## List of Tables

Table	No. Table Captions	Page No.
CHAI	PTER 3	
3.1	Percentage composition of MoS <sub>2</sub> from EDX spectrum	61
3.2	Determination of phonon lifetime in MoS <sub>2</sub> NPs sample from the Rama spectrum	an 65
3.3	Optical Energy BG calculation of MoS <sub>2</sub> NPs using KM plot	68
3.4	Percentage composition of WS <sub>2</sub> from EDX spectrum	69
3.5	Determination of phonon lifetime in WS <sub>2</sub> NPs sample from Rama spectrum	an 73
3.6	Optical Energy BG calculation of WS <sub>2</sub> NPs using KM plot	73
3.7	$2\theta$ , Millar planes and d-spacing values for MoW-disulfide1 NPs	75
3.8	$2\theta$ , Miller planes and d-spacing values for MoW-disulfide2 NPs	77
3.9	Percentage composition of MoW-disulfide1 from EDX spectrum	79
3.10	Percentage composition of MoW-disulfide2 from EDX spectrum	79
3.11	Determination of phonon lifetime in MoW-disulfide1 and MoW	V- 83
	disulfide2 sample from the Raman spectra	

**3.12** Optical Energy BG calculation MoW-disulfide1 and MoW-disulfide2 85 using KM plot

### **CHAPTER 4**

4.1	BET surface area and BJH pore size values of the as-synthesized catalysts	101
4.2	Optical energy BG values of all the as-prepared catalyst	101
4.3	Different parameters (%D, RC, $R^2$ and $t_{1/2}$ ) of the pseudo first order, zero order and polynomial regression for photocatalytic degradations of MO and RB using catalysts MoS <sub>2</sub> , MoW-disulfide1 and WS <sub>2</sub> NPs	110

### **CHAPTER 5**

5.1	Cell volume of minimized Mo <sub>8</sub> S <sub>16</sub> , Mo <sub>8</sub> WS <sub>16</sub> and Mo <sub>8</sub> W <sub>8</sub> S <sub>16</sub> systems	122
-----	--	-----

5.2 Cell parameters of minimized  $Mo_8S_{16}$ ,  $Mo_8WS_{16}$  and  $Mo_8W_8S_{16}$  122 systems

# List of Figures

Figure	No. Figure Captions	Page No.	
СНАР	TER 1		
1.1	Figure shows the position of the elements forming TMDs in the mode periodic table	ern 4	
1.2	Figure shows 1T, 2H and 3R structures of 2D $MoS_2$ . Many other TMDs like $WS_2$ also exist as these similar structures	2D 6	
CHAP	TER 2		
2.1	(a) Schematic of the experimental set-up for material synthesis. In synthesis process, the powdered raw materials are mixed thorough and heated at 500°C for 3hours followed by cooling to root temperature under $N_2$ gas environment inside a furnace to produce final product and (b) a photograph of the experimental set-up material synthesis	hly om the	
2.2	Schematic diagram of the X-ray diffractometer technique for analysis of powder sample	the 35	
2.3	Visualization of TEM technique producing a magnified image of the specin	nen 37	
2.4	SEM used to obtain a magnified image and EDX spectrum	39	
2.5	Schematic diagram showing the mechanism of Raman spectrometer	41	
2.6	Energy level diagram showing transitions in Raman spectra	41	
2.7	Schematic diagram of a UV-vis spectrometer showing its difference components	ent 43	
2.8	Schematic diagram to visualize Beer-Lambert Law	43	
2.9	Schematic diagram of the PL spectrometer technique	45	
2.10	Schematic diagram of BET measurement technique	45	
2.11	(a) Schematic diagram of photocatalytic measurement set-up and (b photograph of the experimental photocatalytic measurement set-up.	o) a 48	
CHAP	CHAPTER 3		
3.1	(a) XRD spectrum of $MoS_2$ NPs (experimental) and (b) Comparison XRD of $MoS_2$ with simulated PXRD of $MoS_2$	of 59	
3.2	TEM image showing (a) different crystal planes, (b) a bunch of gra and (c) SAED pattern in $MoS_2$ NPs sample	ins 60	
3.3	(a) SEM image, (b) particle size distribution histogram and (c) EI spectrum of $MoS_2$ NPs sample. The noise peak observed below 0.5k is not taken into consideration		
3.4	EDX spot Elemental mapping of $MoS_2$ NPs. The Bright spots represented the presence of respective elements in the image of Mo and S mapping		
3.5	(a) Raman spectrum of $MoS_2$ NPs sample showing characteristics	64	

# **Figure Captions**

modes of vibration, (b) schematic to visualize prominent  $E^{1}_{\ 2g}$  and  $A_{1g}$  modes of vibration in  $MoS_{2}$ 

3.6	Optical BG determination by using KM plot of $MoS_2$ NPs (inset is UV-vis spectrum)	67
3.7	Schematic of 'A', 'B' and 'C' excitonic transition in TMDs	67
3.8	(a) XRD pattern of WS <sub>2</sub> NPs showing different characteristic peaks corresponding to Miller crystal planes and (b) Comparison of XRD pattern of WS <sub>2</sub> with simulated PXRD of WS <sub>2</sub>	70
3.9	(a) TEM micrograph and (b) SAED pattern of $WS_2 NPs$ sample	71
3.10	(a) SEM image, (b) particle size distribution and (c) EDX spectrum of $WS_2$ NPs sample. The noise peak observed below 0.5keV is not taken into consideration	71
3.11	EDX elemental mapping of $WS_2$ NPs sample. The bright spots in a black background in the second and third image represent the positions of respective elements W and S in the selected area	72
3.12	Raman spectrum of $WS_2$ NPs showing prominent Raman active modes in the sample	74
3.13	Optical BG determination by using KM plot of $WS_2$ NPs (inset is UV-vis spectrum)	74
3.14	XRD patterns of (i) $MoS_2$ , (ii) $WS_2$ , (iii) MoW-disulfide1 and (iv) MoW-disulfide2 NPs sample	76
3.15	TEM micrograph of (a) MoW-disulfide1 and (b) MoW-disulfide2 showing different Miller planes	78
3.16	Figure shows (a) SEM image, (b) particle size distribution and (c) EDX spectrum of MoW-disulfide1 NPs and (d) SEM image, (e) particle size distribution and (f) EDX spectrum of MoW-disulfide2 NPs	80
3.17	EDX Elemental mapping of MoW-disulfide1. The bright spots in black background in the second, third and fourth images represent the positions of respective elements S, Mo and W in the selected area	81
3.18	EDX Elemental mapping of MoW-disulfide2. The bright spots in black background in the second, third and fourth images represent the positions of respective elements S, Mo and W in the selected area	82
3.19	Raman spectra of (a) MoW-disulfide1 NPs and (b) MoW-disulfide2 NPs	84
3.20	Optical BG determination by using KM plot of compound (a) MoW- disulfide1and (b) MoW-disulfide2 NPs (inset is UV-vis spectra)	86
3.21	PL spectra of $MoS_2$ , $WS_2$ , MoW-disulfide1 and MoW-disulfide2 at (a) 300nm (4.13eV) and (b) 500nm (2.48eV). The enhancement of PL peak is observed in case of ternary compound MoW-disulfide1 having largest normalized intensity	88

Figure No.

#### **Figure Captions**

**3.22** The figure shows (a) the excitation of a direct BG semiconductor by light radiation generating electron-hole pairs and (b) re-emission of light by the process of radiative recombination of electron and holes

### **CHAPTER 4**

- 4.1  $N_2$  adsorption/desorption isotherm and the BJH pore size distribution 99 (inset) of (a) MoS<sub>2</sub>, (b) WS<sub>2</sub> and (c) MoW-disulfide1 NPs as photocatalysts
- **4.2** (a) and (b) represent  $MoS_2$  and  $WS_2$  system respectively having no 100 defect states. (c) a schematic of the generation of lattice vacancy due to the size mismatch of W and Mo in the ternary compound system
- **4.3** (a) The UV-vis spectra and (b) KM plot showing different values of 102 optical BGs of all the as-prepared catalysts
- **4.4** Absorption spectra of MO (a, b & c) and RB (d, e & f) degraded by 105 MoS<sub>2</sub>, MoW-disulfide1, and WS<sub>2</sub> NPs catalysts respectively under light irradiation
- **4.5** Comparison of percentage degradation measurements of (a) MO and (b) 107 RB using all the catalysts, Decolourisation of (c) MO and (d) RB using MoW-disulfide1 photocatalyst
- **4.6** A photocatalytic mechanism for a catalyst having Multiple BGs 108 showing transfer of electron-holes with the oxidation-reduction process
- **4.7** Schematic diagram showing different steps of the heterogeneous 108 photocatalytic reaction
- **4.8** Photocatalytic degradation kinetics of MO for (a) pseudo first order, 111 (b) polynomial and (c) zero order regression using MoS<sub>2</sub> NPs catalyst and of RB for (d) pseudo first order, (e) polynomial and (f) zero order regression using MoS<sub>2</sub> NPs catalyst
- 4.9 Photocatalytic degradation kinetics of MO for (a) pseudo first order, 112
  (b) polynomial and (c) zero order regression using WS<sub>2</sub> NPs catalyst and of RB for (d) pseudo first order, (e) polynomial and (f) zero order regression using MoS<sub>2</sub> NPs catalyst
- 4.10 Photocatalytic degradation kinetics of MO for (a) pseudo first order, 113
  (b) polynomial and (c) zero order regression using MoW-disulfide1
  NPs catalyst and of RB for (d) pseudo first order, (e) polynomial and (f) zero order regression using MoW-disulfide1 NPs catalyst
- **4.11** (a) XRD and (b) EDX spectra of the compound catalyst recycled after 115 seven consecutive photocatalytic reactions. The noise below 0.5keV is not taken into consideration

#### **CHAPTER 5**

5.1 DFT model of (a)  $Mo_8S_{16}$ , (b)  $Mo_8WS_{16}$  and (c)  $Mo_8W_8S_{16}$  systems 123

Figure	No. Figure Captions	Page No.
5.2	(a) Band structure plot of $Mo_8S_{16}$	125
5.2	Band structure plot of (b) $Mo_8WS_{16}$ and (c) $Mo_8W_8S_{16}$ . The inset each plot shows that the system transits from indirect to direct band g system in $Mo_8W_8S_{16}$	
5.3	TDOS plot of $Mo_8S_{16}$ , $Mo_8WS_{16}$ and $Mo_8W_8S_{16}$	129
5.4	PDOS plot of $Mo_8S_{16}$ showing (a) various states of Mo and (b) states of S	tes 130
5.5	PDOS plot of $Mo_8WS_{16}$ showing (a) various states of Mo and W, a (b) states of S	und 131
5.6	PDOS plot of $Mo_8W_8S_{16}$ showing (a) various states of Mo and various states of S	(b) 132
5.6	(c) PDOS plot of $Mo_8W_8S_{16}$ showing various states of W	133

# List of symbols and abbreviations

2D	Two dimensional
TMD	Transition metal dichalcogenide
SC	Semiconductor
BG	Band gap
MBG	Multiple band gap
PL	Photoluminescence
DFT	Density functional theory
VASP	Vienna Ab initio Simulation Package
LDA	Local density approximation
GGA	Generalized gradient approximation
PBE	Perdew-Burke-Ernzerhof
NP	Nanoparticle
UV-vis	Ultra violet and visible
RB	Rhodamine B
MO	Methyl Orange
d or $d_{hkl}$	Crystal plane spacing or interplanar spacing
λ	Wavelength
θ	Bragg's angle
JCPDS	Joint committee on powder diffraction standards
SAED	Selected area electron diffraction
BET	Brunauer-Emmett-Teller
BJH	Berrett-Joyner-Halenda
K.E.	Kinetic energy
L	Crystallite size
$a(\lambda)$	Wavelength dependent absorptivity constant
KM	Kubelka-Munk
F(R)	Kubelka-Munk function
KS	Kohn-Sham
С	Concentration

c	Speed of light in vacuum
μΜ	Micro molar
eV	Electron volt
rpm	Rotation/revolution per minute
%D	Percentage of degradation
$A_0$	Initial absorbance
A <sub>t</sub>	Absorbance at time t
ps	picosecond
n	Electron density
DOS	Density of states
TDOS	Total density of states
PDOS	Partial density of states
τ	Phonon lifetime
F.W.H.M	Full width at half maximum
VB	Valence band
CB	Conduction band
BZ	Brillouin zone
Eg	Band gap energy value
υ	frequency
e <sup>-1</sup>	electron
$\mathbf{h}^+$	hole
RC	Rate constant
$V_{\text{eff}}$	Kohn-Sham potential or effective potential
3	Eigenenergy
V <sub>xc</sub>	Exchange correlation potential
K or k	momentum
E-K	Energy-momentum
$H_2MoO_4$	Molybdic acid
$H_2WO_4$	Tungstic acid
NH <sub>2</sub> CSNH <sub>2</sub>	Thiourea