DEVELOPMENT OF THE PEROVSKITE-POLYMER INKS AND UNDERSTANDING THEIR STRUCTURE-PROPERTY RELATIONSHIP FOR OPTOELECTRONIC APPLICATIONS

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by

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TO MY PARENTS, TEACHERS AND FRIENDS

CERTIFICATE

This is to certify that the thesis entitled '**DEVELOPMENT OF THE PEROVSKITE-POLYMER INKS AND UNDERSTANDING THEIR STRUCTURE-PROPERTY RELATIONSHIP FOR OPTOELECTRONIC APPLICATIONS'** being submitted by **Ms. Kartiki Chandratre** to the Indian Institute of Technology Delhi in fulfilment of the requirements for the award of the degree of **Doctor of Philosophy** is a record of Bonafide research work performed by him under my guidance and supervision at Department of Energy Science and Engineering, Indian Institute of Technology Delhi, India. The results obtained herein have not been submitted in part or in full to any other university or institute for the award of any degree to the best of my knowledge.

Professor Supravat Karak, PhD
Department of Energy Science and Engineering
Indian Institute of Technology, Delhi, India

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ABSTRACT

The functionality of perovskite-based opto-electronic devices, including solar cells, LEDs, transistors, and sensors, is significantly influenced by the fabrication of the perovskite active layer, its integration into suitable device architectures, and the optimization of device performance through various component adjustments. Understanding the structure-property correlation is essential for the development of this technology.

This thesis investigates the effects of macroscale material fabrication modifications on microscale charge carrier dynamics. By employing the '*polymer-in-perovskite*' approach, micro grains larger than 100µm were achieved for the PMMA-incorporated triple cation perovskite precursor, resulting in a compact film morphology without anti-solvent treatment. Detailed investigations of crystallization dynamics led to an enhancement in radiative recombination lifetime from 0.88 µs (for pristine FAMACs film) to 1.45 µs (for FAMACs film with PMMA incorporation). Additionally, microstructural findings of the photoactive layer were appraised against operating conditions in a device through transient photocurrent measurements, aiming to gain a deeper understanding of the '*polymer-in-perovskite*' approach for precursor development.

Furthermore, a methodology utilizing ligands and surfactants to engineer colloidal suspensions of perovskite was explored. This foundational approach, using methylammonium lead triiodide (MAPI) and polymethyl methacrylate (PMMA), offers an accessible alternative to post-treatment of the photoactive layer. By integrating the properties of polymers and perovskites with selective additives, a novel '*perovskite-in-polymer matrix*' solution was developed for one-step coating of colloidal perovskite, enabling the production of distinct and tailored morphologies. This solvent system, featuring various additives, serves as a template to achieve similar morphologies, provided the additives contain related functional groups. These inks can

be adjusted to produce different surface morphologies, governed by the control of colloidal composition and molecular arrangement dynamics, which are explored in detail in this dissertation. The study also investigates phase segregation observed in quasi-2D-3D perovskite polycrystalline films formed using these template inks.

Overall, this thesis delves into colloidal chemistry, molecular arrangement, film morphology, and the properties of particle structure, size, and shape, as well as their optoelectronic characteristics. Comprehensive analyses of these aspects are provided through a range of measurements, including X-ray diffraction (XRD), scanning electron microscopy (SEM), steady-state photoluminescence (PL), UV-vis absorbance, confocal laser scanning microscopy (CLSM), and small-angle X-ray scattering (SAXS), etc.

सारांश

सौर सेल, एलईडी, ट्रांजिस्टर और सेंसर सहित पेरोव्स्काइट-आधारित ऑप्टो-इलेक्ट्रॉनिक उपकरणों की कार्यक्षमता पेरोव्स्काइट सक्रिय परत के निर्माण, उपयुक्त डिवाइस आर्किटेक्चर में इसके एकीकरण और विभिन्न घटक समायोजन के माध्यम से डिवाइस के प्रदर्शन के अनुकूलन से काफी प्रभावित होती है। इस तकनीक के विकास के लिए संरचना-गुण सहसंबंध को समझना आवश्यक है।

यह थीसिस माइक्रोस्केल चार्ज कैरियर डायनेमिक्स पर मैक्रोस्केल सामग्री निर्माण संशोधनों के प्रभावों की जांच करती है। *'पॉलिमर-इन-पेरोव्स्काइट'* दृष्टिकोण को नियोजित करके, PMMA-शामिल ट्रिपल केशन पेरोव्स्काइट अग्रदूत के लिए 100μm से बड़े माइक्रोग्रेन प्राप्त किए गए, जिसके परिणामस्वरूप एंटी-सॉल्वेंट उपचार के बिना एक कॉम्पैक्ट फिल्म आकृति विज्ञान प्राप्त हुआ। क्रिस्टलीकरण गतिकी की विस्तृत जांच से विकिरण पुनर्संयोजन जीवनकाल में 0.88μs (प्राचीन FAMACs फिल्म के लिए) से 1.45μs (PMMA समावेश के साथ FAMACs फिल्म के लिए) तक की वृद्धि हुई। इसके अतिरिक्त, फोटोएक्टिव परत के सूक्ष्म संरचनात्मक निष्कर्षों का क्षणिक फोटोकरंट माप के माध्यम से एक उपकरण में परिचालन स्थितियों के विरुद्ध मूल्यांकन किया गया, जिसका उद्देश्य अग्रदूत विकास के लिए *'पॉलीमर-इन-पेरोव्स्काइट'* दृष्टिकोण की गहरी समझ हासिल करना था। इसके अलावा, पेरोव्स्काइट के कोलाइडल निलंबन को इंजीनियर करने के लिए लिगैंड और सर्फेक्टेंट का उपयोग करने वाली एक पद्धति का पता लगाया गया। मिथाइलमोनियम लीड ट्राईआयोडाइड (MAPI) और पॉलीमेथिल मेथैक्रिलेट (PMMA) का उपयोग करने वाला यह मूलभूत दृष्टिकोण, फोटोएक्टिव परत के पोस्ट-ट्रीटमेंट के लिए एक सुलभ विकल्प प्रदान करता है। पॉलिमर और पेरोव्स्काइट के गुणों को चुनिंदा योजकों के साथ एकीकृत करके, कोलाइडल पेरोव्स्काइट की एक-चरण कोटिंग के लिए एक उपन्यास *'पेरोव्स्काइट-इन-पॉलिमर मैट्रिक्स'* समाधान विकसित किया गया था, जो अलग और अनुरूप आकारिकी के उत्पादन को सक्षम करता है। विभिन्न योजकों की विशेषता वाली यह विलायक प्रणाली समान आकारिकी को प्राप्त करने के लिए एक

टेम्पलेट के रूप में कार्य करती है, बशर्ते कि योजकों में संबंधित कार्यात्मक समूह हों। इन स्याही को विभिन्न सतह आकृति विज्ञान का उत्पादन करने के लिए समायोजित किया जा सकता है, जो कोलाइडल संरचना और आणविक व्यवस्था गतिशीलता के नियंत्रण द्वारा नियंत्रित होते हैं, जिन्हें इस शोध प्रबंध में विस्तार से खोजा गया है। अध्ययन इन टेम्पलेट स्याही का उपयोग करके बनाई गई अर्ध-2D-3D पेरोव्स्काइट पॉलीक्रिस्टलाइन फिल्मों में देखे गए चरण पृथक्करण की भी जांच करता है। कुल मिलाकर, यह थीसिस कोलाइडल रसायन विज्ञान, आणविक व्यवस्था, फिल्म आकृति विज्ञान और कण संरचना, आकार और आकृति के गुणों के साथ-साथ उनकी ऑप्टोइलेक्ट्रॉनिक विशेषताओं में गहराई से जाती है। इन पहलुओं का व्यापक विश्लेषण माप की एक श्रृंखला के माध्यम से प्रदान किया जाता है, जिसमें एक्स-रे विवर्तन (एक्स.आर.डी), स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी (एस.ई.एम), स्थिर-अवस्था फोटोल्यूमिनेसेंस (पी.एल), यूवी-विज़ अवशोषण, कॉन्फोकल लेजर स्कैनिंग माइक्रोस्कोपी (सी.एल.एस.एम), और छोटे-कोण एक्स-रे बिखराव (एस.ए.एक्स.एस), आदि शामिल हैं।

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4/6/8amine	N-butyl/n-hexyl/n-octyl amine
ABX_3	Empirical formula for 3D halide perovskites
ACN	Acetonitrile
AFBn	4-Amino-2,5-difluorobenzonitrile
AFM	Atomic force microscopy
AM	Air mass
ASTM	American Society for Testing and Materials
CB	Chlorobenzene
CLSM	Confocal laser scanning microscopy
DLS	Dynamic light scattering
DMF	N,N'-dimethylformamide
DMSO	Dimethyl sulfoxide
E/HTL	Electron/Hole transport layer
FAMACs	Triple cation perovskite
FF	Fill factor
FTFA	4-Fluoro-3-(trifluoromethyl)aniline
GBL	γ-butyrolactone
HP	Halide perovskite
HRTEM	High resolution transmission electron microscopy
IPA	Iso propyl alcohol
I_{sc}	Short circuit current
ITO	Indium tin oxide
J-V plot	Current density versus voltage plot
MAPI	Methylammonium lead triiodide
MAX	Maximum
meV	Milli electron volt
MIN	Minimum
MOC	Manders overlap coefficient
NMP	N-methyl-2-pyrrolidone
OA	Oleic acid

P30ACN200	200 mg ml^{-1} MAPI microparticles in 30 mg ml^{-1} of PMMA in ACN
P3HT	Poly(3-hexylthiophene-2,5-diyl)
PC61BM	[6,6]-Phenyl C61 butyric acid methyl ester
PCC	Pearson's correlation coefficient
PCE	Power conversion efficiency
PEDOT complex	Poly(3,4-ethylenedioxythiophene) complex
PMMA	Poly(methyl methacrylate)
PSC	Perovskite solar cell
PxACN	PMMA in acetonitrile in x mg ml^{-1}
RMS	Root mean square
SAED	Selected area electron diffraction
SAXS	Small angle X-ray scattering
SEM	Scanning electron microscopy
STC	Standard test and conditions
tBP	4-tert-butylpyridine
tDoS	Transient density of states
TPV/C	Transient photo voltage/current
TRPL	Time resolved photoluminescence
UV-vis-PL/UV-PL	Ultraviolet-visible absorption and photoluminescence spectrum
V_{oc}	Open circuit voltage
XRD	X-ray diffraction