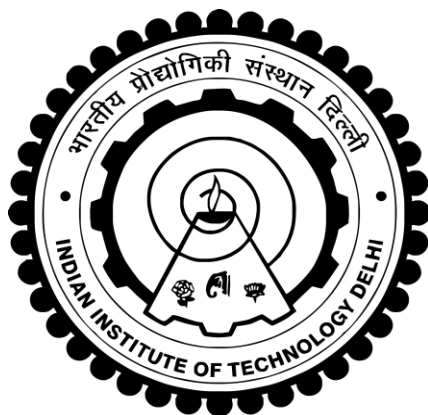


**NANOHETEROSTRUCTURES BASED ON THE LAYERED
TRANSITION METAL DICHALCOGENIDE MOLYBDENUM
DISELENIDE FOR CATALYTIC AND OPTOELECTRONIC
APPLICATIONS**

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**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
OCTOBER 2020**

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by

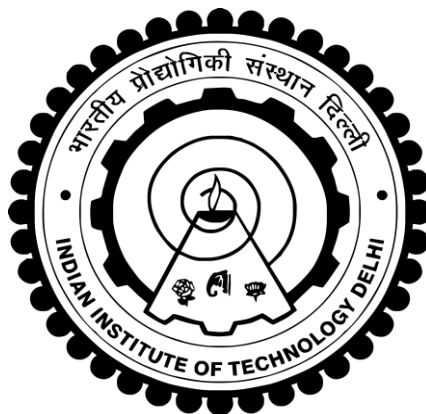
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Submitted

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

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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 MoSe₂ 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-MoSe₂ 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 MoSe₂-Cu₂S nanoheterostructures (NHSs) using defect-rich MoSe₂ NSs. These MoSe₂-Cu₂S 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-matter interaction, passivation of surface defects, and formation of p-n junction. In **Chapter 5**, we have investigated the catalytic activities of MoSe₂-Cu₂S NHSs in water splitting and as counter electrode in QDSCs. We have shown that the decoration of basal planes of MoSe₂ NSs with a catalytic active material and interfacial charge transfer phenomenon enhance the electrocatalytic activities. In **Chapter 6**, we have presented the synthesis of MoSe₂-CsPbBr₃ 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 MoSe₂-CsPbBr₃ 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 पदार्थों के अनुप्रयोग सतह साइटों पर अत्यधिक निर्भर हैं, अर्थात्, छत साइट और किनारे साइट। पार्श्व सतह पर किनारा साइटें विभिन्न उत्प्रेरक अनुप्रयोगों के लिए उपयोगी हैं, जबकि बेसल सतह में छत साइटें कई ऑटोइलेक्ट्रॉनिक उपकरणों में अनुप्रयोगों के लिए उपयोगी हैं। वर्तमान थीसिस इस बात पर केंद्रित है कि सिंथेटिक प्रोटोकॉल विकसित करके विभिन्न उत्प्रेरक और ऑटोइलेक्ट्रॉनिक 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 पदार्थों 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 पदार्थों को संयोजित किया जा सके। कई अनुप्रयोगों 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 पदार्थों 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 विद्युत्प्रवाह के रूप में किया है। **अध्याय 4** में, एक कोलाइडल मार्ग को $\text{MoSe}_2\text{-Cu}_2\text{S}$ नैनोहेटरोस्ट्रक्चर(NHSs) को डिफैक्ट -समृद्ध MoSe_2 NSs का उपयोग करके संश्लेषित करने के लिए विकसित किया गया है। इन $\text{MoSe}_2\text{-Cu}_2\text{S}$ NHSs को बेहतर प्रकाश प्रतिक्रिया विशेषताओं के साथ प्रकाशडेटेक्टर्स के निर्माण के लिए नियोजित किया गया है। इन निर्मित 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 $\text{MoSe}_2\text{-Cu}_2\text{S}$ NHSs की उत्प्रेरक गतिविधियों को जल विभाजन में और QDSCs में विरोधक विद्युत्प्रवाह के रूप में जांच की है। हमने दिखाया है कि एक उत्प्रेरक सक्रिय पदार्थ और उक्त तलों के बीच चार्ज ट्रांसफर के साथ MoSe_2 NSs के बेसल सतह की सजावट इलेक्ट्रोउत्प्रेरक गतिविधियों को बढ़ाती है। **अध्याय 6** में, हमने एक द्विभाषी लिगेंड यानी 4-अमीनोथायोफिनाल का उपयोग करके $\text{MoSe}_2\text{-CsPbBr}_3$ 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। $\text{MoSe}_2\text{-CsPbBr}_3$ नैनोहाइब्रिड्स, उच्च आवेश और परिवहन 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 ऑप्टोइलेक्ट्रॉनिक 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।

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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