

**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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By

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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 MoS₂, WS₂, and MoSe₂ 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 MoS₂, WS₂, MoSe₂, TiS₂ and NbS₂ 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-TaS₂ based heterostructure for broadband photodetector applications and its photoelectrochemical properties have been designed. The

photoelectrochemical measurements illustrate that the 2D-TaS₂/SnS₂-rGO heterostructure shows 10 times enhancement in the photocurrent density than that of the bare 2D- TaS₂. These results establish the feasibility of the fabrication of the 2D-TaS₂/SnS₂-rGO heterostructure at room temperature for broadband photodetection in the ultra-violet (UV)- Near IR region. Similarly, the fabrication of inorganic TaS₂ and organic rGO and g-C₃N₄ 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 TaS₂.

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 फोटोडिटेक्टर 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 फोटोडिटेक्टर 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 एक्सफोलीएटेड 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 फोटोडिटेक्टर की बढ़ी हुई प्रतिक्रिया। इसके अलावा, ब्रॉडबैंड फोटोडिटेक्टर अनुप्रयोगों और इसके फोटोइलेक्ट्रोकेमिकल गुणों के लिए 2D-TaS₂ आधारित हेटरोस्ट्रक्चर को डिजाइन किया गया है। फोटोइलेक्ट्रॉनिक माप बताते हैं कि 2D-TaS₂/SnS₂-rGO हेटरोस्ट्रक्चर नंगे 2D-TaS₂ की तुलना में फोटोकॉरंट 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-TaS₂/SnS₂-rGO हेटरोस्ट्रक्चर के निर्माण की व्यवहार्यता स्थापित करते हैं। इसी तरह, समाधान-संसाधित मार्ग का उपयोग करके फोटोइलेक्ट्रॉनिक गुणों और फोटोडिटेक्टर 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 TaS₂ की तुलना में 35 गुना अधिक फोटोकॉरंट 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।

TABLE OF CONTENTS

CERTIFICATE	i
ACKNOWLEDGEMENTS	ii-iv
ABSTRACT	v-viii
TABLE OF CONTENTS	ix-xiv
LIST OF FIGURES	xv-xxi
LIST OF TABLES	xxii
ABBREVIATIONS AND SYMBOLS	xxiii-xxiv

Chapter 1	Introduction	
1.1	Looking for Renewable Energy Sources	1-3
1.2	Photodetectors based on solution-processed semiconductors	3-5
1.3	2D Materials	5-6
1.3.1	Graphene	6-7
1.3.1.1	Structure of graphene	7-8
1.3.1.2	Properties of graphene	8
1.3.1.3	Applications of graphene	9
1.3.2	Transition Metal Dichalcogenides (TMDs)	9-10
1.3.2.1	The chemical formula and structure of TMDs	10-11
1.3.2.2	Properties of the TMDs	11-12
1.3.2.3	Applications of the TMDs	12-13
1.3.2.4	Challenges associated with TMDs	13-14
1.3.3	Other 2D materials	14
1.4	Preparation Methods of 2D materials	15
1.4.1	Mechanical exfoliation method	15

1.4.2	Liquid exfoliation method	16
1.4.3	High—temperature routes to 2D materials	16-17
1.5	Photocurrent Generation Mechanism	17-20
1.5.1	Photovoltaic Effect (PVE)	
1.5.2	Photoconductive Effect (PCE)	
1.5.3	Photogating Effect (PGE)	
1.5.4	Photothermoelectric Effect (PTE)	
1.5.5	Photobolometric Effect (PBE)	
1.6	Motivation of the thesis	20-22
1.7	References	22

Chapter 2 Methodology and Characterization Techniques

2.1	Synthesis Methodology	28
2.1.1	Ultrasonication-assisted liquid phase exfoliation	28-30
2.1.2	Sol-gel Method	30
2.2	Characterization Techniques	31
2.2.1	Powder X-Ray Diffraction (XRD)	31-33
2.2.2	Field emission scanning electron microscopy (FESEM)	33-35
2.2.3	Energy Dispersive X-ray Spectroscopy (EDX)	35-36
2.2.4	Transmission Electron Microscopy (TEM)	36-37
2.2.5	Atomic Force Microscopy (AFM)	37-38
2.2.6	Raman spectroscopy	39-40
2.2.7	Ultraviolet-Visible (UV-Vis) spectroscopy	40-41
2.2.8	Fourier-transform infrared spectroscopy (FT-IR)	
	Spectroscopy	41
2.2.9	NMR spectroscopy	42
2.3	Photoelectrochemical (PEC) Measurements	43
2.3.1	Working electrode preparation	44
2.3.2	Linear Sweep Voltammetry (LSV)	44-45
2.3.3	Transient photocurrent response (TPR)	45

2.3.4	Electrochemical Impedance Spectroscopy (EIS)	45
2.3.5	Mott-Schottky Plot (M-S)	46
2.4	Photodetector Measurements	47
2.4.1	Figure of Merit of a Photodetector	48-49
2.5	References	50

Chapter 3 A Biodegradable Polymer-Assisted Efficient and Universal Exfoliation Route to a Stable Few Layer Dispersion of Transition Metal Dichalcogenides

	Abstract	55
3.1	Introduction	56-60
3.2	Experimental section	60
3.2.1	Exfoliation	61-62
3.3	Characterization	62-63
3.3.1	Transmission Electron Microscopy (TEM) and Selected Area Electron Diffraction (SAED)	
3.3.2	Atomic Force Microscopy (AFM)	
3.3.3	Raman Spectroscopy	
3.3.4	¹³ C NMR Spectroscopy	
3.4	Results and Discussion	63-75
3.5	Conclusions	75
3.6	References	75

Chapter 4 Large-scale solution-processed ultrathin 2D tri-layer heterostructures for photodetector applications

	Abstract	80
4.1	Introduction	81-83
4.2	Experimental Section	84-85

4.2.1	Synthesis and deposition of films	
4.2.2	Fabrication of photodetector	
4.3	Characterization	85-86
4.3.1	Field Emission Scanning Electron Microscope (FESEM) and Energy Dispersive X-ray analysis (EDX)	
4.3.2	Atomic Force Microscopy (AFM)	
4.3.3	Raman Spectroscopy	
4.3.4	Powder X-ray Diffraction (PXRD)	
4.3.5	Photodetection studies	
4.4	Results and Discussion	
4.4.1	Characterization of as-fabricated photodetector	86-89
4.4.2	Essential parameters for device characterization	90-91
4.4.3	Photodetector measurements	91-99
4.5	Conclusions	99
4.6	References	99

**Chapter 5 SnS₂/rGO decorated 2D-TaS₂ for broadband photodetector
application and its photoelectrochemical properties**

	Abstract	105
5.1	Introduction	106-107
5.2	Experimental	108-109
5.2.1	Exfoliation of 2D-TaS ₂	
5.2.2	Synthesis of SnS ₂	
5.2.3	Synthesis of 2D-TaS ₂ /SnS ₂ and 2D-TaS ₂ /SnS ₂ -rGO	
5.3	Characterization	110-111
5.3.1	Powder X-ray Diffraction (Powder XRD)	
5.3.2	Atomic Force Microscopy (AFM)	
5.3.3	Raman Spectroscopy	
5.3.4	Field Emission Scanning Electron Microscope (FESEM) and Energy-Dispersive X-ray Spectroscopy (EDX)	

5.3.5	High Resolution Transmission Electron Microscopy (HRTEM)	
5.3.6	Diffuse reflectance spectroscopy (DRS)	
5.3.7	Fourier Transform Infra-red Spectroscopy (FT-IR)	
5.3.8	Photoelectrochemical Studies	111
5.3.9	Photodetection measurements	112
5.4	Results and Discussion	
5.4.1	Characterization of synthesized samples	112-118
5.4.2	Photoelectrochemical Measurements	119-122
5.4.3	Photodetection Measurements	122-127
5.5	Conclusions	128
5.6	References	129

Chapter 6 Synthesis of an organic-inorganic hybrid using rGO and g-C₃N₄ with 2D TaS₂ to study its photoelectrochemical and photodetector properties

	Abstract	132
6.1	Introduction	132-134
6.2	Experimental	134-136
6.2.1	Exfoliation of 2D-TaS ₂	
6.2.2	Synthesis of rGO	
6.2.3	Synthesis of g-C ₃ N ₄	
6.2.4	Synthesis of g-C ₃ N ₄ /2D-TaS ₂	
6.2.5	Synthesis of rGO/2D-TaS ₂	
6.2.6	Synthesis of g-C ₃ N ₄ /2D-TaS ₂ ; rGO/2D-TaS ₂	
6.3	Characterization	137
6.3.1	Powder X-ray Diffraction (Powder XRD)	
6.3.2	Field Emission Scanning Electron Microscope (FESEM) and Energy-Dispersive X-ray Spectroscopy (EDX)	

6.3.3	Fourier Transform Infra-red Spectroscopy (FT-IR)	
6.3.4	Photoelectrochemical Studies	137
6.3.5	Photodetection measurements	138
6.4	Results and Discussion	
6.4.1	Characterization of synthesized samples	139-142
6.4.2	Photoelectrochemical Measurements	142-145
6.4.3	Photodetection Measurements	146-148
6.5	Conclusions	148
6.6	References	149
Chapter 7	Conclusions and Future Prospects	151-152
	PUBLICATIONS, PATENTS, AND CONFERENCES	153-154
	BIO-DATA OF THE AUTHOR	155-158

LIST OF FIGURES

Figure No.	Figure Captions	Page. No.
Figure 1.1	Sustainable energy development and research.	2
Figure 1.2	Schematic view of 2D materials from insulators to metals and semiconductors with varied bandgaps.	6
Figure 1.3	Honeycomb lattice structure and bonding in atomic thick graphene nanosheet.	8
Figure 1.4	Structure and phases of TMDs.	11
Figure 1.5	Applications of TMDs based heterostructures for optoelectronic, electrical, sensors, and energy devices.	13
Figure 1.6	Existing library of 2D materials.	14
Figure 1.7	Schematic representation of (a) Photovoltaic Effect, (b) Photoconductive Effect, (c) and (d) Photogating Effect.	18
Figure 2.1	Derivation of Bragg's law.	32
Figure 2.2	Schematic illustration of electron matter interaction.	34
Figure 2.3	Schematic Illustration of Atomic Force Microscopy	38
Figure 2.4	Schematic representation of Raman scattering processes.	39
Figure 2.5	Schematic of the PEC setup used for photoelectrochemical measurements.	43
Figure 2.6	Schematic representation of a general linear sweep voltammogram (LSV) curve.	45
Figure 2.7	The probe station and semiconductor parameter analyzer (SCS 4200 A) used for photodetector measurements.	48

Figure 3.1	Generalized structure of a class of cellulose based biodegradable polymer.	61
Figure 3.2	Scheme to illustrate the exfoliation process.	64
Figure 3.3	Exfoliated suspensions of different TMDs in BuOH/HPC system	64
Figure 3.4	TEM images and SAED patterns of (a-e) bulk and (f-j) exfoliated MoS ₂ , TiS ₂ , NbS ₂ , WS ₂ and MoSe ₂ respectively, with projected zone axis [001].	65
Figure 3.5	(a-d) TEM images and AFM analysis (e-h) reconstructed image and depth profiling of exfoliated MoS ₂ in different solvent-polymer systems: (I) MoS ₂ /CMC/BuOH, (II) MoS ₂ /HPMC/BuOH, (III) MoS ₂ /HPC/IBA and (IV) MoS ₂ /HPC/EG respectively.	66
Figure 3.6	AFM analysis (reconstructed image and depth profile) of exfoliated (a) MoS ₂ , (b) TiS ₂ and (c) MoSe ₂ (d) WS ₂ and (e) NbS ₂ respectively.	67
Figure 3.7	Raman analysis of exfoliated and bulk (a) MoS ₂ , (b) WS ₂ , (c) TiS ₂ , (d) NbS ₂ and (e) MoSe ₂ respectively.	69
Figure 3.8	¹³ C NMR spectra of 1-BuOH solvent.(a) depicts the ¹³ C NMR of pure 1-butanol in CDCl ₃ while (b) depicts the corresponding data for 1-butanol in the exfoliated suspension.	71
Figure 3.9	Exfoliated suspensions after 6 months of different TMDs in BuOH/HPC system.	74
Figure 3.10	TEM images of exfoliated (a-e) MoS ₂ , TiS ₂ , NbS ₂ , WS ₂ and MoSe ₂ respectively.	74

Figure 4.1	Schematic illustration of tri-layer ($\text{TiS}_2/\text{MoSe}_2/\text{MoS}_2$) heterostructure fabrication and measurement setup	85
Figure 4.2	FESEM and EDAX analysis (side view) of tri-layer ($\text{TiS}_2/\text{MoSe}_2/\text{MoS}_2$) heterostructure	87
Figure 4.3	Powder XRD of tri-layer ($\text{TiS}_2/\text{MoSe}_2/\text{MoS}_2$) heterostructure.	87
Figure 4.4	AFM top-view analysis and depth profiling of the surface of tri-layer ($\text{TiS}_2/\text{MoSe}_2/\text{MoS}_2$) heterostructure.	88
Figure 4.5	Raman mapping and analysis of tri-layer ($\text{TiS}_2/\text{MoSe}_2/\text{MoS}_2$) heterostructure	89
Figure 4.6	Optical (left) and FESEM image (right) of tri-layer ($\text{TiS}_2/\text{MoSe}_2/\text{MoS}_2$) heterostructure device (M= Metal contacts).	89
Figure 4.7	I-V characteristics of heterojunction device measured at 660 and 785 nm laser source.	92
Figure 4.8	I-V characteristics of heterojunction device measured using 660 and 785 nm laser source upon increasing illumination time with maximum power density.	93
Figure 4.9	Transient photocurrent response of heterojunction device is measured by 660 nm laser source.	94
Figure 4.10	Transient photocurrent response of heterojunction device measured at different input power using a 785 nm laser source.	94
Figure 4.11	I-V characteristics of heterojunction device measured using 660 nm laser source with varying laser power.	95

Figure 4.12	Photocurrent vs intensity measured at different input power using 660 nm and 785 nm laser source (left side) and charge transfer diagram of the 2D-Tri-layer (TiS ₂ /MoSe ₂ /MoS ₂) heterostructure (right side).	97
Figure 5.1	Schematic illustration for the synthesis of heterostructure.	109
Figure 5.2	Powder XRD patterns of (a) (i) bare SnS ₂ , (ii) 2D-TaS ₂ , (iii) 2D-TaS ₂ /SnS ₂ and (iv) 2D-TaS ₂ /SnS ₂ -rGO heterostructures. (b) (008) reflection indicating shift in the position due to strain generated after heterostructure formation.	113
Figure 5.3	(a-c) represent the FESEM images of bare 2D-TaS ₂ , bare SnS ₂ and 2D-TaS ₂ /SnS ₂ -rGO heterostructure and (d) depicts the elemental mapping of the 2D-TaS ₂ /SnS ₂ -rGO heterostructure respectively.	114
Figure 5.4	(a) FTIR analysis of bare 2D-TaS ₂ , bare SnS ₂ , 2D-TaS ₂ /SnS ₂ and 2D-TaS ₂ /SnS ₂ -rGO heterostructure respectively, (b) Inset- FTIR analysis peak indicating shift in the carbonyl peak, (c) Raman analysis (d) diffuse reflectance spectrum of bare 2D-TaS ₂ , bare SnS ₂ , 2D-TaS ₂ /SnS ₂ and 2D-TaS ₂ /SnS ₂ -rGO heterostructure respectively.	115
Figure 5.5	Exfoliated suspensions of bulk TaS ₂ in Nitro benzene and TEM image of exfoliated TaS ₂ .	117
Figure 5.6	Absorbance plot of exfoliated TaS ₂ .	117

Figure 5.7	HRTEM of the 2D-TaS ₂ /SnS ₂ -rGO heterostructure.	118
Figure 5.8	AFM analysis-reconstructed image and depth profiling of exfoliated TaS ₂ .	119
Figure 5.9	(a) Photoelectrochemical current density measurements of bare 2D-TaS ₂ , bare SnS ₂ , 2D-TaS ₂ /SnS ₂ and 2D-TaS ₂ /SnS ₂ -rGO heterostructures under light (l) and dark (d) conditions, (b) applied bias to photon-to-current efficiency (ABPE%) plot for bare 2D-TaS ₂ , bare SnS ₂ , 2D-TaS ₂ /SnS ₂ and 2D-TaS ₂ /SnS ₂ -rGO heterostructures respectively.	120
Figure 5.10	a) EIS measurements (b) chronoamperometric studies for bare 2D-TaS ₂ , bare SnS ₂ , 2D-TaS ₂ /SnS ₂ and 2D-TaS ₂ /SnS ₂ -rGO heterostructures respectively.	122
Figure 5.11	(a) Pictorial representation of device fabricated on IDEs (b-d) I-V measurements 2D-TaS ₂ /SnS ₂ -rGO heterostructure using solar simulator by varying wavelengths from 200- 1550 nm with a power of 100 μW (Inset shows the logarithmic plot for the corresponding I-V plot).	123
Figure 5.12	(a) Responsivity and (b)Detectivity of heterostructure device measured at different wavelengths from 200-1550 nm, (c-f) Transient photocurrent response of heterostructure device analysed for rise/fall time at 405 nm and 660 nm wavelengths.	124
Figure 5.13	Time response of 2D-TaS ₂ /SnS ₂ -rGO heterostructure at different	127

	wavelength of light source.	
Figure 5.14	I-V measurements and Responsivity of 2D-TaS ₂ /SnS ₂ -rGO heterostructure by varying power at 660 nm light source.	127
Figure 6.1	Schematic procedure and different composition for optimization of the heterostructures.	136
Figure 6.2	Powder XRD patterns of 2D-TaS ₂ , different percentage compositions of rGO/2D-TaS ₂ , and g-C ₃ N ₄ /2D-TaS ₂ respectively.	139
Figure 6.3	FESEM images of 50%-rGO/2D-TaS ₂ , and 5%-g-C ₃ N ₄ /2D-TaS ₂ heterostructures and depicts their elemental mapping respectively.	141
Figure 6.4	FTIR analysis of of 2D-TaS ₂ , different percentage compositions of rGO/2D-TaS ₂ ,(left) and g-C ₃ N ₄ /2D-TaS ₂ (right) respectively.	142
Figure 6.5	Photoelectrochemical current density measurements of bare 2D-TaS ₂ , all the compositions of rGO/2D-TaS ₂ and g-C ₃ N ₄ /2D-TaS ₂ heterostructures under light (l) and dark (d) conditions (left) and their corresponding electrochemical impedance spectroscopic measurements respectively (right)	144
Figure 6.6	Photoelectrochemical current density measurements of 50%-rGO/2D-TaS ₂ , 5%-g-C ₃ N ₄ /2D-TaS ₂ and 50%-rGO/2D-TaS ₂ : 5%-g-C ₃ N ₄ /2D-TaS ₂ heterostructures under light (l) and dark (d) conditions (left) and their corresponding electrochemical impedance spectroscopic measurements respectively (right)	145
Figure 6.7	I-V characteristics of heterojunction device measured from 350-	146

	1550 nm light source (left) and their corresponding photoresponsivity values at 0.04 mW	
Figure 6.8	Transient photocurrent response of heterojunction device is measured at 750 nm, 850 nm and white light source (left) and transient photocurrent response of heterojunction device measured at different input power using a 750 nm light source (right).	148

LIST OF TABLES

Table No.	Table Captions	Page No.
Table 1.1	List of few photodetectors commercially available for broadband photodetection.	4
Table 3.1	Hansen solubility parameters at 25°C	58
Table 3.2	Comparative study of the exfoliation yield of various TMDs using different solvent-polymer systems.	73
Table 4.1	Comparative studies of characteristic parameters for photodetectors from the present heterojunction and previous reports.	98
Table 5.1	Comparative analysis of Responsivity from the 2D-TaS ₂ /SnS ₂ -rGO heterostructure and earlier reports.	126
Table 6.1	Photocurrent density values of 50%-rGO/2D-TaS ₂ , 5%-g-C ₃ N ₄ /2D-TaS ₂ and 50%-rGO/2D-TaS ₂ : 5%-g-C ₃ N ₄ /2D-TaS ₂ heterostructures at -1.0 V.	145

Abbreviations and Symbols

Å	Angstroms
°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
°	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