COLLOIDALLY SYNTHESIZED HETEROSTRUCTURES BASED ON 2D LAYERED SEMICONDUCTORS

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by

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Submitted

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Dedicated to
My Parents

CERTIFICATE

This is to certify that the thesis entitled, "**Colloidally Synthesized Heterostructures of 2D Layered Semiconductors**" being submitted by **Mr. AJEET SINGH** to the **Indian Institute of Technology Delhi** for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of bonafide research work carried out by him. Mr. AJEET SINGH has worked under my guidance and supervision. He has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

Every time the study presented is based on the findings of other researchers, proper acknowledgement has been made in accordance with the standard procedure for publishing scientific observations. Any omission that may have resulted from a mistake or a lack of judgement is regrettable.

PROF. SAMEER SAPRA
DEPARTMENT OF CHEMISTRY

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AJEET SINGH

ABSTRACT

The unique and tunable material properties of two-dimensional (2D) molybdenum diselenide include quantum-well structures with a thickness-dependent indirect to direct band transitions, high in-plane charge carrier mobility. Terrace sites at $MoSe_2$ nanosheets' (NS) basal planes are terminated with fewer dangling bonds and are useful for a variety of applications in optoelectronic devices, supercapacitors, and spintronic devices, whereas edge sites on the side surface have more dangling bonds and are active sites for catalytic reactions. Due to ultrathin nature of monolayer of $MoSe_2$ NS, the light-matter interactions decreases and presence of defect in colloidally synthesized NS is also known to affect the optoelectronic properties. To avoid these issues, we synthesized heterostructure of $MoSe_2$ NS with various metal chalcogenide nanoparticles to increase the light matter interaction and passivate the Se-vacancy defects. Like $MoSe_2$, the hybrid organic-inorganic layered halide perovskites (LH-PVSK) also have quasi-2D layered structure with alternating organic and inorganic layers. These LH-PVSK display excellent opto-electronic properties with high mobility of charge carriers. Whereas lead-free layered halide double perovskite (DP-PVSK) analogs of LH-PVSK exhibit very weak and broad white light emission arising due to STE and defects. We synthesized a system by combining the LH-PVSK – DP-PVSK into a core-shell morphology to make it possible to study the anion migration in our weakly emitting DP-PVSK by monitoring the fluorescence spectra of highly emitting LH-PVSK. The work in this thesis emphasizes how to utilize these different 2D materials to realize various heterostructures.

In this thesis, **chapters 1 & 2** provide the detailed introduction of materials and characterization methods. In **chapter 3**, we discuss the synthesis and characterization of 2D/2D $MoSe_2$/SnS NHS and 2D/3D $MoSe_2$/PbE (E=S, Se or Te) NHS using hot-injection synthesis route. The NHS were synthesized in a two-step colloidal route: defect rich (Se-vacancies) pure $MoSe_2$ NS were

synthesized and followed by growth of metal chalcogenide nanocubes (NC) on top of $MoSe_2$ NS. The Se-vacancies in $MoSe_2$ NS were passivated by chalcogenide anions followed by addition of metal precursor. The passivation of Se-vacancies was found to be a thermodynamically controlled process as a high temperature of ≥180°C was required to produce $MoSe_2$/SnS NHS and $MoSe_2$/PbE NHS with intimate contact. The layered crystal structure of SnS allows for the growth of SnS NS on top of $MoSe_2$ NS resulting in a unique 2D/2D NHS. We utilized the as synthesized type-II $MoSe_2$/SnS NHS in electrocatalytic water splitting and found that the $MoSe_2$/SnS NHS is a better electrocatalyst in comparison to both pure $MoSe_2$ NS and SnS NC due to the in-built potential at the interface which reduces the charge transfer resistance. In **chapter 4**, we discuss the synthesis and the ultrafast charge transfer in 1D/2D CdS/$MoSe_2$ nanorod (NR) on NS NHS. Unlike chapter 3, the synthesis scheme here involves growth of $MoSe_2$ NS on top of NR surface. As a promising heterostructure for the application in photocatalytic water splitting, we took the opportunity to synthesize, characterize and study the charge transfer at the interface of $MoSe_2$ NS and CdS NR in CdS/$MoSe_2$ NHS. The NHS was synthesized using a two-step synthesis route: CdS NR were synthesized using hydrothermal route and followed by growth of $MoSe_2$ NS around CdS NR using hot-injection colloidal method. Transient absorption (TA) spectroscopy was used to understand the charge carrier dynamics at the interface of CdS NR and $MoSe_2$ NS. The observed ultrafast charge transfer from CdS NR to $MoSe_2$ NS showed the ultrafast charge separation in the CdS/$MoSe_2$ NHS. In **chapter 5**, we discuss the synthesis and characterization of heterostructures of layered halide perovskites. We synthesized 16 different core/shell heterostructures of non-emitting or weakly emitting DP-PVSK as shell, and highly emitting LH-PVSK as core. We investigated the evolution of morphology of shell as a function of number of times the shell growth reaction is repeated on same set of particles. We analyzed electron diffraction patterns obtained

from pure LH-PVSK core and the core-shell LH-PVSK – DP-PVSK heterostructure to understand the crystal orientation of the heterostructure particles. This core-shell morphology provides a unique opportunity to study the structure-property relationship of non-emitting or weakly emitting DP-PVSK. The anion diffusion in DP-PVSK shell was studied by monitoring the changes in fluorescence spectra of lead-based layered halide perovskite. We established that the choice of organic spacer cation as well as the metal cation affects the anion diffusion.

In summary, we have successfully synthesized the $MoSe_2$ NS based $MoSe_2$/PbE and $MoSe_2$/SnS NHS, characterized and utilized the $MoSe_2$/SnS NHS in electrocatalytic water splitting. We also realized the growth of $MoSe_2$ NS on CdS NC and established the ultrafast hot electron transfer from CdS to $MoSe_2$ NS. We have synthesized a core-shell heterostructure of lead-based and lead-free layered halide perovskites to study the structure-property relationship in lead-free layered halide perovskite using fluorescence spectroscopy.

सारांश

द्वि-आयामी (2 डी) $MoSe_2$ के अद्वितीय और बदलने योग्य सामग्री गुणों में क्वांटम-कुंआ संरचनाएं शामिल हैं, जिनमें मोटाई-निर्भर अप्रत्यक्ष से प्रत्यक्ष ऊर्जा अंतराल संक्रमण, उच्च अंतर्निर्मित-सतह चार्ज वाहक गतिशीलता शामिल है। $MoSe_2$ नैनोशीट्स (एनएस) आधार वाला सतह में छत साइटें कम झूलते बंधनों के साथ समाप्त हो जाती हैं और ऑप्टोइलेक्ट्रोनिक उपकरणों, सुपरकैपेसिटर और स्पिनट्रोनिक उपकरणों में विभिन्न अनुप्रयोगों के लिए उपयोगी होती हैं, जबकि पार्श्व सतह पर किनारे की साइटों में अधिक झूलते बंधन होते हैं और उत्प्रेरक प्रतिक्रियाओं के लिए सक्रिय साइटें होती हैं। $MoSe_2$ एनएस के एक परत की बेहद पतली प्रकृति के कारण, प्रकाश-पदार्थ इंटरैक्शन कम हो जाता है और कोलाइडल रूप से संश्लेषित एनएस में दोष की उपस्थिति को ऑप्टोइलेक्ट्रॉनिक गुणों को प्रभावित करने के लिए भी जाना जाता है। अंतर्निर्मित मुद्दों से बचने के लिए, हमने प्रकाश पदार्थ की परस्पर क्रिया को बढ़ाने और सी-रिक्ति दोषों को दूर करने के लिए विभिन्न धातु चाल्कोजेनाइड नैनोकणों के साथ $MoSe_2$ एनएस के विषम संरचना को संश्लेषित किया। $MoSe_2$ की तरह, संकर कार्बनिक-अकार्बनिक स्तरित हलाइड पेरोवेक्साइट (एलएच-पीवीएसके) में वैकल्पिक कार्बनिक और अकार्बनिक परतों के साथ अर्ध-2 डी स्तरित संरचना भी होती है। ये एलएच-पीवीएसके चार्ज वाहक की उच्च गतिशीलता के साथ उत्कृष्ट ऑप्टो-इलेक्ट्रॉनिक गुणों को प्रदर्शित करते हैं। जबकि एलएच-पीवीएसके के लेड-फ्री बहुस्तरीय हैलाइड दोहरा पेरोवेक्साइट (डीपी-पीवीएसके) अनुरूप एसटीई और दोषों के कारण उत्पन्न होने वाले बहुत कमजोर और व्यापक सफेद प्रकाश उत्सर्जन का प्रदर्शन करते हैं। हमने एलएच-पीवीएसके - डीपी-पीवीएसके को आन्तरक-आवरण आकृति विज्ञान में जोड़कर एक प्रणाली को संश्लेषित किया ताकि अत्यधिक उत्सर्जक एलएच-पीवीएसके के प्रतिदीप्ति स्पेक्ट्रा की निगरानी करके हमारे कमजोर उत्सर्जक डीपी-पीवीएसके में आयनप्रवास का अध्ययन करना संभव हो सके। इस

थीसिस में काम इस बात पर जोर देता है कि विभिन्न विषम संरचना को प्राप्त करने के लिए अंतर्निर्मित विभिन्न 2 डी सामग्रियों का उपयोग कैसे किया जाए।

इस थीसिस में, **अध्याय 1 और 2** सामग्री और लक्षण वर्णन विधियों का विस्तृत परिचय प्रदान करते हैं। **अध्याय 3** में, हम गर्म-अन्तःक्षेपण संश्लेषण मार्ग का उपयोग करके 2 डी / 2 डी $MoSe_2$ /SnS एनएचएस और 2 डी / 3 डी $MoSe_2$ /PbE (E = S, Se या Te) एनएचएस के संश्लेषण और लक्षण वर्णन पर चर्चा करते हैं। एनएचएस को दो-चरणीय कोलाइडल मार्ग में संश्लेषित किया गया था: दोष समृद्ध (Se-रिक्तियां) शुद्ध $MoSe_2$ एनएस को संश्लेषित किया गया था और इसके बाद $MoSe_2$ एनएस के शीर्ष पर धातु चाल्कोजेनाइड नैनोक्यूब्स (एनसी) की वृद्धि हुई थी। $MoSe_2$ एनएस में Se-रिक्तियों को धातु अग्रदूत के अलावा चाल्कोजेनाइड आयनों द्वारा पारित किया गया था। Se-रिक्तियों की निष्क्रियता एक ऊष्मप्रवैगिकी रूप से नियंत्रित प्रक्रिया पाई गई क्योंकि अंतरंग संपर्क के साथ $MoSe_2$/SnS एनएचएस और $MoSe_2$/PbE एनएचएस का उत्पादन करने के लिए $\geq$180 डिग्री सेल्सियस के उच्च तापमान की आवश्यकता थी। SnS की स्तरित क्रिस्टल संरचना $MoSe_2$ एनएस के शीर्ष पर SnS एनएस के विकास की अनुमति देती है जिसके परिणामस्वरूप एक अद्वितीय 2 डी / 2 डी एनएचएस होता है। हमने विद्युत द्वारा उत्पन्न रासायनिक विघटन जल विभाजन में संश्लेषित प्रकार-2 $MoSe_2$/SnS एनएचएस का उपयोग किया और पाया कि $MoSe_2$/SnS एनएचएस अंतराफलक पर अंतर्निर्मित क्षमता के कारण शुद्ध $MoSe_2$ एनएस और SnS एनसी दोनों की तुलना में बेहतर विद्युत उत्प्रेरक है जो चार्ज स्थानांतरण प्रतिरोध को कम करता है। **अध्याय 4** में, हम एनएस एनएचएस पर 1 डी / 2 डी CdS/ $MoSe_2$ नैनोरोड (एनआर) में संश्लेषण और अति तेज चार्ज स्थानांतरण पर चर्चा करते

हैं। अध्याय 3 के विपरीत, यहां संश्लेषण योजना में एनआर सतह के शीर्ष पर $MoSe_2$ एनएस का विकास शामिल है। प्रकाश उत्प्रेरक जल विभाजन में आवेदन के लिए एक आशाजनक संरचना के रूप में, हमने $CdS/MoSe_2$ एनएचएस में $MoSe_2$ एनएस और CdS एनआर के अंतराफलक पर चार्ज स्थानांतरण को संश्लेषित, चिह्नित और अध्ययन करने का अवसर लिया । एनएचएस को दो-चरण संश्लेषण मार्ग का उपयोग करके संश्लेषित किया गया था: CdS एनआर को जलतापीय मार्ग का उपयोग करके संश्लेषित किया गया था और इसके बाद गर्म-अन्तःक्षेपण कोलाइडल विधि का उपयोग करके CdS एनआर के आसपास $MoSe_2$ एनएस की वृद्धि हुई थी। क्षणिक अवशोषण (टीए) किरणों के वर्ण-क्रम को मापने की विद्या का उपयोग CdS एनआर और $MoSe_2$ एनएस के अंतराफलक पर चार्ज वाहक गतिशीलता को समझने के लिए किया गया था। CdS एनआर से $MoSe_2$ एनएस में देखे गए अति तेज चार्ज स्थानांतरण ने $CdS/MoSe_2$ एनएचएस में अति तेज चार्ज पृथक्करण को दिखाया। **अध्याय 5** में, हम स्तरित हलाइड पेरोवेक्साइट के विषम संरचना के संश्लेषण और लक्षण वर्णन पर चर्चा करते हैं। हमने आवरण के रूप में गैर-उत्सर्जक या कमजोर रूप से उत्सर्जित डीपी-पीवीएसके के 16 अलग-अलग आन्तरक/आवरण विषम संरचना को संश्लेषित किया, और आन्तरक के रूप में अत्यधिक उत्सर्जित एलएच-पीवीएसके। हमने आवरण के आकृति विज्ञान के विकास की जांच की, कणों के एक ही सेट पर आवरण विकास प्रतिक्रिया को दोहराया है। हमने शुद्ध एलएच-पीवीएसके आन्तरक और आन्तरक-आवरण एलएच-पीवीएसके - डीपी-पीवीएसके से प्राप्त विद्युदअणु विवर्तन प्रतिमा आकार का विश्लेषण किया ताकि खगोल कणों के क्रिस्टल अभिविन्यास को समझा जा सके। यह आन्तरक-आवरण आकृति विज्ञान गैर-उत्सर्जक या कमजोर उत्सर्जक डीपी-पीवीएसके की संरचना-संपत्ति संबंध का अध्ययन करने का एक अनूठा अवसर प्रदान करता है। डीपी-पीवीएसके आवरण में आयन प्रसार का अध्ययन

लेड-आधारित स्तरित हैलाइड पेरोवेक्साइट के प्रतिदीप्ति स्पेक्ट्रा में परिवर्तन की निगरानी करके किया गया था। हमने स्थापित किया कि कार्बनिक स्पेसर केशन के साथ-साथ धातु केशन का विकल्प आयन प्रसार को प्रभावित करता है।

सारांश में, हमने सफलतापूर्वक $MoSe_2$ एनएस आधारित $MoSe_2$/PbE और $MoSe_2$/SnS एनएचएस को संश्लेषित किया है, जो विद्युत द्वारा उत्पन्न रासायनिक विघटन जल विभाजन में $MoSe_2$/SnS एनएचएस की विशेषता और उपयोग करता है। हमने CdS एनसी पर $MoSe_2$ एनएस के विकास को भी प्राप्त किया और CdS से $MoSe_2$ एनएस तक अति तेज गर्म विद्युदअणु स्थानांतरण की स्थापना की। हमने प्रतिदीप्ति किरणों के वर्ण-क्रम को मापने की विद्या का उपयोग करके लेड-फ्री बहुस्तरीय हैलाइड पेरोवेक्साइट में संरचना-संपत्ति संबंध का अध्ययन करने के लिए लेड-आधारित और लेड-फ्री बहुस्तरीय हैलाइड पेरोवेक्साइट के एक आन्तरक-आवरण विषम संरचना को संश्लेषित किया है।

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GLOSSARY OF SYMBOL AND ABBREVIATIONS

NC	nanocrystals
NS	nanosheets
NHS	nanoheterostructures
TMDC	transition metal dichalcogenides
MC	metal chalcogenides
DP-PVSK	Layered lead-free halide perovskite
LH-PVSK	Layered lead-based halide perovskite
EIS	electron impedance spectra
LSV	linear sweep voltammetry
HER	hydrogen evolution reaction
OER	oxygen evolution reaction
CB	conduction band
VB	valence band
PL	photoluminescence
DFT	density functional theory
DOS	density of state
nm	nanometer
g	gram
h	hour
min	minute

i.e.,	that is
eV	electron volt
°C	degree centigrade
M	molar