

Table of Contents

<i>Acknowledgements</i>	<i>i</i>
<i>Table of Contents</i>	<i>iii</i>
<i>List of Figures</i>	<i>vii</i>
<i>List of Tables</i>	<i>xi</i>
<i>List of Abbreviations</i>	<i>xiii</i>
<i>List of Symbols</i>	<i>xv</i>
<i>Preface</i>	<i>xvii</i>
Chapter 1 Introduction and Literature Survey	1-26
1.1 Introduction.....	1
1.2 Overview of 2D TMDs.....	2
1.2.1 Structure of MoS ₂	3
1.2.2 Different Phase of MoS ₂	4
1.2.3 Raman Study of MoS ₂	5
1.3 Synthesis of MoS ₂ Nanostructures.....	6
1.3.1 Top-down Approach for MoS ₂ Synthesis.....	6
1.3.1.1 Mechanical Exfoliation.....	7
1.3.1.2 Liquid Exfoliation.....	7
1.3.1.3 Lithium Ion Intercalation.....	8
1.3.2 Bottom-up Approach for MoS ₂ Synthesis.....	8
1.3.2.1 Physical Vapor Deposition (PVD).....	8
1.3.2.2 Chemical Vapor Deposition (CVD).....	9
1.3.2.3 Solution Chemical Process.....	9
1.4 Properties and Applications of MoS ₂ Nanostructures.....	9
1.4.1 Electronic Properties.....	10
1.4.2 Optical Properties.....	10
1.4.3 Thermal Properties.....	11
1.4.4 Applications of 2D MoS ₂ Nanomaterials.....	12
1.5 Thermal Conductivity of 2D MoS ₂ Nanostructure.....	13

1.5.1	Different Technique to Determine Thermal Conductivity.....	13
1.5.2	Literature Survey on Thermal Conductivity of MoS ₂ Nanostructures by OTR Method.....	16
1.6	Photodetection Applications of MoS ₂ Nanostructure.....	17
1.6.1	Basic Principle of Photodetection Process.....	18
1.6.2	Literature Survey on Photodetection Application of MoS ₂ Nanostructure.....	20
1.7	Surface Enhanced Raman Spectroscopy.....	22
1.7.1	Theories for SERS Enhancement.....	23
1.7.2	Literature Survey on SERS Application of MoS ₂ Nanostructures.....	24
1.8	Scope and Objective of the Present Work.....	25
Chapter 2 Synthesis and Characterization Techniques.....		27-44
2.1	Materials Synthesis.....	27
2.1.1	CVD Synthesis of MoS ₂ Nanostructures.....	28
2.1.1.1	Horizontally Grown Interconnected Network Few-Layer MoS ₂ Nanostructure	31
2.1.1.2	Horizontally Grown Triangular Bi-Layer MoS ₂ Nanostructure.....	31
2.1.1.3	Vertically Grown Few-Layer MoS ₂ Nanostructure.....	32
2.2	Characterization Techniques.....	33
2.2.1	X-ray Diffraction (XRD).....	34
2.2.2	Scanning Electron Microscope (SEM).....	35
2.2.3	Transmission Electron Microscope (TEM).....	37
2.2.4	Atomic Force Microscopy (AFM).....	38
2.2.5	Raman Spectroscopy.....	39
2.2.6	Photoluminescence (PL) Spectroscopy.....	42
2.2.7	UV-Visible Spectrophotometer.....	43
2.2.8	Current Voltage (IV) Measurement.....	43
2.2.9	SERS Measurement.....	44

Chapter 3	Thermal Conductivity of MoS₂ Nanostructures using Optothermal Raman Spectroscopy Technique.....	45-66
3.1	Introduction.....	45
3.2	Results and Discussion.....	48
3.2.1	Thermal Conductivity of Triangular Supported Bi-Layer MoS ₂	48
3.2.1.1	Characterization of Triangular Bi-Layer MoS ₂	48
3.2.1.2	Calculation of Thermal Conductivity of Supported Bi-Layer MoS ₂ Film.....	49
3.2.2	Thermal Conductivity of Vertically Oriented Few-Layer MoS ₂ Film.....	58
3.2.2.1	Characterization of VFL-MoS ₂ Film.....	58
3.2.2.2	Calculation of Thermal Conductivity of VFL-MoS ₂ Film.....	60
3.3	Conclusions.....	66
Chapter 4	Thermal Sensitive Quantum Confinement of MoS₂ Nanostructures.....	67-80
4.1	Introduction.....	67
4.1.1	Origin of Photoluminescence and Variation of Bandgap in 2D Materials.....	69
4.2	Results and Discussion.....	71
4.2.1	Origin of Photoluminescence in MoS ₂ Nanostructures.....	71
4.2.2	Temperature Dependent PL Study of Horizontally Grown Triangular Shaped Bi-Layer MoS ₂	73
4.2.3	Temperature Dependent PL Study of Vertically Grown Few-Layer MoS ₂	77
4.3	Conclusions.....	79
Chapter 5	Photodetection Application of MoS₂ Nanostructures.....	81-96
5.1	Introduction.....	81
5.2	Results and Discussion.....	83
5.2.1	Photodetection Behaviour of Horizontally Grown Interconnected Network of Few-Layer MoS ₂	83
5.2.1.1	Characterization of Horizontally Grown Interconnected Few-Layer MoS ₂	83

5.2.1.2	Photoresponse of Few-Layer MoS ₂ /Si Heterojunction.....	85
5.2.2	Photodetection Behaviour of Vertically Oriented Few-Layer MoS ₂	90
5.2.2.1	Characterization of Vertically Oriented Few-Layer MoS ₂	90
5.2.2.2	Photoresponse of Vertically Oriented Few-Layer MoS ₂ /Si Heterojunction.....	92
5.3	Conclusions.....	95
Chapter 6	SERS Application of MoS₂ Nanostructures.....	97-116
6.1	Introduction.....	97
6.1.1	Enhancement Factor (EF).....	99
6.1.2	Mechanism for SERS Signal using MoS ₂ Substrates.....	100
6.2	Results and Discussion	103
6.2.1	Characterization of Dye Molecules.....	103
6.2.2	SERS Application of Horizontally Grown Interconnected Network of Few-Layer MoS ₂	105
6.2.3	SERS Application of Horizontally Grown Triangular Bi-Layer MoS ₂	108
6.2.4	SERS Application of Vertically Oriented Few-layer MoS ₂	111
6.3	Conclusions.....	116
Chapter 7	Conclusion and Scope for Future Work.....	117-119
7.1	Conclusions.....	117
7.2	Future Scope of the Work.....	119
References.....		121
List of Publications.....		141

List of Figures

Figure 1.1 Schematic diagram of periodic table with highlighted transition metals (green in colour) and three chalcogen elements (yellow in colour) [21].....	2
Figure 1.2 Schematic diagram of (a) Side view of MoS ₂ and (b) Top view of MoS ₂	3
Figure 1.3 Schematic diagram of MoS ₂ polytypes (a) 1T phase (tetragonal symmetry, one layer per repeat unit, octahedral coordination) (b) 2H phase (hexagonal symmetry, two layers per repeat unit, trigonal prismatic coordination) (c) 3R phase (rhombohedral symmetry, three layers per repeat unit, trigonal prismatic coordination) [11]	4
Figure 1.4 Schematic representation of different Raman active modes of MoS ₂ [31].....	5
Figure 1.5 Applications of 2D MoS ₂ nanostructures.....	12
Figure 1.6 Schematic diagram of optothermal Raman technique. Black arrow shows the direction of heat flow [72].....	14
Figure 1.7 The electromagnetic spectrum of 2D TMDs [91].....	18
Figure 1.8 Band alignment of p-n junction under photoconductive mode [92].	19
Figure 1.9 Band alignment of p-n junction under photovoltaic mode [92].	20
Figure 1.10 Hypothetical example of the spectral dependence of SERS [119].	24
Figure 2.1 Schematic diagram of synthesis process for 2D-MoS ₂ nanostructures.	28
Figure 2.2 Schematic diagram of MoS ₂ growth via CVD method.	29
Figure 2.3 Schematic diagram of experimental condition of synthesis of different morphologies of 2D-MoS ₂ nanostructures.	30
Figure 2.4 Schematic diagram of growth mechanism of triangular bi-layer MoS ₂ nanostructure over SiO ₂ /Si substrate.	32
Figure 2.5 Schematic diagram of growth mechanism of vertically oriented few-layer MoS ₂ nanostructure over Si substrate.	33
Figure 2.6 Schematic diagram of incident and diffracted X-rays from the crystal.....	35
Figure 2.7 Schematic diagram of core component of SEM microscope [138].....	36

Figure 2.8 (a) Schematic diagram of core component of TEM microscope. Transmitted and diffracted electrons for (b) Bright field and (c) Dark field imaging in TEM [138]	38
Figure 2.9 Schematic diagram of the atomic force microscope [141].....	39
Figure 2.10 Schematic representation of the scattering process in Raman scattering (Rayleigh, stokes and anti-stokes line) [119].....	40
Figure 2.11 Schematic diagram of Raman spectrometer.	41
Figure 2.12 Schematic representation of the photoluminescence spectroscopy [119].....	42
Figure 2.13 Schematic diagram of UV-Visible spectrometer [145].....	43
Figure 3.1 Schematic representation of optothermal Raman technique.	46
Figure 3.2 (a) Optical image, (b) Raman spectrum (Lorentzian fitting of A_{1g} and E_{2g}^1 as inset, (c) AFM image and (d) Corresponding height profile of triangular bi-layer MoS_2 over SiO_2/Si substrate.	49
Figure 3.3 (a) Schematic diagram of temperature dependent Raman study. (b) Temperature dependent Raman spectra of triangular bi-layer MoS_2 on SiO_2/Si substrate using LWD 50x. Variations of (c) Peak position and (d) FWHM with respect to temperature of triangular bi-layer MoS_2 on SiO_2/Si substrate.	53
Figure 3.4 (a) Schematic diagram of power dependent Raman study. (b) Power dependent Raman spectra of triangular bi-layer MoS_2 on SiO_2/Si substrate using LWD 50x lens. Variations of (c) Peak position and (d) FWHM with incident laser power for triangular bi-layer MoS_2	55
Figure 3.5 (a) Temperature dependent Raman spectra of triangular bi-layer MoS_2 on SiO_2/Si substrate using 100x objective lens. (b) Variation of peak position with respect to temperature. (c) Power dependent Raman spectra of triangular bi-layer MoS_2 on SiO_2/Si substrate using 100x objective lens. (d) Variation of peak position with respect to laser power.	56
Figure 3.6 (a) HRSEM (b) AFM (2D view) and (c) Height profile of VFL- MoS_2 over Si-substrate. (d) HRTEM image of edge cross sectional view of VFL- MoS_2 (e) XRD pattern and (f) Raman spectrum of VFL- MoS_2	59
Figure 3.7 (a) Schematic of temperature dependent Raman study of VFL- MoS_2 (b) Raman spectra of VFL- MoS_2 at different temperatures (c) Raman shifts and (d) FWHM of E_{2g}^1 and A_{1g} modes as a function of temperature.	62

Figure 3.8 (a) Schematic of heat conduction through VFL-MoS ₂ (b) Raman spectra of VFL-MoS ₂ at different laser powers (c) Raman shifts and (d) FWHM of E _{12g} ¹ and A _{1g} modes as a function of laser power.....	63
Figure 4.1 Schematic diagram of the temperature dependent PL measurement process.	68
Figure 4.2 Common transitions in photoluminescence process [170].....	69
Figure 4.3 A schematic representation of A and B excitons in 2D materials.	72
Figure 4.4 (a) Optical image of triangular bi-layer MoS ₂ over SiO ₂ /Si substrate. (b) Room temperature PL spectra (Gaussian fitted) of triangular bi-layer MoS ₂ over SiO ₂ /Si substrate (c) SEM image of vertically oriented few-layer MoS ₂ nanosheets (d) Room temperature PL spectra (Gaussian fitted) of VFL- MoS ₂ over Si substrate.	73
Figure 4.5 (a) Optical image of triangular bi-layer MoS ₂ over SiO ₂ /Si substrate. (b) Gaussian fitted PL spectra of triangular bi-layer MoS ₂ on SiO ₂ /Si substrate at different temperatures. Variation of (c) Total PL intensity (d) FWHM for A exciton with temperature. (e) Variation of spin-orbit splitting between A and B exciton with temperature. (f) Fitting of variation in bandgap with temperature.....	75
Figure 4.6 (a) SEM image of VFL-MoS ₂ (b) Gaussian fitted PL spectra of VFL-MoS ₂ on Si substrate at different temperatures. Variation of (c) Total PL intensity (d) FWHM for A exciton with temperature for VFL-MoS ₂ . Variation of (e) Spin-orbit splitting between A and B exciton with temperature of VFL-MoS ₂ . (f) Fitting of variation in bandgap with temperature of VFL-MoS ₂	79
Figure 5.1 Schematic representation of p-n junction-based photodetector.	83
Figure 5.2 (a) SEM image (b) AFM image (c) Corresponding height profile and (d) Raman spectrum of interconnected network of few-layer MoS ₂ over Si substrate.....	84
Figure 5.3 (a) Photoluminescence spectrum of interconnected network of few-layer MoS ₂ grown over Si substrate (b) Current-Voltage (I-V) characteristics curve of few-layer MoS ₂ /Si heterojunction at dark conditions. (c) Current-Voltage (I-V) curve under dark and white light illumination. (d) Reverse bias current vs reverse bias voltage.....	87
Figure 5.4 Schematic band diagram of p-type Si and n-MoS ₂ (a) Before contact (b) Equilibrium (c) Forward bias and (d) Reverse bias conditions. E _C , E _V , and E _F denote the conduction band, valence band, and Fermi energy level, respectively.	89
Figure 5.5 (a) Photograph of VFL-MoS ₂ grown over Si indicating 1x1 cm ² growth region, (b) SEM image, (c) HRTEM image, (d) SAED pattern, (e) XRD pattern and (f) Photoluminescence spectrum of VFL-MoS ₂ grown over Si substrate	91

Figure 5.6 (a) I-V characteristics of VFL-MoS ₂ /Si p-n junction photodiode under dark condition. (b) I-V curves of VFL-MoS ₂ /Si photodiode under dark and different illumination. (c) Photocurrent vs laser intensities at -2V. (d) Switching behaviour of photodiode at -3V.....	94
Figure 6.1 Schematic diagram of SERS process.	98
Figure 6.2 The coupling diagram for B-term and C-term in semiconductor-molecule system [36].....	102
Figure 6.3 The photograph of aqueous solutions of (a) R6G and (b) MO dye at two different concentrations.	103
Figure 6.4 UV-Vis spectra of (a) R6G in DI water and (b) MO in DI water (c) Corresponding Tauc plot of R6G. (d) Corresponding Tauc plot of MO.	104
Figure 6.5 Raman spectra of (a) Bulk R6G and (b) Bulk MO on glass slide.	105
Figure 6.6 (a) SEM image of few-layer MoS ₂ /Si substrate, (b) SERS spectrum showing characteristic peaks of MoS ₂ , Si and R6G, (c) SERS spectra of R6G molecules on interconnected network of few-layer MoS ₂ /Si substrate at different concentrations (10 ⁻³ to 10 ⁻⁹ M), (d) Raman intensity of 1362 cm ⁻¹ peak for R6G as a function of the R6G concentrations.	106
Figure 6.7 Raman spectra of R6G molecules (10 ⁻³ M) on Si substrates.	107
Figure 6.8 (a) Optical image, (b) AFM image and (c) Corresponding height profile of triangular bi-layer MoS ₂ . (d) Full range SERS spectrum of R6G on bi-layer MoS ₂ over SiO ₂ /Si substrate. (e) Raman spectra of R6G molecules on triangular bi-layer MoS ₂ over SiO ₂ /Si substrates with different concentrations from 10 ⁻⁶ to 10 ⁻⁹ M (f) Raman intensity of 612 and 1365 cm ⁻¹ peaks for R6G as a function of the concentration of R6G.	109
Figure 6.9 Raman spectra of R6G molecules (10 ⁻³ M) on SiO ₂ /Si substrates.	110
Figure 6.10 (a) SEM image, (b) Le-Bail fitting of XRD pattern, (c) Raman spectrum and (d) Room temperature PL spectrum (Gauss fitted) of VFL-MoS ₂	112
Figure 6.11 SERS spectra of (a) R6G molecules and (b) MO molecules over VFL-MoS ₂ on Si substrate. (c) SERS of R6G molecule and (d) SERS of MO molecule on pure Si substrates.	113
Figure 6.12 SERS signals of (a) R6G and (c) MO dyes over VFL-MoS ₂ at different concentrations. Raman intensity vs dye concentration of (b) R6G and (d) MO molecules for two different peaks.	114

List of Tables

Table 3.1 Thermal Conductivity of MoS ₂ Nanostructure with First-Order Temperature Coefficients (χ_T) using OTR Technique.	65
Table 5.1 Comparison of Responsivity of MoS ₂ /Si Heterojunction Photodiodes.	95
Table 6.1 Comparison of the SERS Detection Limit of Pristine MoS ₂ Nanostructures	115