carried out by her. **Ms. Satakshi Gupta** has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to our knowledge has reached the requisite standard. The results contained in this thesis are original and have not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.

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Abstract

High optical absorption coefficient, high mobility and long diffusion length of electrons and holes, optimal band gap (typically around 1.1 to 1.5 eV), tunable properties and stability under harsh environmental conditions are some of the most desirable properties of a material to be used in solar cells. Halide perovskites such as methylammonium lead iodide (MAPI) and formamidinium lead iodide (FAPI) possess most of these properties, thereby making them popular materials for use in and as an active layer material in solar cells. Likewise, there are multiple variants of these hybrid perovskites that are being researched for different aspects of the solar cell specifications. However, the persistent stability challenge has long hindered its commercial viability, driving continuous efforts to overcome this limitation. The use of additive engineering as a powerful way to enhance the efficiency and stability of solar cells has long been a subject of research. Despite the high number of studies on MAPI and FAPI, the complete understanding of the photocarrier dynamics and the related mechanisms in these hybrid materials is still evolving. Hence, the investigation carried out in this thesis endeavours to unravel the photophysics of these additive-engineered hybrid perovskites, specifically MAPI and FAPI, to enhance the understanding of the research community.

Three fluorinated cations with different alkyl chain lengths (2,3,4,5,6-pentafluorophenyl) methylammonium iodide (FMAI), 2-(2,3,4,5,6-pentafluorophenyl) ethylammonium iodide (FEAI), and 3-(2,3,4,5,6-pentafluorophenyl) propylammonium iodide (FPAI), when incorporated in the perovskite precursor solution at small concentrations, have led to enhanced performance and stability of the solar cell devices. A combination of optical, electrical and spectroscopic techniques was used to study the control film and observe the changes in the presence of the additives. The absorption and emission characteristics of the control and modified films have been enhanced in the presence of additives. The results of temperature-dependent photoluminescence (measured down to 77 K) demonstrated that the exciton binding energy of the modified MAPI films remained unchanged. Femtosecond Transient Absorption Spectroscopy (TAS) revealed the dependence of the charge recombination process on the alkyl chain length of the additives. Femtosecond Transient Reflection Spectroscopy (TRS) provided deeper insight into the surface recombination mechanisms, and a comparison of the results with those obtained for the bulk was done. While the TRS data for MAPI at the low fluence showed

a longer lifetime in the presence of FMAI for the first few tens of picoseconds, the bulk measurement data at high fluence demonstrated that the longer chain cations FEAI and FPAI were effective in suppressing the contribution from the Auger recombination process.

Incorporation of additives in the precursor solution of FAPI affected the crystallization process of the films. With an increase in the concentration of the additive, the annealing time of the films was increased to complete the crystallization process and obtain the photoactive black phase of the FAPI films. The dependence of film crystallization on the additives was not observed in MAPI, highlighting that additives can affect the film quality of materials based on their molecular interaction. The average performance and stability of the FAPI devices were highest for those containing the additive FPAI (propyl chain). The peak performance obtained for the devices with ethyl and propyl linking chain additives was 14.4% compared to 13.1% for the control FAPI-based devices. Also, the devices with C_{60} as the electron transport layer (ETL) exhibited higher stability as compared to the devices with phenyl-C61-butyric acid methyl ester (PCBM) as the ETL. The behaviour of additives and their impact on the photovoltaic properties was found to be dependent on the perovskite material. While for MAPI, the highest performance of 16.3% was obtained for FMAI at a concentration of 0.2 mol%, the outcome was a little different in FAPI, with the longest chain additive, FPAI, achieving the highest performance of 14.4% at 0.2 mol%.

The photophysical investigation of FAPI demonstrated that the effect of additives was similar on both the bulk and surface dynamics. The lifetime of charge carriers present in bulk increased with chain length, with the largest change in FEAI followed by the longest chain length additive FPAI. A similar impact was observed on the surface dynamics, too, where FEAI led to an increase in the lifetime of carriers, closely followed by FPAI. The carrier dynamics also revealed the contrasting effect of additives on the surface and bulk properties of MAPI and FAPI. FMAI led to the longer recombination lifetime as revealed by the surface measurement of MAPI. Whereas FEAI aided in achieving the longest recombination lifetime in FAPI. The work in this thesis has distinguished the surface dynamics from those of the bulk and demonstrated the influence of fluorinated additives on the photophysical properties of the perovskite materials through TAS and TRS.

Abstract in Hindi

सौर सेल में उपयोग किए जाने वाले किसी भी सामग्री की कुछ सबसे वांछनीय विशेषताएँ होती हैं: उच्च ऑप्टिकल अवशोषण गुणांक, उच्च गतिशीलता, इलेक्ट्रॉनों और होल्स की लंबी विसरण लंबाई, उपयुक्त बैंड गैप (आमतौर पर 1.1 से 1.5 eV के बीच), अनुकूलनीय गुणधर्म, और कठोर पर्यावरणीय परिस्थितियों में स्थिरता। हेलाइड पेरोव्स्काइट्स, जैसे मेथाइलअमोनियम लेड आयोडाइड (MAPI) और फॉर्मामिडिनियम लेड आयोडाइड (FAPI), इन गुणों में से अधिकांश को प्रदर्शित करते हैं, जिससे वे सौर सेल में सक्रिय परत सामग्री के रूप में उपयोग के लिए सबसे अधिक पसंद की जाने वाली सामग्री बन गए हैं। इसी प्रकार, इन संकर पेरोव्स्काइट्स के कई संस्करण विभिन्न सौर सेल विनिर्देशों के पहलुओं के लिए अनुसंधान के अंतर्गत हैं। हालांकि, स्थायित्व की लगातार बनी रहने वाली चुनौती ने लंबे समय से इसके वाणिज्यिक उपयोग की संभावनाओं को बाधित किया है, और इस सीमा को पार करने के लिए निरंतर प्रयास जारी हैं। ऐडिटिव इंजीनियरिंग का उपयोग सौर सेल की दक्षता और स्थिरता बढ़ाने के लिए एक प्रभावी तरीका माना गया है और यह लंबे समय से अनुसंधान का विषय रहा है। यद्यपि MAPI और FAPI पर अनेक अध्ययन किए गए हैं, फिर भी इन संकर सामग्रियों में फोटोकैरियर डायनामिक्स और संबंधित तंत्रों की पूर्ण समझ अभी भी विकसित हो रही है। अतः, इस शोध प्रबंध में किया गया अध्ययन इन ऐडिटिव-इंजीनियर्ड संकर पेरोव्स्काइट्स, विशेष रूप से MAPI और FAPI की फोटोफिज़िक्स को स्पष्ट करने का प्रयास करता है, जिससे शोध समुदाय की समझ को और अधिक गहराई मिल सके।

तीन फ्लोरीनेटेड धनायन, जिनमें अलग-अलग लंबाइयों वाली एल्काइल श्रृंखला हैं — (2,3,4,5,6-पेंटाफ्लोरोफिनाइल) मेथाइलअमोनियम आयोडाइड (FMAI), 2-(2,3,4,5,6-पेंटाफ्लोरोफिनाइल) एथाइलअमोनियम आयोडाइड (FEAI), और 3-(2,3,4,5,6-पेंटाफ्लोरोफिनाइल) प्रोपाइलअमोनियम आयोडाइड (FPAI) — को जब पेरोव्स्काइट प्रीकर्सर विलयन में थोड़ी मात्रा में सम्मिलित किया गया, तो इससे सौर सेल डिवाइसेज़ की प्रदर्शन क्षमता और स्थिरता में उल्लेखनीय सुधार देखा गया। नियंत्रण फिल्म (control film) का अध्ययन करने और ऐडिटिव्स की उपस्थिति में होने वाले परिवर्तनों को देखने के लिए ऑप्टिकल, इलेक्ट्रिकल और स्पेक्ट्रोस्कोपिक तकनीकों का संयोजन उपयोग में लाया गया। ऐडिटिव्स की उपस्थिति में नियंत्रण और संशोधित फिल्मों के अवशोषण और उत्सर्जन गुणों में सुधार देखा गया। तापमान-आधारित फोटोल्यूमिनेसेंस (जो 77 K तक मापा गया) के परिणामों से यह स्पष्ट हुआ कि संशोधित MAPI फिल्मों में एक्साइटॉन बाइंडिंग एनर्जी अपरिवर्तित रही। फेम्टोसेकंड ट्रांज़िएंट एब्जॉर्प्शन स्पेक्ट्रोस्कोपी (TAS) से यह पता चला कि चार्ज रिकॉम्बिनेशन प्रक्रिया ऐडिटिव्स की ऐल्किल श्रृंखला की लंबाई पर निर्भर करती है। फेम्टोसेकंड ट्रांज़िएंट रिफ्लेक्शन स्पेक्ट्रोस्कोपी (TRS) का उपयोग सतह पर होने वाली रिकॉम्बिनेशन प्रक्रियाओं की गहराई से समझ प्राप्त करने और उन्हें बल्क में प्राप्त

परिणामों से तुलना करने के लिए किया गया। जहाँ MAPI के लिए TRS डेटा ने कम फ्लूएंस पर FMAI की उपस्थिति में पहले कुछ पिकोसेकंड के दौरान लंबी लाइफटाइम दर्शाई, वहीं उच्च फ्लूएंस पर बल्क माप में पाया गया कि लंबी चेन कैटायन, जैसे FEAI और FPAI, ऑगर रिकॉम्बिनेशन प्रक्रिया के प्रभाव को कम करने में प्रभावी थे।

FAPI के प्रीकर्सर विलयन में ऐडिटिव्स को शामिल करने से फिल्मों की क्रिस्टलीकरण प्रक्रिया प्रभावित हुई। जैसे-जैसे ऐडिटिव की सांद्रता बढ़ाई गई, क्रिस्टलीकरण प्रक्रिया को पूर्ण करने और FAPI फिल्मों के फोटोएक्टिव ब्लैक फेज को प्राप्त करने के लिए फिल्मों की तापानुशीतन (एनिंलिंग) अवधि भी बढ़ गई। हालाँकि, यह निर्भरता MAPI में नहीं देखी गई, जिससे यह स्पष्ट होता है कि ऐडिटिव्स का प्रभाव सामग्री की मॉलिक्यूलर इंटरैक्शन पर आधारित होता है और वे फिल्म की गुणवत्ता को प्रभावित कर सकते हैं। FAPI डिवाइसेज़ में, FPAI (प्रोपाइल श्रृंखला) युक्त ऐडिटिव के साथ औसत प्रदर्शन और स्थिरता सबसे अधिक पाई गई। एथाइल और प्रोपाइल लिंकिंग चेन वाले ऐडिटिव्स के साथ प्राप्त शीर्ष प्रदर्शन 14.4% था, जबकि नियंत्रण FAPI डिवाइसेज़ (बिना ऐडिटिव) के लिए यह 13.1% था। साथ ही, जिन डिवाइसेज़ में C_{60} को इलेक्ट्रॉन ट्रांसपोर्ट लेयर (ETL) के रूप में उपयोग किया गया, उन्होंने PCBM (फेनिल-C61-ब्यूटिरिक एसिड मेथाइल एस्टर) आधारित डिवाइसेज़ की तुलना में अधिक स्थिरता दिखाई। ऐडिटिव्स का व्यवहार और उनका फोटोवोल्टाइक गुणों पर प्रभाव पेरोव्स्काइट सामग्री पर निर्भर पाया गया। जहाँ MAPI के लिए FMAI (0.2 mol%) पर 16.3% का उच्चतम प्रदर्शन प्राप्त हुआ, वहीं FAPI के मामले में सबसे लंबी चेन ऐडिटिव, FPAI, ने 0.2 mol% सांद्रता पर सबसे उच्च प्रदर्शन प्रदर्शित किया।

FAPI के फोटोफिज़िकल अध्ययन से यह स्पष्ट हुआ कि ऐडिटिव्स का प्रभाव बल्क और सतह दोनों डायनामिक्स पर समान था। बल्क में उपस्थित चार्ज कैरियर्स की लाइफटाइम ऐल्किल चेन की लंबाई के साथ बढ़ी — जिसमें सबसे बड़ा परिवर्तन FEAI के साथ और उसके बाद सबसे लंबी चेन वाले FPAI के साथ देखा गया। सतह डायनामिक्स पर भी इसी प्रकार का प्रभाव देखा गया, जहाँ FEAI ने कैरियर्स की लाइफटाइम को बढ़ाया, और उसके बाद FPAI का प्रभाव रहा। चार्ज कैरियर डायनामिक्स ने यह भी उजागर किया कि MAPI और FAPI की सतह और बल्क विशेषताओं पर ऐडिटिव्स का प्रभाव विपरीत था। MAPI की सतह माप में FMAI ने लंबी रिकॉम्बिनेशन लाइफटाइम प्रदान की, जबकि FAPI में FEAI ने सबसे लंबी रिकॉम्बिनेशन लाइफटाइम प्राप्त करने में सहायता की। इस शोध प्रबंध में किए गए कार्य ने बल्क और सतह डायनामिक्स के बीच स्पष्ट अंतर स्थापित किया है और TAS और TRS तकनीकों के माध्यम से यह दर्शाया है कि कैसे फ्लोरीनेटेड ऐडिटिव्स पेरोव्स्काइट सामग्री के फोटोफिज़िकल गुणों को प्रभावित करते हैं।

Declaration by the author

This thesis is composed of my original work and contains no material previously published or written by another person except where due reference has been made in the text. I have clearly stated the contribution by others to jointly authored works that I have included in my thesis.

I have clearly stated the contribution of others to my thesis as a whole, including statistical assistance, survey design, data analysis, significant technical procedures, professional editorial advice, financial support and any other original research work used or reported in my thesis. The content of my thesis is the result of work I have carried out since the commencement of my higher degree by research candidature and does not include a substantial part of work that has been submitted to qualify for the award of any other degree or diploma in any university or other tertiary institution. I have clearly stated which parts of my thesis, if any, have been submitted to qualify for another award.

I acknowledge that an electronic copy of my thesis must be lodged with the University Library and, subject to the policy and procedures of The University of Queensland, the thesis be made available for research and study in accordance with the Copyright Act 1968 unless a period of embargo has been approved by the Dean of the Graduate School.

I acknowledge that copyright of all material contained in my thesis resides with the copyright holder(s) of that material. Where appropriate, I have obtained copyright permission from the copyright holder to reproduce material in this thesis and have sought permission from co-authors for any jointly authored works included in the thesis.

Publications included in this thesis

Submitted manuscripts included in this thesis

Gupta, S., Li, H., Burn, P. L., Kumar, S., & Shaw, P. E. (2023). Exploring the interplay of bulk and surface carrier dynamics in additive-engineered halide perovskites. *Advanced Optical Materials (under review)*.

Other publications during candidature

Li, H., Chu, R., Bati, A. S., **Gupta, S**., Burn, P. L., Gentle, I. R., & Shaw, P. E. (2023). Efficient inverted perovskite solar cells using dual fluorinated additive modification. *Advanced Materials Interfaces*, *10*(13), 2201939.

Contributions by others to the thesis

All chapters

Editorial suggestions were provided by the candidate's supervisors, Assoc. Prof. Paul Shaw (UQ), Assoc. Prof. Sunil Kumar (IITD), Prof. Paul Burn (UQ) and PhD committee, Prof. Pramit K. Chowdhury (Chairperson), Prof. Ian Gentle (UQ Expert) and Prof. Vamsi Krishna (IITD Expert).

Assoc. Prof. Paul Shaw – Concept and design of the project, collection, analysis and interpretation of data, critical review of the thesis.

Assoc. Prof. Sunil Kumar – Concept and design of the project, analysis and interpretation of data, critical review of the thesis.

Prof. Paul Burn – Advisory supervision of the project, analysis and interpretation of data, critical review of the thesis.

Chapter 3

Dr Hui Li – Synthesis of additives

Dr Hellen Jin – Atomic Force Microscopy and Ellipsometry measurement, data fitting for ellipsometry

Dr Guanran Zhang and Dr Isaac Etchells – Help with Transient Absorption and Reflection Spectroscopy measurement

Chapter 4

Dr Neil Mallo – Synthesis of additive

Dr Hellen Jin – Atomic Force Microscopy, Ellipsometry measurement and data fitting, Stability measurement for devices

Mr Oliver Lindsay - X-ray photoelectron spectroscopy, X-ray powder diffraction, and grazing incidence wide-angle X-ray scattering measurements, data analysis

Statement of parts of the thesis submitted to qualify for the award of another degree

No works submitted towards another degree have been included in this thesis.

Research involving human or animal subjects

No animal or human subjects were involved in this research.

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Inverted perovskite solar cell, additive engineering, transient absorption spectroscopy, transient reflection spectroscopy, methylammonium lead triiodide, formamidinium lead triiodide, 2,3,4,5,6-pentafluorophenyl ammonium cation.

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Fields of research classification

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FoR code: 0205, Optical Physics, 60%

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