STABILIZATION OF THE LEAD HALIDE PEROVSKITE NANOCRYSTALS VIA FORMING NANOHETEROSTRUCTURES

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by

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DEPARTMENT OF CHEMISTRY

Submitted

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

to the

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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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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 $CsPbBr_3$−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 seperation. 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 $CsPbBr_3$−PbSe nanoheterostructures (NHSs) and other derivatives of LHPs-based NHSs using defect-rich $MoSe_2$ nanosheets (NSs) and selenium powder as selenium precursors and discussed the mechanism of the formation of NHSs. In $MoSe_2$-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 $CsPbBr_3$ NCs. Despite having type-I band alignment, the huge PL enhancement in $MoSe_2$-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 $CsPbBr_3$/$CsPbI_3$ NHSs. Spatially resolved elemental analysis reveals that the halides do not diffuse across the heterostructure interface, whereas in case of pristine $CsPbBr_3$/$CsPbI_3$ 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 $CsPbBr_3$ and $CsPbI_3$ 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 $CsPbBr_3$/$CsPbI_3$ heterostructures, which exhibits stable luminescence from both the $CsPbBr_3$ and $CsPbI_3$ 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 $CsPbBr_3$-PbE and $CsPbI_3$-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, $CsPbBr_3$-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 ऑप्टोइलेक्ट्रॉनिक 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 सामग्रियां 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 हेटरोस्ट्रक्चर 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-नैफ्थोइक 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 लिगैंड 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, $CsPbBr_3$–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 संरेखण 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 $CsPbBr_3/CsPbI_3$ 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 हेटरोस्ट्रक्चर इंटरफ़ेस में फैलते नहीं हैं, जबकि प्राचीन $CsPbBr_3/CsPbI_3$ NHS के मामले में, हैलाइड का तेजी से समरूपीकरण होता है, जिससे तेज इंटरफेस 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 हेटरोस्ट्रक्चर को गर्म करने पर भी हैलाइड इंटरडिफ्यूजन बाधित होता है। इसके अलावा, हमने PbSe से सुसज्जित $CsPbBr_3/CsPbI_3$ हेटरोस्ट्रक्चर 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 = S, Se, Te) के साथ उनकी हेटरोस्ट्रक्चर 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 $CsPbBr_3$-PbE और $CsPbI_3$-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, $CsPbBr_3$-PbE NHS पानी की उपस्थिति में बेहतर स्थिरता प्रदर्शित करते हैं और कई महीनों तक परिवेशी परिस्थितियों में ख़राब 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	methylammonium
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
μs	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