

**TUNING ELECTRONIC PROPERTIES OF NIOBIUM
DISELENIDE VIA DOPING AND HETEROSTRUCTURE
DESIGN FOR ELECTROCATALYTIC APPLICATIONS**

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

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by

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Submitted

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Doctor of Philosophy
to the



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JUNE 2026

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**Dedicated to
My Parents**

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This is to certify that the thesis entitled, “**TUNING ELECTRONIC PROPERTIES OF NIOBIUM DISELENIDE VIA DOPING AND HETEROSTRUCTURE DESIGN FOR ELECTROCATALYTIC APPLICATIONS**” being submitted by **Varsha Jha** 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 her. Varsha Jha has worked under our guidance and supervision. She has fulfilled the requirements for the submission of this thesis, which to our knowledge has reached the requisite standard.

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ABSTRACT

Transition metal dichalcogenides (TMDs) form a class of two-dimensional layered materials comprising of one metal layer (M = groups IV to VII transition metal) sandwiched between two chalcogenide layers (X = S, Se, Te) resulting in a MX_2 stoichiometry. Layered structure offers advantages such as high specific surface area, and superior in-plane charge carrier mobility which are crucial for electro-catalysis. While the highly explored group VI (M = Mo, W) based TMDs exhibit semiconducting behavior in their thermodynamic stable phase; their phase transition to metallic 1T phase shows enhanced electrocatalytic activity owing to high electrical conductivity. However, the 1T phase of group VI chalcogenides are metastable and readily converted into the stable 2H phase leading to relative inhibition in their electrochemical activity. In this respect, group V based Nb dichalcogenides show inherent metallic characteristics in all phases, characterized by absence of band gap which triggers attention towards their exploration for wide range of electrochemical applications. The thesis focuses on manipulating the electronic and catalytic properties of Niobium Diselenide ($NbSe_2$) TMDs via strategies such as doping, alloying and heterostructure formation. We attempt to provide insights into the factors contributing to enhanced catalytic activity via experimental and theoretical results.

The first chapter (**Chapter 1**) is dedicated to the extensive literature survey of research work related to TMDs, their nano heterostructures and their electrochemical applications. **Chapter 2** describes the synthetic methodologies of these materials, electrode fabrication procedures, along with various techniques employed for the structural and electrochemical characterization of as-synthesized materials. **Chapter 3** examines the effect of isovalent chalcogen alloying in $Nb(S_xSe_{1-x})_2$ nanosheets and demonstrates that $NbSSe$ exhibits enhanced hydrogen evolution reaction (HER) activity. Building upon these findings, **Chapter 4** explores the incorporation of transition metal dopants, specifically cobalt (Co), into the $NbSSe$ lattice. Given the critical role of metal d-electrons

in tailoring electronic properties, Co doping was investigated and found to significantly improve HER performance at an optimal concentration while preserving the structural integrity of the host lattice. Moreover, the multiple accessible oxidation states of cobalt make it an ideal dopant for investigating both faradaic and non-faradaic charge storage mechanisms in layered NbSSe for supercapacitor applications. In **Chapter 5**, structural engineering of NbSe₂ is achieved through the fabrication of NbSe₂–NiSe heterostructures, and their electrocatalytic performance toward HER is systematically evaluated. In addition to HER catalysis, the potential of NbSe₂ based materials for anodic oxidation reactions is also explored. **Chapter 6** focuses on Ni doped NbSe₂ nanosheets for the urea oxidation reaction (UOR), where the material acted as a pre-catalyst, consistent with the well-known transformation of transition metal dichalcogenides into oxide phases under strongly alkaline conditions. Finally, **Chapter 7** summarizes the key findings of the thesis and outlines prospective research directions, including the exploration of alternative dopants and heterostructure designs, as well as the extension of these materials to other electrochemical applications.

संक्षेपण

संक्रमण धातु डाइचैल्कोजेनाइड्स (TMDs) दो-आयामी परतदार पदार्थों का एक वर्ग बनाते हैं, जिनमें एक धातु परत (M = समूह 4 से 7 संक्रमण धातु) दो चैल्कोजेनाइड परतों ($X = S, Se, Te$) के बीच सैंडविच होती है, जिसके परिणामस्वरूप MX_2 स्टॉइकियोमेट्री बनती है। परतदार संरचना उच्च विशिष्ट सतह क्षेत्र और बेहतर इन-प्लेन चार्ज कैरियर गतिशीलता जैसे लाभ प्रदान करती है, जो इलेक्ट्रो-कैटेलिसिस के लिए महत्वपूर्ण हैं। जबकि अत्यधिक खोजे गए समूह VI ($M = Mo, W$) आधारित TMDs अपने थर्मोडायनामिक स्थिर अवस्था में अर्धचालक व्यवहार प्रदर्शित करते हैं; धात्विक 1T अवस्था में उनका चरण संक्रमण उच्च विद्युत चालकता के कारण बढ़ी हुई इलेक्ट्रो-कैटेलिटिक गतिविधि को दर्शाता है। हालांकि, समूह VI चैल्कोजेनाइड्स की 1T अवस्था मेटास्टेबल होती है और आसानी से स्थिर 2H अवस्था में परिवर्तित हो जाती है, जिससे उनकी इलेक्ट्रोकेमिकल गतिविधि में सापेक्षिक अवरोध उत्पन्न होता है। इस संदर्भ में, समूह V आधारित Nb डाइचैल्कोजेनाइड्स सभी अवस्थाओं में अंतर्निहित धात्विक गुण प्रदर्शित करते हैं, जिनकी विशेषता बैंड गैप की अनुपस्थिति है, जो इलेक्ट्रोकेमिकल अनुप्रयोगों की व्यापक श्रेणी के लिए उनके अन्वेषण की ओर ध्यान आकर्षित करती है। यह शोध प्रबंध डोपिंग, मिश्रधातुकरण और हेटरोस्ट्रक्चर निर्माण जैसी रणनीतियों के माध्यम से नियोबियम डिसेलेनाइड ($NbSe_2$)TMDs के इलेक्ट्रॉनिक और उत्प्रेरक गुणों में हेरफेर करने पर केंद्रित है। हम प्रायोगिक और सैद्धांतिक परिणामों के माध्यम से बढ़ी हुई उत्प्रेरक गतिविधि में योगदान देने वाले कारकों के बारे में जानकारी प्रदान करने का प्रयास करते हैं।

पहला अध्याय (अध्याय 1) टीएमडी, उनके नैनो हेट्रोस्ट्रक्चर और उनके इलेक्ट्रोकेमिकल अनुप्रयोगों से संबंधित शोध कार्यों के व्यापक साहित्य सर्वेक्षण को समर्पित है। **अध्याय 2** इन सामग्रियों की संश्लेषणात्मक कार्यप्रणालियों, इलेक्ट्रोड निर्माण प्रक्रियाओं और संश्लेषित सामग्रियों के संरचनात्मक और इलेक्ट्रोकेमिकल लक्षण वर्णन के लिए उपयोग की जाने वाली विभिन्न तकनीकों का वर्णन करता है। **अध्याय 3**

एनबी(एसएसएसई¹-एक्स)₂ नैनोशीट्स में आइसोवेलेंट चैल्कोजेन मिश्रधातु के प्रभाव की जांच करता है और दर्शाता है कि एनबीएसएसई बढ़ी हुई हाइड्रोजन विकास प्रतिक्रिया (एचईआर) गतिविधि प्रदर्शित करता है। इन निष्कर्षों के आधार पर, **अध्याय 4** एनबीएसएसई जाली में संक्रमण धातु डोपेंट, विशेष रूप से कोबाल्ट (कोबाल्ट) के समावेश का अन्वेषण करता है। इलेक्ट्रॉनिक गुणों को अनुकूलित करने में धातु डी-इलेक्ट्रॉनों की महत्वपूर्ण भूमिका को देखते हुए, कोबाल्ट डोपिंग का अध्ययन किया गया और पाया गया कि यह मेजबान जाली की संरचनात्मक अखंडता को बनाए रखते हुए इष्टतम सांद्रता पर एचईआर प्रदर्शन में उल्लेखनीय सुधार करता है। इसके अलावा, कोबाल्ट की कई सुलभ ऑक्सीकरण अवस्थाएँ इसे सुपरकैपेसिटर अनुप्रयोगों के लिए स्तरित NbSSe में फैराडिक और नॉन-फैराडिकचार्ज भंडारण तंत्र दोनों की जांच के लिए एक आदर्श डोपेंट बनाती हैं। **अध्याय 5** में, NbSe₂-NiSe हेटरोस्ट्रक्चर के निर्माण के माध्यम से NbSe₂ की संरचनात्मक अभियांत्रिकी की जाती है, और विद्युत ऊष्मा प्रतिरोध (HER) के प्रति उनके विद्युत उत्प्रेरक प्रदर्शन का व्यवस्थित मूल्यांकन किया जाता है। HER उत्प्रेरण के अलावा, एनोडिक ऑक्सीकरण अभिक्रियाओं के लिए NbSe₂ आधारित सामग्रियों की क्षमता का भी पता लगाया जाता है। **अध्याय 6** यूरिया ऑक्सीकरण अभिक्रिया (UOR) के लिए Ni डोपड NbSe₂ नैनोशीट्स पर केंद्रित है, जहां यह सामग्री एक पूर्व-उत्प्रेरक के रूप में कार्य करती है, जो प्रबल क्षारीय परिस्थितियों में संक्रमण धातु डाइचैल्कोजेनाइड्स के ऑक्साइड चरणों में सुप्रसिद्ध परिवर्तन के अनुरूप है। अंत में, **अध्याय 7** शोध प्रबंध के प्रमुख निष्कर्षों का सारांश प्रस्तुत करता है और संभावित अनुसंधान दिशाओं की रूपरेखा तैयार करता है, जिसमें वैकल्पिक डोपेंट और हेटरोस्ट्रक्चर डिज़ाइनों की खोज, साथ ही इन सामग्रियों का अन्य विद्युत रासायनिक अनुप्रयोगों तक विस्तार शामिल है।

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GLOSSARY OF SYMBOLS AND ABBREVIATIONS

0D	Zero-dimensional
1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
NSs	nanosheets
NHSs	nanoheterostructures
TMDs	transition metal dichalcogenides
DOS	density of states
NbSe ₂	niobium diselenide
NiSe	nickel selenide
EIS	electron impedance spectra
LSV	linear sweep voltammetry
CV	cyclic voltammetry
EDLC	electric double layer capacitance
GCD	galvanostatic charge discharge
CA	chronoamperometry
HER	hydrogen evolution reaction
OER	oxygen evolution reaction
UOR	urea oxidation reaction
SCs	supercapacitors
DFT	density functional theory
DOS	density of state
PAW	projected augmented wave
FWHM	full width half maximum
ΔG_H	Gibbs free energy
<i>RHE</i>	reversible hydrogen evolution
<i>E</i>	energy density
<i>P</i>	power density
η	overpotential
<i>b</i>	tafel slope

C_{dl}	double layer capacitance
nm	nanometer
mL	millilitre
μL	microlitre
mg	milligram
h	hour
min	minute
i.e.	that is
V	volts
mV	millivolts
$^{\circ}\text{C}$	degree centigrade
M	molar