SYNTHESIS OF QUASI TWO-DIMENSIONAL TRANSITION METAL DICHALCOGENIDES (2D TMDs) FOR EFFICIENT PHOTO-ELECTROCHEMICAL AND PHOTODETECTOR APPLICATIONS

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Synthesis of Quasi Two-Dimensional Transition metal dichalcogenides (2D TMDs) for Efficient Photo-electrochemical and Photodetector Applications

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Dedicated
To
My Mother

CERTIFICATE

This is to certify that the thesis entitled, "Synthesis of Quasi Two-Dimensional Transition metal dichalcogenides (2D TMDs) for Efficient Photo-electrochemical and Photodetector Applications", is being submitted by Ms. Priyanka Yadav, 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. Ms. Priyanka Yadav has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard. The results contained in this dissertation have not been submitted in part or full, to any other university or institute for the award of any degree or diploma.

Date: 12 July 2023

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ABSTRACT

In the past ten years, optoelectronic devices have undergone rapid development and a significant increase in their efficacy, revealing a growing need for new-type of materials at their core. Optoelectronic devices are those that employ electric charges to generate light, such as light-emitting diodes (LEDs) or lasers, or light to generate electric currents, such as photodetectors or solar cells. 2D transition metal dichalcogenides (2D TMDs) like MoS_2, WS_2, and $MoSe_2$ belong to a broad family of layered materials that have varying band gaps or transition from indirect to direct band gaps when scaled down from 3D to 2D. Thus, these atomically thin 2D semiconductors are promising for future electrical and optoelectronic devices. Layered 2D heterostructures offer a unique opportunity to create photodetectors with a wide spectral range and exceptional figures of merit that are not possible with discrete materials due to their ultrathin sharp interfaces and quantum confinement. 2D materials such as graphene and TMDs have demonstrated intriguing physical features as well as promising optoelectronic applications.

In this thesis, a scalable synthesis route for high-performance, 2D TMD nanosheets of MoS_2, WS_2, $MoSe_2$, TiS_2 and NbS_2 is designed at room-temperature via liquid phase exfoliation method that leads to a stable dispersion of a few layers 2D-TMDs and remains stable in suspension form for several months. The polymers chosen to stabilize 2D nanosheets in dispersion were cellulose based which are environment friendly and biodegradable. Further, the fabrication is carried out for a thin film device based on the heterojunction of the above exfoliated 2D TMDs via a solution-processable route and their photodetection properties have been explored. The enhanced response of the as-fabricated photodetector of tri-layer heterojunction results from the effective decrease in recombination rate and efficient electron–hole separation. Further, 2D-TaS_2 based heterostructure for broadband photodetector applications and its photoelectrochemical properties have been designed. The

photoelectrochemical measurements illustrate that the 2D-TaS_2/SnS_2-rGO heterostructure shows 10 times enhancement in the photocurrent density than that of the bare 2D- TaS_2. These results establish the feasibility of the fabrication of the 2D-TaS_2/SnS_2-rGO heterostructure at room temperature for broadband photodetection in the ultra-violet (UV)- Near IR region. Similarly, the fabrication of inorganic TaS_2 and organic rGO and g-C_3N_4 photocatalyst with optimized composition is carried out for photoelectrochemical properties and photodetector properties using the solution-processed route. The photoelectrochemical activity of optimized composition shows 35 times higher photocurrent density compared to the bare 2D TaS_2.

The main objective of this thesis work is to design a solution route that may help in the scalability of high-performance 2D TMDs nanosheets and solution-processed fabrication of large-area devices to achieve better spectral response for a wide range of the electromagnetic spectrum.

(ABSTRACT) सारांश

पिछले दस वर्षों में, ऑप्टोइलेक्ट्रॉनिक उपकरणों का तेजी से विकास हुआ है और उनकी प्रभावकारिता में उल्लेखनीय वृद्धि हुई है, जिससे उनके मूल में नए प्रकार की सामग्रियों की बढ़ती आवश्यकता का पता चलता है। ऑप्टोइलेक्ट्रॉनिक डिवाइस वे हैं जो प्रकाश उत्पन्न करने के लिए विद्युत आवेशों का उपयोग करते हैं, जैसे कि प्रकाश उत्सर्जक डायोड (LED) या लेजर, या विद्युत धाराओं को उत्पन्न करने के लिए प्रकाश, जैसे कि फोटोडेटेक्टर या सौर सेल। MoS_2, WS_2, और $MoSe_2$ जैसे 2D ट्रांज़िशन मेटल डाइक्लोजेनाइड्स (2D TMDs) स्तरित सामग्रियों के एक व्यापक परिवार से संबंधित हैं, जिनमें 3D से 2D तक स्केल किए जाने पर अलग-अलग बैंड अंतराल या अप्रत्यक्ष से प्रत्यक्ष बैंड अंतराल में संक्रमण होता है। इस प्रकार, ये परमाणु रूप से पतले 2D अर्धचालक भविष्य के विद्युत और ऑप्टोइलेक्ट्रॉनिक उपकरणों के लिए आशाजनक हैं। स्तरित 2D हेटरोस्ट्रक्चर एक विस्तृत वर्णक्रमीय रेंज और योग्यता के असाधारण आंकड़ों के साथ फोटोडेटेक्टर बनाने का एक अनूठा अवसर प्रदान करते हैं जो उनके अल्ट्राथिन शार्प इंटरफेस और क्वांटम कारावास के कारण असतत सामग्री के साथ संभव नहीं है। ग्राफीन और टीएमडी जैसी 2D सामग्री ने पेचीदा भौतिक विशेषताओं के साथ-साथ ऑप्टोइलेक्ट्रॉनिक अनुप्रयोगों का वादा किया है। इस थीसिस में, MoS_2, WS_2, $MoSe_2$, TiS_2 और NbS_2 के उच्च-प्रदर्शन, 2D TMD नैनोशीट्स के लिए एक स्केलेबल सिंथेसिस रूट को कमरे के तापमान पर तरल चरण एक्सफोलिएशन विधि के माध्यम से डिज़ाइन किया गया है जो कुछ परतों 2D-TMDs के स्थिर फैलाव की ओर जाता है। और कई महीनों तक निलंबन के रूप में स्थिर रहता है। फैलाव में 2D नैनोशीट को स्थिर करने के लिए चुने गए पॉलिमर सेलुलोज आधारित थे जो पर्यावरण के अनुकूल और बायोडिग्रेडेबल हैं। इसके अलावा, एक समाधान-प्रक्रिया योग्य मार्ग के माध्यम से उपरोक्त एक्सफ़ोलीएटेड 2D TMDs के विषमता के आधार पर एक पतली फिल्म डिवाइस के लिए निर्माण किया जाता है और उनके फोटोडिटेक्शन गुणों का पता लगाया गया है। पुनर्संयोजन दर और कुशल इलेक्ट्रॉन-छेद पृथक्करण में प्रभावी कमी से त्रि-परत

विषम परिणाम के रूप में निर्मित फोटोडेटेक्टर की बढ़ी हुई प्रतिक्रिया। इसके अलावा, ब्रॉडबैंड फोटोडिटेक्टर अनुप्रयोगों और इसके फोटोइलेक्ट्रोकेमिकल गुणों के लिए 2D-TaS_2 आधारित हेटरोस्ट्रक्चर को डिजाइन किया गया है। फोटोइलेक्ट्रॉनिक माप बताते हैं कि 2D-TaS_2/SnS_2-rGO हेटरोस्ट्रक्चर नंगे 2D-TaS_2 की तुलना में फोटोकरंट घनत्व में 10 गुना वृद्धि दर्शाता है। ये परिणाम अल्ट्रा-वायलेट (UV) - IR क्षेत्र के पास ब्रॉडबैंड फोटोडिटेक्शन के लिए कमरे के तापमान पर 2D-TaS_2/SnS_2-rGO हेटरोस्ट्रक्चर के निर्माण की व्यवहार्यता स्थापित करते हैं। इसी तरह, समाधान-संसाधित मार्ग का उपयोग करके फोटोइलेक्ट्रॉनिक गुणों और फोटोडेटेक्टर गुणों के लिए अनुकूलित संरचना के साथ अकार्बनिक टीएएस2 और कार्बनिक आरजीओ और जी-सी3एन4 फोटोकैटलिस्ट का निर्माण किया जाता है। अनुकूलित रचना की फोटोइलेक्ट्रॉनिक गतिविधि नंगे 2D TaS_2 की तुलना में 35 गुना अधिक फोटोकरंट घनत्व दिखाती है। इस थीसिस कार्य का मुख्य उद्देश्य एक समाधान मार्ग को डिजाइन करना है जो उच्च-प्रदर्शन 2D TMDs नैनोशीट्स की मापनीयता में मदद कर सकता है और विद्युत चुम्बकीय स्पेक्ट्रम की एक विस्तृत श्रृंखला के लिए बेहतर वर्णक्रमीय प्रतिक्रिया प्राप्त करने के लिए बड़े क्षेत्र के उपकरणों के समाधान-संसाधित निर्माण में मदद कर सकता है।

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Abbreviations and Symbols

Å	Angstroms
^{o}C	Degree Celsius
µm	Micrometer
nm	Nanometer
min	Minutes
sec	Seconds
h	Hours
mL	milliliter
M	molar
XRD	X-ray diffraction
PXRD	Powder X-ray diffraction
TEM	Transmission Electron Microscopy
HRTEM	High Resolution Transmission Electron Microscopy
FESEM	Field Emission Scanning Electron Microscopy
EDX	Energy Dispersive X-ray Spectroscopy
AFM	Atomic Force Microscopy
VB	Valence band
CB	Conduction band
eV	Electron – Volt
K	Kelvin
^{o}	Degree (angle)
λ	Wavelength

UV	Ultraviolet -visible
FT-IR	Fourier-transform infrared spectroscopy
SAED	Selected Area Electron Diffraction
DRS	Diffuse reflectance spectroscopy
TMDs	Transition Metal Dichalcogenides
2D	Two- dimensional
PEC	Photoelectrochemical
HER	Hydrogen Evolution Reaction
OER	Oxygen Evolution Reaction
STH	Solar-to-hydrogen efficiency
LSV	Linear sweep voltammetry
M-S	Mott-Schottky
EIS	Electrochemical Impedance spectroscopy
TPR	Transient Photocurrent Response
PVE	Photovoltaic Effect
PCE	Photoconductive Effect
PGE	Photogating Effect
PTE	Photothermoelectric Effect
PBE	Photobolometric Effect