

**STABILIZATION OF THE LEAD HALIDE
PEROVSKITE NANOCRYSTALS VIA FORMING
NANOHETEROSTRUCTURES**

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**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
JUNE 2024**

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by

SWATI KHURANA

DEPARTMENT OF CHEMISTRY

Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

JUNE 2024

Dedicated to
my parents

CERTIFICATE

This is to certify that the thesis entitled, “**STABILIZATION OF THE LEAD HALIDE PEROVSKITE NANOCRYSTALS VIA FORMING NANOHETEROSTRUCTURES**” being submitted by **Ms. Swati Khurana** to the **Indian Institute of Technology Delhi** for the award of the degree of **Doctor of Philosophy** in Chemistry, represents genuine research conducted by her. Ms. Swati Khurana has conducted this research under my guidance and supervision. She has successfully met the submission requirements for this thesis, which, to the best of my knowledge, meets the necessary standards.

Date

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ACKNOWLEDGEMENTS

After five years of being part of NANOLAB, I have finally reached a significant milestone by completing my doctoral research journey at the Department of Chemistry, IIT Delhi. The completion of this thesis owes much to the guidance, support, and encouragement of several people. At this moment, I am truly grateful to express my heartfelt appreciation and profound gratitude to all those who have offered their indispensable contributions to this thesis.

First and foremost, I wish to express my sincere and profound gratitude to my supervisor, ***Prof. Sameer Sapra*** from IIT Delhi, for his exceptional mentorship, unwavering motivation, unconditional support, insightful suggestions, and continuous encouragement throughout my doctoral research. His meticulous guidance helped me in all aspects during my experimental work as well as writing manuscripts of my thesis and research articles. I am profoundly inspired by his inquisitive and passionate approach to research. He consistently offered his support and motivation during challenging phases of my research endeavours. He makes himself always available for the constructive discussions and offers invaluable insights. He generously provided me freedom and time to explore innovative ideas throughout my PhD pursuit. Apart from this, I am grateful for his compassionate, remarkable, and benevolent nature. His genuine concern for both my academic and personal welfare is deeply appreciated.

In addition to my supervisor, I would like to express my heartfelt appreciation to all our wonderful collaborators *Prof. Dibyajyoti Ghosh, Prof. Pralay K. Santra, and Prof. Manash R. Das* for providing the facilities and engaging in fruitful discussions, both of which have greatly contributed to the advancement of my research. I express my sincere gratitude to *Prof. Dibyajyoti Ghosh* for his intellectual contributions in enhancing my understanding of theoretical studies. Also, my sincere thanks to *Prof. Pralay K. Santra, and Prof. Manash R. Das* for helping me with the characterization techniques that have contributed immensely towards my research work.

I wish to convey my heartfelt gratitude to both past and present heads of our department *Prof. Ashok K. Ganguly, Prof. Anil J. Elias, Prof. Narayanan D Kurur and Prof. Siddharth Pandey* for providing all the necessary facilities in the department. I would like to take this opportunity to express my gratitude to all the SRC members *Prof. Ashok K. Ganguly, Prof. Pramit K. Chowdhury, and Prof. Nirat Ray* for their unwavering encouragement and support.

I would also like to extend my appreciation to the Central Research Facility (CRF), Sophisticated Analytical and Technical Help Institutes (SATHI) Foundation at IIT Delhi, for generously providing access to a wide array of characterization techniques. Their support has been instrumental in facilitating the smooth progress of my research work.

I would like to express my genuine appreciation to all the administrative and instrumentation lab staff for their assistance and cooperation with all official and instrumental activities. I express my sincere gratefulness to IIT Delhi for providing me with the funding during my PhD work, also for the international travel grant.

It gives me great pleasure to extend my heartfelt gratitude to all my wonderful lab mates who have made significant contributions to this thesis. I have gained valuable skills and knowledge from each of my esteemed fellow lab members. First and foremost, I express my heartfelt gratitude to all the senior members of my lab: *Dr. Md Samim Hassan, Dr. Ajeet Singh, Dr. Raman Singh Lamba, Dr. Priyesh Yadav, and Sahil Singh*. I deeply value their guidance, motivation, warm affection, and constant support during difficult times, as well as the invaluable scientific interactions we have shared. I would like to extend my heartfelt gratitude to all the post-doctoral fellows in the lab, namely *Dr. Puspanjali Tripathy, Dr. Arkajyoti Chakrabarty, Dr. Jitendra Kumar, Dr. Sushma Yadav, and Dr. Rajyashree Chithajallu, and Dr. Umesh Yadav*. Their invaluable contributions in terms of experience, knowledge, and skills

have profoundly influenced my personal and academic growth. I feel privileged to have delightful and jovial colleagues and juniors: *Rachna, Kriti Choudhary, Varsha Jha, Shubham Kumar, Jyoti Yadav, and Twinkle Jain*. I take this opportunity to express my gratitude to all the M.Sc. and M.Tech students: *Sagar, Utkarsh, Sunil, Animesh, Priyanka, Shashank, Vidya, Ashutosh, Komal, Aakansha, Reetika, Faisal, and Pulkit, Deepak Kumar Pradhan, Suvadip Saha*.

Indeed, I have gleaned a wealth of knowledge from my seniors, and I am grateful to acknowledge their invaluable guidance and mentorship. I extend my sincere thanks to *Dr. Arkajyoti Chakrabarty* for his unwavering encouragement, guidance, support, and invaluable scientific insights. I am indebted to *Dr. MD Samim Hassan* for his steadfast support and exhaustive discussions regarding scientific complexities, especially for providing me with important suggestions to improve my writing skills. He makes himself always available to check my write-up and share insightful scientific discussions related to them. I express my heartfelt thanks to *Dr. Priyesh Yadav*, senior-cum-like best friend for his continuous encouragement, support, motivation, and invaluable scientific arguments, which sharpened my critical thinking of the subject. He consistently dedicates his time to review my written work and partake in insightful scientific dialogues related to them. I consider myself fortunate to have a friend who consistently supports and motivates me. I appreciate his genuine concern for both my academic and personal well-being. I would also like to extend my gratitude to *Dr. Raman Singh Lamba* for his valuable discussions, suggestions, and engaging in both scientific and non-scientific arguments.

I have no words to express my sincere thanks to all my friends at IIT Delhi. Life at IIT Delhi would have been considerably dull without the presence of my wonderful friends. Their friendship has added vibrancy and joy to my life. I am lucky to have friends like Priyesh, Samim, Raman, Sahil, Neha, Swati, Rajat, Jyoti, Vikas, Shashank, Sonia. I mustn't overlook

my friends outside of IIT Delhi, who have always stood by me regardless of the circumstances. I am grateful to Ankit Bhoriya for his constant support and motivation, Garima Sindwani, and Jyoti Yadav for their presence in my life.

I wish to extend my heartfelt gratitude to my family members, whose influence has been pivotal in shaping my thesis. Their enduring love, support, motivation, and unwavering confidence in me have been invaluable throughout this journey. I am truly grateful for their presence and steadfast belief in my abilities. Words cannot fully express my deep gratitude for them. I consider myself incredibly fortunate to have the blessings of my late grand-parents **Mr. Jagdish Chander Khurana** and **Mrs. Bhagwanti Khurana** and parents **Mr. Rajesh Khurana** and **Mrs. Seema Khurana**. They always bless me with their unwavering care and affection, instilling strong moral values within me. These values empower me to confront life's challenges with resilience and strength. Their sacrifices and dedication have inspired me to strive for excellence. I am indebted to them for their immeasurable contributions to my education and personal growth. I am deeply grateful to my brother **Parveen Khurana**, for his unwavering love, support, encouragement, and belief in my abilities throughout my academic journey. His constant motivation and understanding have been instrumental in my academic journey, and I am deeply appreciative of his presence in my life.

Finally, I wish to express my gratitude to all individuals who have played integral roles in the successful completion of this thesis. I sincerely apologize if I have inadvertently overlooked or not adequately recognized anyone's contributions.

Last but certainly not least, I extend my heartfelt thanks to God for blessing me with the patience and strength required to complete my Ph.D. journey.

Swati Khurana

ABSTRACT

All inorganic lead halide perovskites (LHPs) have triggered much attention for energy harvesting applications owing to their interesting optoelectronic properties, such as high absorption coefficient, high photoluminescence quantum yield (PLQY), tunable band gap, long charge carrier diffusion length, and high charge carrier mobility. However, these materials are enriched with surface defects due to the presence of large number of halide vacancies which acts as the trapping centers for charge carriers, resulting in the lowering of PLQY and stability of LHPs. Additionally, these LHPs suffer from poor power conversion efficiency as compared to their organic-inorganic counterparts owing to their faster charge carrier recombination and narrow absorption window, which limits their photovoltaic performance. The present thesis focuses on enhancing the stability, rate of charge transport, and absorption windows of the perovskites via coupling it with other semiconducting materials. In this regard, we have used both in-situ and ex-situ methods to synthesize the nanoheterostructures of perovskite with other semiconducting materials, which results in the improved optical properties, enhancement of stability. Additionally, these heterostructures can be further utilized in the energy harvesting or photovoltaic application.

The first two chapters (**Chapter 1 and 2**) are dedicated to the extensive literature survey of research work related to LHPs, metal chalcogenides, their structure, applications, challenges, and possible solutions, along with summary of various techniques used for the characterization of as-synthesized materials. In **Chapter 3**, we have developed a route for the synthesis of $\text{CsPbBr}_3\text{-CdSe/CdS/ZnS}$ (CSS) mixed dimensional nanohybrids (MDNHs) using various bifunctional ligands, such as 4-aminothiophenol (4-ATP), p-aminobenzoic acid (PABA), and 6-amino-2-naphthoic acid (ANA), which results in the increased absorption windows and better charge separation. These MDNHs form donor-bridge-acceptor systems, where the electronic interaction is greatly influenced by the nature of ligands. We observe that in the case

of 4-ATP, the charge transfer rate is most efficient as compared to other ligands because of smaller size and stronger binding affinity. In **Chapter 4**, a colloidal route is developed for designing CsPbBr₃-PbSe nanoheterostructures (NHSs) and other derivatives of LHPs-based NHSs using defect-rich MoSe₂ nanosheets (NSs) and selenium powder as selenium precursors and discussed the mechanism of the formation of NHSs. In MoSe₂-synthesized NHSs, the size of PbSe is ~2.0 nm, whereas, for synthesis involving Se powder, the size is approximately 3.4 nm. A nearly 3-fold PL enhancement is observed in the former case, whereas Se powder resulted in negligible PL enhancement, as compared to pure CsPbBr₃ NCs. Despite having type-I band alignment, the huge PL enhancement in MoSe₂-synthesized NHSs suggests very strong passivation of defects, which is also corroborated with all photophysical studies. In **Chapter 5**, we have utilized the PbSe decorated perovskite to prevent the halide diffusion in CsPbBr₃/CsPbI₃ NHSs. Spatially resolved elemental analysis reveals that the halides do not diffuse across the heterostructure interface, whereas in case of pristine CsPbBr₃/CsPbI₃ NHSs, rapid homogenization of the halides occur, leading to the loss of sharp interfaces. Inhibition of ion diffusion is further evidenced from spectroscopic measurements, revealing consistent emission from both CsPbBr₃ and CsPbI₃ within the nanoheterostructures for several months. Moreover, halide interdiffusion is inhibited even upon heating the PbSe decorated heterostructure for several hours at high temperature. Furthermore, we have fabricated a phosphor converted white light emitting diode (pc-LED) using PbSe decorated CsPbBr₃/CsPbI₃ heterostructures, which exhibits stable luminescence from both the CsPbBr₃ and CsPbI₃ layers, with no evidence of ion diffusion during operation. In **Chapter 6**, we study the impact of various lead chalcogenides on the stability and optical properties of perovskite via making their heterostructures with PbE (E = S, Se, Te). In this synthesis route, lead chalcogenides are formed at an early stage of reaction which then undergoes consumption to form CsPbBr₃-PbE and CsPbI₃-PbE NHSs. Optical and structural characterization confirmed

the formation of NHSs. The resultant NHSs exhibited enhanced optical properties, indicating the passivation of surface defects of perovskite in all three NHSs. The maximum enhancement is observed in case of PbTe passivated NHSs, owing to the more covalent nature of PbTe as compared to other lead chalcogenides. Moreover, CsPbBr₃-PbE NHSs exhibit improved stability in the presence of water and do not degrade under ambient conditions for several months. **Chapter 7** provides a comprehensive summary of the thesis, with particularly emphasizing on enhancing the stability and overall photovoltaic performance of perovskites via coupling it with other semiconductors and provides an insightful glimpse into the future prospects and potential implications of the whole work described herein.

संक्षेपण

सभी अकार्बनिक लेड हैलाइड पेरोव्स्काइट्स (एलएचपी) ने अपने दिलचस्प ऑटोइलेक्ट्रॉनिक गुणों, जैसे उच्च अवशोषण गुणांक, उच्च फोटोल्यूमिनेशन क्वांटम उपज (पीएलक्यूवाई), ट्यूनेबल बैंड गैप, लंबी चार्ज वाहक प्रसार लंबाई और उच्च चार्ज वाहक गतिशीलता के कारण ऊर्जा संचयन अनुप्रयोगों पर अधिक ध्यान आकर्षित किया है। हालाँकि, बड़ी संख्या में हैलाइड रिक्तियों की उपस्थिति के कारण ये सामग्रियाँ सतह दोषों से समृद्ध होती हैं जो चार्ज वाहक के लिए ट्रैपिंग केंद्र के रूप में कार्य करती हैं, जिसके परिणामस्वरूप पीएलक्यूवाई कम हो जाती है और एलएचपी की स्थिरता होती है। इसके अतिरिक्त, ये एलएचपी अपने तेज चार्ज वाहक पुनर्संयोजन और संकीर्ण अवशोषण विंडो के कारण अपने कार्बनिक-अकार्बनिक समकक्षों की तुलना में खराब बिजली रूपांतरण दक्षता से ग्रस्त हैं, जो उनके फोटोवोल्टिक प्रदर्शन को सीमित करता है। वर्तमान थीसिस अन्य अर्धचालक सामग्रियों के साथ युग्मित करके पेरोव्स्काइट्स की स्थिरता, चार्ज परिवहन की दर और अवशोषण खिड़कियों को बढ़ाने पर केंद्रित है। इस संबंध में, हमने अन्य अर्धचालक सामग्रियों के साथ पेरोव्स्काइट के नैनोहेटेरोस्ट्रक्चर को संश्लेषित करने के लिए इन-सीटू और एक्स-सीटू दोनों तरीकों का उपयोग किया है, जिसके परिणामस्वरूप ऑप्टिकल गुणों में सुधार हुआ है, स्थिरता में वृद्धि हुई है। इसके अतिरिक्त, इन हेटेरोस्ट्रक्चर का उपयोग ऊर्जा संचयन या फोटोवोल्टिक अनुप्रयोग में किया जा सकता है।

पहले दो अध्याय (अध्याय 1 और 2) एलएचपी, धातु चाल्कोजेनाइड्स, उनकी संरचना, अनुप्रयोगों, चुनौतियों और संभावित समाधानों से संबंधित शोध कार्यों के व्यापक साहित्य सर्वेक्षण के साथ-साथ इनके लक्षण वर्णन के लिए उपयोग की जाने वाली विभिन्न तकनीकों के सारांश के लिए समर्पित हैं। -संश्लेषित सामग्री अध्याय 3 में, हमने 4-एमिनोथियोफेनोल (4-ATP), पी-एमिनोबेंजोइक एसिड (PABA), और 6-अमीनो-2-नैफथोइक एसिड (ANA), जिसके परिणामस्वरूप अवशोषण विंडो में वृद्धि होती है और बेहतर चार्ज पृथक्करण होता है। ये एमडीएनएच डोनर-ब्रिज-स्वीकर्ता सिस्टम बनाते हैं, जहां इलेक्ट्रॉनिक इंटरैक्शन लिगेंड की प्रकृति से काफी प्रभावित होता है। हमने देखा कि 4-ATP के मामले में, छोटे आकार

और मजबूत बाइंडिंग एफ़िनिटी के कारण चार्ज ट्रांसफर दर अन्य लिगेंड की तुलना में सबसे कुशल है। अध्याय 4 में, $\text{CsPbBr}_3\text{-PbSe}$ नैनोहेटेरोस्ट्रक्चर (NHS) और LHPs-आधारित NHS के अन्य डेरिवेटिव को सेलेनियम अग्रदूतों के रूप में दोष-समृद्ध MoSe_2 नैनोशीट्स (NSs) और सेलेनियम पाउडर का उपयोग करके डिजाइन करने के लिए एक कोलाइडल मार्ग विकसित किया गया है और NHS के गठन के तंत्र पर चर्चा की गई है। MoSe_2 -संश्लेषित NHS में, PbSe का आकार ~ 2.0 एनएम है, जबकि, Se पाउडर से जुड़े संश्लेषण के लिए, आकार लगभग 3.4 एनएम है। पहले मामले में लगभग 3 गुना पीएल वृद्धि देखी गई है, जबकि शुद्ध सीएसपीबीबीआर₃ एनसी की तुलना में एसई पाउडर के परिणामस्वरूप नगण्य पीएल वृद्धि हुई है। टाइप-I बैंड संरक्षण होने के बावजूद, MoSe_2 -संश्लेषित एनएचएस में भारी पीएल वृद्धि दोषों के बहुत मजबूत निष्क्रियता का सुझाव देती है, जो सभी फोटोफिजिकल अध्ययनों से भी पुष्टि होती है। अध्याय 5 में, हमने $\text{CsPbBr}_3/\text{CsPbI}_3$ NHS में हैलाइड प्रसार को रोकने के लिए PbSe सजाए गए पेरोव्स्काइट का उपयोग किया है। स्थानिक रूप से हल किए गए तात्विक विश्लेषण से पता चलता है कि हैलाइड हेटेरोस्ट्रक्चर इंटरफ़ेस में फैलते नहीं हैं, जबकि प्राचीन $\text{CsPbBr}_3/\text{CsPbI}_3$ NHS के मामले में, हैलाइड का तेजी से समरूपीकरण होता है, जिससे तेज इंटरफ़ेस का नुकसान होता है। स्पेक्ट्रोस्कोपिक माप से आयन प्रसार में अवरोध का और भी प्रमाण मिलता है, जिससे कई महीनों तक नैनोहेटेरोस्ट्रक्चर के भीतर CsPbBr_3 और CsPbI_3 दोनों से लगातार उत्सर्जन का पता चलता है। इसके अलावा, उच्च तापमान पर कई घंटों तक PbSe सजाए गए हेटेरोस्ट्रक्चर को गर्म करने पर भी हैलाइड इंटरडिफ्यूजन बाधित होता है। इसके अलावा, हमने PbSe से सुसज्जित $\text{CsPbBr}_3/\text{CsPbI}_3$ हेटेरोस्ट्रक्चर का उपयोग करके एक फॉस्फोर परिवर्तित सफेद प्रकाश उत्सर्जक डायोड (पीसी-एलईडी) बनाया है, जो CsPbBr_3 और CsPbI_3 दोनों परतों से स्थिर ल्यूमिनेसेंस प्रदर्शित करता है, जिसमें ऑपरेशन के दौरान आयन प्रसार का कोई सबूत नहीं होता है। अध्याय 6 में, हम PbE ($E = \text{S, Se, Te}$) के साथ उनकी हेटेरोस्ट्रक्चर बनाकर पेरोव्स्काइट की स्थिरता और ऑप्टिकल गुणों पर विभिन्न लेड चॉकोजेनाइड्स के प्रभाव का अध्ययन करते हैं। इस संश्लेषण मार्ग में, प्रतिक्रिया के प्रारंभिक चरण में लेड चॉकोजेनाइड्स

बनते हैं जो फिर $\text{CsPbBr}_3\text{-PbE}$ और $\text{CsPbI}_3\text{-PbE}$ NHS बनाने के लिए खपत से गुजरते हैं। ऑप्टिकल और संरचनात्मक लक्षण वर्णन ने एनएचएस के गठन की पुष्टि की। परिणामी एनएचएस ने उन्नत ऑप्टिकल गुणों का प्रदर्शन किया, जो तीनों एनएचएस में पेरोव्स्काइट के सतह दोषों के पारित होने का संकेत देता है। अन्य लेड चॉकोजेनाइड्स की तुलना में PbTe की अधिक सहसंयोजक प्रकृति के कारण, PbTe निष्क्रिय एनएचएस के मामले में अधिकतम वृद्धि देखी गई है। इसके अलावा, $\text{CsPbBr}_3\text{-PbE}$ NHS पानी की उपस्थिति में बेहतर स्थिरता प्रदर्शित करते हैं और कई महीनों तक परिवेशी परिस्थितियों में खराब नहीं होते हैं। अध्याय 7 थीसिस का एक व्यापक सारांश प्रदान करता है, जिसमें विशेष रूप से स्थिरता और समग्र फोटोवोल्टिक को बढ़ाने पर जोर दिया गया है। अन्य अर्धचालकों के साथ युग्मित करके पेरोव्स्काइट्स का प्रदर्शन और यहां वर्णित संपूर्ण कार्य की भविष्य की संभावनाओं और संभावित प्रभावों की एक अंतर्दृष्टिपूर्ण झलक प्रदान करता है।

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GLOSSARY OF SYMBOLS AND ABBREVIATIONS

MHP	Metal halide perovskites
PLQY	photoluminescence quantum yield
FWHM	Full width at half-maximum
NCs	nanocrystals
3D	Three-dimensional
MA	methyllummonium
FA	formamidinium
t	tolerance factor
RT	Room temperature
μ	octahedral factor
DOS	Density of states
PL	photoluminescence
$D_{n,p}$	diffusion coefficient
$\mu_{n,p}$	carrier mobility
VBM	Valence band maximum
SOC	Spin-orbit coupling
PeLEDs	perovskite LEDs
LCDs	liquid-crystal displays
LEDs	light-emitting diodes
PCE	power conversion efficiency
NPLs	nanoplatelets
TMDs	transition metal dichalcogenides
NSs	nanosheets

NIR	near-infrared region
CVD	chemical vapor deposition
QDs	quantum dots
NRs	nanorods
ASE	amplified spontaneous emission
CB	conduction band
VB	valence band
PbE	lead chalcogenide
CSS	CdSe/CdS/ZnS
4-ATP	4-aminothiophenol
PABA	p-aminobenzoic acid
ANA	6-amino-2-naphthoic acid
LHPs	Lead Halide Perovskites
XRD	X-ray diffraction
TEM	transmission electron microscopy
FESEM	field emission scanning electron microscopy
¹ H-NMR	Proton nuclear magnetic resonance
TRPL	time resolved photoluminescence
EDX	Energy dispersive X-ray
FTIR	Fourier transform infrared
XPS	X-ray photoelectron spectroscopy
ICP-OES	inductively coupled plasma optical emission spectroscopy
HRTEM	High-Resolution Transmission Electron Microscopy HRTEM
K.E.	kinetic energy
B.E.	binding energy

A	absorbance
T	transmittance
UV	ultraviolet
ps	picosecond
ns	nanoseconds
μ s	microseconds
ms	milliseconds
IC	internal conversion
ISC	intersystem crossing
Γ	fluorescence lifetime
MDNHs	Mixed dimensional nanohybrids
0D	zero-dimensional
2D	two-dimensional
DFT	density functional theory
cALD	colloidal atomic layer deposition
TCSPC	time correlated single photon counting
VASP	Vienna ab initio Simulation Package
PAW	projected augmented wave
GGA	generalized gradient approximations
PBE	Perdew-Burke-Ernzerhof functionals
OLAM	oleylamine
Γ_{avg}	average PL lifetime
VBM	Valence band maximum
CBM	conduction band minimum
NHSs	Nanoheterostructures

NPs	nanoparticles
TOP	trioctyl phosphine
OA	oleic acid
FFT	fast Fourier transform
STEM	Scanning transmission electron microscopy
pDOS	partial density of states
Pc-LED	phosphor converted light emitting diodes
eV	electron volts