NANOHETEROSTRUCTURES BASED ON THE LAYERED TRANSITION METAL DICHALCOGENIDE MOLYBDENUM DISELENIDE FOR CATALYTIC AND OPTOELECTRONIC APPLICATIONS

MD. SAMIM HASSAN

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
OCTOBER 2020

NANOHETEROSTRUCTURES BASED ON THE LAYERED TRANSITION METAL DICHALCOGENIDE MOLYBDENUM DISELENIDE FOR CATALYTIC AND OPTOELECTRONIC APPLICATIONS

by

MD. SAMIM HASSAN

Department of Chemistry

Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the

INDIAN INSTITUTE OF TECHNOLOGY DELHI

OCTOBER 2020

Dedicated to

My Parents

CERTIFICATE

This is to certify that the thesis entitled, "**NANOHETEROSTRUCTURES BASED ON THE LAYERED TRANSITION METAL DICHALCOGENIDE MOLYBDENUM DISELENIDE FOR CATALYTIC AND OPTOELECTRONIC APPLICATIONS**" being submitted by **Mr. MD. SAMIM HASSAN** 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. MD. SAMIM HASSAN 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.

Prof. Sameer Sapra
Professor
Department of Chemistry
Indian Institute of Technology Delhi

ACKNOWLEDGEMENTS

It took almost six years since my joining the NANOLAB, to achieve this much-vaunted milestone and finish my journey as a doctoral research scholar at the department of Chemistry, IIT Delhi. This thesis owes its existence to the help, support, and inspiration of several people. Now, At this juncture, I feel privileged to express my sincere gratitude towards all those who have extended their valuable assistance and contributed to this thesis in an indispensable manner.

First and foremost, I would like to express my deep and sincere gratitude to my supervisor ***Prof. Sameer Sapra*,** IIT Delhi for his exalting guidance, motivation, unconditional support, suggestions, and encouragement throughout my doctoral research. He introduced me to the scientific community with high-impact researchers and their path-breaking as well as conventional research work and instilled a critical viewpoint toward the scientific problems in me. His careful guidance helped me in all aspects during my experimental work as well as writing manuscripts of my thesis and research articles. I am thoroughly inspired by his curious and enthusiastic nature towards research. He had always been my support and motivation when things did not move as well as expected in my research. He makes himself always ready for the discussions and provides very important suggestions. In his calming presence, a very friendly and stress free work atmosphere is maintained inside the lab, and this is why I never felt embarrassed or low morale during my PhD and my passion in research kept growing day by day in these years. His words '*Enjoy the Science*', are an inspiration to me to enjoy my works and stay in *Nanolab*. He give me full freedom and time to explore new ideas during my PhD. Apart from this, I thank him for being a caring, wonderful, and generous person and also for showing interests in my academic and personal well-being.

In addition to my supervisor, I would like to extend my heartfelt gratitude to all our wonderful and esteemed collaborators *Prof. Nadja C Bigall, Prof. Pravin P. Ingole, Prof. Saswata Bhattacharya, Prof. Samit K. Ray, Prof. Madhusudan Singh* for providing the facilities and useful discussions that have contributed immensely towards my research work. I express my sincere gratitude to *Prof. Nadja C Bigall*, Leibnitz Universität, Germany for giving me an opportunity to work in his lab through scholar exchange visits. It was my great pleasure to learn new things from her research group. Also, my sincere thanks to *Prof. Pravin P. Ingole* for giving me the opportunity to learn the Electrochemistry in his lab. Furthermore, my heartfelt thanks to *Prof. Saswata Bhattacharya* for his intellectual inputs toward understanding the concepts of theoretical studies. I am immensely thankful to *Prof. Samit K. Ray, Prof. Madhusudan Singh, Prof. Pramit K. Chowdhury, Prof. Kamal K. Pant* for providing me with the characterization facilities that have contributed hugely towards my research work. I am grateful to *Prof. Nirat Ray* for her support and help.

I express my deep sense of gratitude to past and present *heads of our department Prof. A. Ramanan, Prof. Ravi Shankar, Prof. Ashok K. Ganguly, Prof. Anil J. Elias* for providing all the necessary facilities in the department. I would like to take this opportunity to thank SRC members *Prof. Nalin Pant, Prof. Pravin P. Ingole, and Prof. Vamsi K. Komarala* for their encouragement and constant support. I wish to convey my sincere thanks to *Prof. Sasanka Deka*, who was an external member of assessment committee for my senior research fellowship.

I would also like to thank Central Research Facility, IIT Delhi; Advanced Instrumentation Research Facility, JNU for providing me with various characterization techniques, which assisted my research work to progress in a smooth manner.

I wish to extend my sincere acknowledgment to all the office staffs, and instrumentation lab staffs for their help and cooperation regarding all official and instrumental activities.

I express my sincere gratitude to University Grant Commission (UGC) for funding, which has made my PhD work possible over here. I would also like to acknowledge IIT Delhi for the international travel grant. I am thankful to DST-DAAD for providing financial aid for travel and stay in Germany.

It is my great pleasure to express heartfelt thanks to all my awesome lab mates who have immensely contributed to this thesis. I gained a lot of skills and knowledge from all my beloved lab members. First of all, I sincerely thank all seniors of my lab: *Dr. Udit Soni, Dr. Vikas Arora, Dr. Anuushka Pal, Dr. Gurpal Singh*, *Dr. Razi Ahmad, Dr. Sushma Yadav, Dr. Mona Mittal, Jaya Lohani* for their guidance, motivation, warm affection and support during the tough times along with healthy scientific interactions. I would like to thank all post-doc fellows: *Dr. Puspanjali Tripathy, Dr. Arpita Sarkar, Dr. Atanu Jana, Dr. Arkajyoti Chakrabarty, Dr. Priya Kush, Dr. Susnata Bera, Dr. Jitendra Kumar* for sharing their experience, knowledge, and skills. I am fortunate to have wonderful and jovial juniors: *Ajeet, Raman, Isha, Priyesh, Sahil, Swati, Kriti, and Rachna*. I take this opportunity to thank all M.Sc. and M.Tech students: *Prateek, Bhawna, Baristar, Diksha, Krishan, Buban, Liza, Beena, Divya, Preeti, Akanksha, Astita, Pradeep, Shahzad, Umesh, Sowmya, Suneel, Ankita, Sagar, Utkarsh, Animesh, Priyanka* and all project trainee: *Sajan, Mamta, Satya, Pallavi, Khagesh, Aayushi, Diksha, Imran, Girija, Ankita, Lekshmi, Suman, Meenakshi, Komal, Samridhi, Kartikey, Keshav*. Their warm affection, support during tough times, nice scientific interactions, involvement, and useful help have bestowed me with a wonderful time during my PhD.

I have learned a lot from my seniors, need to mention. I am thankful to *Dr. Atanu Jana* for his constant support and exhaustive discussions about new scientific problems. I am grateful to *Dr. Arkajyoti Chakrabarty* for his constant guidance and support, especially for providing me with important suggestions to improve my writing skills. He makes himself available every time to check my write-up and share insightful scientific discussions surrounding it. I express my thanks to *Dr. Anuushka Pal*, senior-cum-like elder sister for her continuous encouragement, guidance, support and valuable scientific arguments, which sharpened my critical thinking on the subject. From *Dr. Sushma Yadav,* I have learned to be well-disciplined in lab to prosper in academic research and she acquainted me with the basics about the reactions. I also thank *Dr. Mona* for useful discussions, suggestions and scientific arguments.

Besides, I would like to thank the people who have made my stay pleasant and memorable in Germany. My sincere thanks to *Dr. Steffy* for making me familiar with German system and sharing a quality time with me. I also thank my German lab mates: *Jan, Patrick, Franziska, Pascal, Axel, Marina, Rasmus, Dominik and Torben*.

Words fail me to express my sincere thanks to all my friends at IIT Delhi. Life in IIT Delhi would have been dull without all my pretty wonderful friends. Their friendship has made my life colorful and enjoyable. I express my heartfelt thanks to *Nimai, Soniya, Pooja, Priya* for their help during experimental works. I am lucky to have friends like *Adeel, Shailesh, Tripti, Arif, Krishna, Kapil, Vipin, Sandeep, Sahnawaz, Sanjeev, Faraz, Preeti, Nusrat, Sahadat, Rajan.* I sincerely acknowledge the enormous assistance and persistent encouragement received from my friends *Pintu, Prabhjot, and Zubair*.

Besides, it is my great pleasure to express heartfelt thanks to my BSc., MSc., and MTech. teachers *Prof. Aminul Islam, Prof. M. Muneer, Prof. Suhail Sabir, Prof. Md. Shahid Nayeem, Prof. Md. Palashuddin Sk, Prof. M. Mohsin Khan* for their continuous encouragement.

Now I would like to thank my family members who played a vital role in shaping up my thesis and their constant love, support, motivation, and ever-lasting confidence in me. Words fail me here also to express my gratitude for them. I am fortunate to have the blessings of my parents ***Mr. Ambu Hossain and Mrs. Anowara Hossain***. They always bless and shower their care and love toward me. They have put high moral values inside me and makes me strong enough to face the hurdles in life. I would like to thank my sister (*Nilufa*) and my jiju (*Nur-e-Alam*) for their unconditional love and infusing faith in me. I would like to thank my nephew (*Neeyaz*) for his presence in my life.

I must definitely thank my wife ***Alima*** for her unconditional love, patience, encouragement and constant support. She helped me a lot in every steps to cross the hurdles, faced during PhD. I would like to appreciate and thank my in laws for their faith in my abilities.

Finally, I would like to thank everyone who were essential to the successful compilation of this thesis, and express my apology if I have missed or not elaborated on something.

Last but not the least, I thank ***GOD*** for providing me enough patience and strength in completing my Ph.D.

Md. Samim Hassan

ABSTRACT

Two dimensional (2D) transition metal dichalcogenides (TMDs) have attracted considerable attention because of their unique and tunable material properties such as quantum-well structures with broad range of indirect to direct band gap crossover, thickness dependent band transitions, in-plane charge carrier mobility, high specific surface area, and enhanced spin-orbit coupling. The applications of these materials are highly dependent on the surface sites, *viz.* terrace sites and edge sites. Edge sites on the side surface are useful for various catalytic applications, whereas the terrace sites at basal planes are useful for applications in several optoelectronic devices. The present thesis focuses on how to utilize these different surface sites for various catalytic and optoelectronic device applications *via* developing a number synthetic protocols. In this regard, defect-rich $MoSe_2$ nanosheets are synthesized *via* colloidal route. Furthermore, these defects are utilized for designing nanoheterostructures with different materials. Lattice matched heterostructures have been grown epitaxially and also it has been possible to combine materials with completely different lattice structures by means of bifunctional ligands. A number of applications such as dye-sensitized solar cell (DSC), quantum-dot sensitized solar cell (QDSC), hydrogen evolution reaction (HER), oxygen evolution reaction (OER) and photodetectors, have been attempted with these nanoheterostructures.

The first two chapters (**Chapter 1 and 2**) are dedicated to the extensive literature survey of research work related to TMDs, perovskites, and copper chalcogenides. The synthetic methodologies of synthesis of these materials and their heterostructures, device fabrication procedures, along with brief accounts of various techniques employed for the characterization of as-synthesized materials. In **Chapter 3**, we have developed a colloidal route for the synthesis of

2H-$MoSe_2$ nanosheets (NSs) having large number of defects and vertically aligned edges. We have used these NSs for electrocatalytic HER and as counter electrode in DSCs. In **Chapter 4**, a colloidal route is developed to synthesize $MoSe_2$–Cu_2S nanoheterostructures (NHSs) using defect-rich $MoSe_2$ NSs. These $MoSe_2$–Cu_2S NHSs have been employed for fabrication of photodetectors with superior photo response characteristics. These fabricated devices exhibit a broadband spectral photoresponse over the visible to near infrared range with a high peak responsivity and photo-to-dark current ratio on account of the combined effect of the pronounced light-mater interaction, passivation of surface defects, and formation of p-n junction. In **Chapter 5**, we have investigated the catalytic activities of $MoSe_2$–Cu_2S NHSs in water splitting and as counter electrode in QDSCs. We have shown that the decoration of basal planes of $MoSe_2$ NSs with a catalytic active material and interfacial charge transfer phenomenon enhance the electrocatalytic activities. In **Chapter 6**, we have presented the synthesis of $MoSe_2$–$CsPbBr_3$ nanohybrid structures using a bifunctional ligand *i.e.* 4-aminothiophenol, which forms a donor-bridge-acceptor system having type-II band alignment, leads to the efficient separation of charge carriers. The $MoSe_2$–$CsPbBr_3$ nanohybrids exhibit much higher photocurrent in the photodiode configuration owing to the synergistic effect of pronounced light-matter interaction followed by efficient charge separation and transportation. **Chapter 7** summarizes the results of present thesis, emphasizing the tuning of catalytic and optoelectronic properties of TMDs for various applications and invites a quick glance toward the future prospects of the whole work described herein.

सार

दो आयामी (2 डी) ट्रानज़िशन धातु डाइचाक्लोजेनाइड्स (टीएमडी) ने अपने अद्वितीय और ट्यून किए गए भौतिक गुणों के कारण काफी ध्यान आकर्षित किया है, जैसे कि क्वांटम-कुंआ संरचनाएँ, जिसमें अप्रत्यक्ष से प्रत्यक्ष बैंड गैप क्रॉसओवर, मोटाई पर निर्भर बैंड ट्रानज़िशन,इन-प्लेन चार्ज वाहक गतिशीलता, उच्च विशिष्ट सतह क्षेत्र, और बढ़ा हुआ स्पिन-कक्षा युग्मन व्यापक रेंज के साथ हैं। । इन पदार्थो के अनुप्रयोग सतह साइटों पर अत्यधिक निर्भर हैं, अर्थात, छत साइटे और किनारे साइटे। पार्श्व सतह पर किनारा साइटें विभिन्न उत्प्रेरक अनुप्रयोगों के लिए उपयोगी हैं, जबकि बेसल सतह में छत साइटें कई ऑप्टोइलेक्ट्रोनिक उपकरणों में अनुप्रयोगों के लिए उपयोगी हैं। वर्तमान थीसिस इस बात पर केंद्रित है कि सिंथेटिक प्रोटोकॉल विकसित करके विभिन्न उत्प्रेरक और ऑप्टोइलेक्ट्रोनिक डिवाइस अनुप्रयोगों के लिए इन विभिन्न सतह साइटों का उपयोग कैसे किया जाए। इस संबंध में, डिफैक्ट -समृद्ध $MoSe_2$ नैनोशीट कोलाइडल मार्ग के माध्यम से संश्लेषित की गई। इसके अलावा, इन डिफैक्ट का उपयोग विभिन्न पदार्थो के साथ नैनोहेटरोस्ट्रक्चर को डिजाइन करने के लिए किया गया है। लैटिस से मेल खाने वाले हेट्रोस्ट्रक्चर को एपिटैक्सियल रूप से उगाया गया है और यह भी संभव है कि द्विभाषी लिगेंड के माध्यम से पूरी तरह से अलग लैटिस संरचनाओं के साथ पदार्थो को संयोजित किया जा सके। कई अनुप्रयोगो का जैसे कि डाई-सेंसिटाइज़्ड सोलर सेल (DSC), क्वांटम-डॉट सेंसिटाइज़्ड सोलर सेल (QDSC), हाइड्रोजन एवोल्यूशन रिएक्शन (HER), ऑक्सीजन इवोल्यूशन रिएक्शन (OER) और फोटोडिटेक्टर्स का इन नैनोहेटरोस्ट्रक्चर के साथ प्रयास किया गया है।

पहले दो अध्याय (**अध्याय 1 और 2**) टीएमडी, पर्कोवसाइट्स, और कॉपर चाक्लोजेनाइड्स से संबंधित अनुसंधान कार्यों के व्यापक साहित्य सर्वेक्षण के लिए समर्पित हैं। इन पदार्थो के संश्लेषण की संश्लेषिक

कार्यप्रणाली और उनके हेट्रोस्ट्रक्चर, उपकरण निर्माण प्रक्रियाओं के साथ-साथ संश्लेषित सामग्री के लक्षण वर्णन के लिए नियोजित विभिन्न तकनीकों के संक्षिप्त विवरण है। **अध्याय 3** में, हमने 2H-$MoSe_2$ नैनोशीट्स (NSs) के संश्लेषण के लिए एक कोलाइडल मार्ग विकसित किया है जिसमें बड़ी संख्या में डिफैक्ट और लंबवत संरेखित किनारे हैं। हमने इन (NSs) का उपयोग इलेक्ट्रोउत्प्रेरक HER के लिए और DSC में विरोधक विद्युदग्र के रूप में किया है। **अध्याय 4** में, एक कोलाइडल मार्ग को $MoSe_2$-Cu_2S नैनोहेटरोस्ट्रक्चर(NHSs) को डिफैक्ट -समृद्ध $MoSe_2$ NSs का उपयोग करके संश्लेषित करने के लिए विकसित किया गया है। इन $MoSe_2$-Cu_2S NHSs को बेहतर प्रकाश प्रतिक्रिया विशेषताओं के साथ प्रकाशडेटेक्टर्स के निर्माण के लिए नियोजित किया गया है। इन र्निमित उपकरणों के पास विज़िबल से निकट इन्फ्रारेड सीमा में एक ब्रॉडबैंड वर्णक्रमीय प्रकाश प्रतिक्रिया है जो एक उच्च शिखर प्रतिक्रिया है और प्रकाश -से-अंधकार विद्युत धारा अनुपात,स्पष्ट प्रकाश-मैटर पारस्परिक क्रिया के संयुक्त प्रभाव, सतह डिफैक्ट के पारित होने और जंक्शन गठन के कारण है। **अध्याय 5** में, हमने $MoSe_2$-Cu_2S NHSs की उत्प्रेरक गतिविधियों को जल विभाजन में और QDSCs में विरोधक विद्युदग्र के रूप में जांच की है। हमने दिखाया है कि एक उत्प्रेरक सक्रिय पर्दाथ और उक्त तलों के बीच चार्ज ट्रांसफर के साथ $MoSe_2$ NSs के बेसल सतह की सजावट इलेक्ट्रोउतप्रेरक गतिविधियों को बढ़ाती है। **अध्याय 6** में, हमने एक द्विभाषी लिगैंड यानी 4-अमीनोथायोफिनॉल का उपयोग करके $MoSe_2$-$CsPbBr_3$ नैनोहाइब्रिड संरचनाओं के संश्लेषण को प्रस्तुत किया है, जो टाइप -2 बैंड संरेखण वाले दाता-स्वीकर्ता पुल प्रणाली बनाता है, जो चार्ज वाहक के कुशल पृथक्करण की ओर जाता है। $MoSe_2$-$CsPbBr_3$ नैनोहाइब्रिड्स, उच्च आवेश और परिवाहन के बाद स्पष्ट प्रकाश-पदार्थ पारस्परिक क्रिया के सहक्रियात्मक प्रभाव के कारण प्रकाश डायोड विन्यास में बहुत अधिक प्रकाश विद्युत धारा प्रदर्शित करते हैं। **अध्याय 7** वर्तमान थीसिस के परिणामों को संक्षेप में प्रस्तुत करता है, विभिन्न अनुप्रयोगों के लिए TMDs के उत्प्रेरक और ऑप्टोइलेक्ट्रोनिक गुणों के

ट्यूनिंग पर जोर देता है और यहां वर्णित पूरे काम की भविष्य की संभावनाओं की ओर एक त्वरित नज़र को आमंत्रित करता है।

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

GLOSSARY OF SYMBOLS AND ABBREVIATIONS

NCs	nanocrystals
NSs	nanosheets
NHSs	nanoheterostructures
2D	two-dimensional
TMDs	transition metal dichalcogenides
MvNHs	mixed-dimensional van der Waals nanohybrids
$MoSe_2$	molybdenum diselenide
DSCs	dye-sensitized solar cells
QDSCs	Quantum dot-sensitized solar cells
CEs	counter electrodes
PCE	power conversion efficiency
FF	fill factor
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
mmol	millimole
E_g	band gap
mL	millilitre
Ar	argon
ns	nanosecond
PXRD	powder X-Ray diffraction
TEM	transmission electron microscopy
SEM	scanning electron microscopy
EDS	energy dispersive spectroscopy
ICP-OES	inductively coupled plasma optical emission spectrometry
TRPL	time resolved photoluminescence
XPS	X-ray photoelectron spectroscopy
FTIR	fourier-transform infrared (FTIR) spectroscopy.
AFM	atomic force microscopy