

List of Tables

Chapter	Table	Title	Page no.
Chapter III			
	3.1	Raman spectra analysis of WS ₂ and WS ₂ /C-dot nanoscale system	58
Chapter IV			
	4.1	Comparison of photocatalytic activity of the systems under study	74
Chapter V			
	5.1	Physical parameters related to thermogravimetric weight loss for nanocomposite systems	91
	5.2	Physical parameters of nanocomposite films determined through UTM	92
	5.3 A	Wetting-dewetting phenomena: Contact angle (CA) parameter and CA hysteresis measured at the nanocomposite film surfaces	96
	5.3 B	Wetting-dewetting phenomena: Surface energy measured at the nanocomposite film surfaces	99
Chapter VI			
	6.1	Electronic and nuclear energy losses and projectile ranges of ions in target materials	107
	6.2	Structural parameters obtained through XRD analyses	109
	6.3 A	Physical parameters obtained from the optical absorption and PL spectra	115
	6.3 B	Raman active modes and mode-assignment	117

List of Figures

Chapter	Figure no.	Caption	Page no.
Chapter I			
	1.1	Schematic representation of the density of states vs energy of 3D, 2D, 1D and 0D nanomaterials	2
	1.2	Schematic representation of band gap of graphene and TMDC systems	3
	1.3	Periodic table showing different groups of TMDC materials	5
	1.4	Schematic representation of trigonal and octahedral coordination	6
	1.5	Schematic representation of the arrangements of atoms in WS ₂	7
	1.6	Schematic diagram of (a) bulk WS ₂ material exfoliated to nanosheets, (b) IF- type WS ₂ nanoparticles	8
	1.7	Schematic representation of stress-strain curve, showing elastic and plastic regions	11
	1.8	Schematic representation of Stribeck curve	11
	1.9	Schematic representation of different processes occur during ion matter interaction	13
Chapter II			
	2.1	Schematic diagram of synthesis of IF-type WS ₂ nanoparticles	28
	2.2	X-ray diffractograms of the prepared samples, and (b) the W-H plot for sample S ₂	30
	2.3	EDX spectra of the as-prepared nano-WS ₂ samples	31
	2.4	SEM micrographs of the as-prepared nano-WS ₂ system: (a) low magnification, (b) high magnification	32
	2.5	(a) TEM micrograph depicting distributed	32

	view of IF-type WS ₂ nanoparticles with a histogram on size distribution (inset), (b) SAED pattern, (c) a single IF nano-WS ₂ structure and (d) enlarged view of a segment showing the bent lattice structure of the WS ₂ nanosystem	
2.6	Raman spectrum of the as-prepared IF-type WS ₂ nanosystem (S ₂)	33
2.7	FTIR spectrum of the as-prepared IF-type WS ₂ nanosystem (S ₂)	35
2.8	(a) UV-Vis optical absorption spectrum along with the Tauc's plot (inset) (b) PL spectrum of the IF nano-WS ₂ system. (c) Schematic diagram showing indirect to direct band gap transition	36
2.9	Representative steps as regards the synthesis of WS ₂ nanosheets	38
2.10	XRD patterns of un-exfoliated WS ₂ (S ₁) and exfoliated WS ₂ nanosheets (S ₂)	39
2.11	SEM micrograph of (a) un-exfoliated WS ₂ powder and (b) exfoliated WS ₂ nanosheets; (c) The EDX micrograph of the un-exfoliated WS ₂ powder	40
2.12	TEM micrograph of (a) WS ₂ nanosheets, (b) magnified view of the sheets, (c) lattice fringe pattern captured at the surface and (d) SAED pattern indicating diffused diffraction rings	40
2.13	UV-Vis optical absorption spectra of the un-exfoliated WS ₂ powder (S ₁) and exfoliated WS ₂ nanosheets (S ₂)	41
2.14	Raman spectra of the un-exfoliated WS ₂ nanopowder (S ₁) and exfoliated WS ₂ nanosheets (S ₂)	42
2.15	(a) The nitrogen gas adsorption-desorption curve and (b) The BJH pore size distribution curve of the unexfoliated WS ₂ and WS ₂ nanosheets	43
2.16	Schematic block diagram of the synthesis steps for processing WS ₂ nanopowder,	46

nanosheets and WS₂/C-dot hybrid nanosystems

- 2.17 (a) X-ray diffractogram and (b-d) scanning electron micrographs of the synthesized nano-WS₂ system. Note the sheets with folds and kinks at higher magnifications. The EDX spectrum is shown as inset in (a) 47
- 2.18 TEM images of (a) nano-WS₂ with C-dots at low magnification, (b) WS₂/C-dot nanohybrid at a higher magnification, and (c) an enlarged view of the isolated C-dots. Information with regard to lattice fringe patterns of the WS₂ and C-dot systems can be noticed in (d) and (e); respectively. The SAED pattern highlighting diffused rings is shown in (f). Whereas, elemental mappings of the WS₂/C dot nanohybrid can be found in (g-i) 48
- 2.19 Schematic figure representing the growth mechanism of the nanosheets and nano hybrid systems 49

Chapter III

- 3.1 Raman spectra of the WS₂ nanosheet and WS₂/C-dot nanohybrid systems. The magnified views of the E'_{2g} and A_{1g} modes are highlighted in (b) 57
- 3.2 (A) (a) UV visible optical absorption and (b) PL emission spectra ($\lambda_{ex} = 360$ nm) of the synthesized WS₂/C dot nanosystems. Digital photographs captured under visible and UV light exposure of the cuvette containing nanohybrid specimen, are shown in (c) 61
- 3.2 (B) A series of (a) excitation dependent PL emission spectra and that of (b) PL excitation spectra of the WS₂/C-dot nanosystem. Since excitation at $\lambda_{ex} = 560$ nm gives a weak emission peak at $\lambda_{em} = 714$ nm, it is shown independently as figure inset of (a) 62
- 3.3 Schematic representation of the effects responsible for excitation dependent PL spectra 62
- 3.4 The fluorescence micrographs under different excitation source: for which (a) 63

white, (b) UV, (c) blue, and (d) green band-pass filters have been used

Chapter IV

4.1	Molecular structure of the harmful organic dyes	68
4.2	Schematic of the photocatalytic mechanism expected in the nano-WS ₂ system	70
4.3	UV-Vis absorption spectra of MG and IF nano-WS ₂ catalyst-loaded dye with different irradiation times: (a) UV illumination, (b) visible light illumination. The respective percentage of degradation and pseudo-first-order plots under the aforesaid conditions are shown in (c) and (d) on a comparative basis	72
4.4	UV-Vis optical absorption spectra of MG and WS ₂ nanocatalyst (nanosheet)-loaded dye with different irradiation times, percentage of photodegradation and pseudo-first-order plots: (a-c) UV light illumination and (d-f) visible light illumination	74
4.5	(A) Optical absorption spectral features illustrating photodegradation of (a) MO and (b) MG dyes under visible light illumination and using WS ₂ nanosheets as the desired nanocatalyst. The exact nature of degradation with exposure time can be found in col.2 and col.3. (B) Optical absorption spectral features illustrating photodegradation of (a) MO and (b) MG dyes under visible light illumination and using WS ₂ /C-dots as the desired nanocatalyst. The exact nature of degradation with exposure time can be found in col.2 and col.3	76
4.6	Schematic illustration of the photocatalytic activity: (a) degradation mechanism and (b) relevant energy scheme	77

Chapter V

5.1	XRD plots of (A) IF-type WS ₂ nanopowder, (B) IF-WS ₂ /PVA nanocomposite films with different loading: (a) 0%, (b) 3 %, (c) 6%, (d) 10%. The W-H plot relevant to diffractogram of the IF-WS ₂ nanosystem is shown in (C)	85
-----	--	----

5.2 (A)	SEM images of IF-WS ₂ /PVA solid films with different nanoparticle loading: (a) 3%, (b) 6% and (c) 10%. The magnified images are shown in (d), (e) and (f); respectively	87
5.2 (B)	TEM micrographs of the IF-WS ₂ nanoparticles at (a) lower magnification, (b,c) higher magnification, and (d) enlarged IF-type WS ₂ highlighting interplanar spacing and bending at the surface. SAED pattern is shown as inset of (a)	87
5.2 (C)	EDX spectra of (a) IF-WS ₂ only and (b) IF-WS ₂ /PVA composite film (6 wt% loading)	88
5.3	FT-IR spectra of (a) pure PVA, (b) pure IF-WS ₂ and (c) IF-WS ₂ /PVA nanocomposites	89
5.4	TGA plots of (a) pure IF-type WS ₂ and (b) pure PVA and specimens with nano-WS ₂ loading at different wt%	91
5.5	(a) Schematic curve of stress strain relationship (b) actual stress-strain plots measured for pure PVA and IF-WS ₂ nanocomposites at different wt% of WS ₂ loading	91
5.6	Stribeck curves for pure PVA and IF-WS ₂ /PVA nanocomposites for (a) pure PVA, and PVA with nano IF-WS ₂ at (b) 3wt%, (c) 6wt% and (d) 10wt% loading	93
5.7	Schematic representation of the three friction mechanisms of IF- particles rolling, sliding and exfoliation	94
5.8	Static water contact angle snap-shots for (a) pure PVA, and PVA with nano IF-WS ₂ at (b) 3wt%, (c) 6wt% and (d) 10wt% loading	95
5.9	Dynamic CA hysteresis obtained for different films: (a) PVA only, and PVA with nano IF-WS ₂ inclusions at (b) 3% wt%, (c) 6 wt% and (d) 10 wt% loading	97
5.10	Curve showing the variation of total surface energy, polar component of surface energy and dispersive component of surface energy for different wt% loading of IF-WS ₂ in PVA	99

Chapter VI

6.1	The schematic representation of the preparation of samples for the irradiation experiment along with the digital photographs of the un-irradiated and post irradiated samples, shown at the extreme right	106
6.2	XRD patterns of the un-irradiated and irradiated nano-WS ₂ samples	108
6.3	TEM micrographs of (a) un-irradiated and irradiated nano-WS ₂ samples with a fluence variation of (b) 1×10^{15} , (c) 5×10^{15} , (d) 1×10^{16} , (e) 5×10^{16} ions/cm ² , while SAED patterns are shown as insets in the mid-column figures. The splitting of nano-stacks into sheets and lattice fringes are evident at higher magnifications. The EDX spectra of the respective systems, with elemental energy spikes are depicted in the extreme right column	110
6.4	Elemental mapping of the sample F4, which illustrates the distribution of W, S and Xe sites spread over an approximate area of 70 $\mu\text{m} \times 50 \mu\text{m}$	111
6.5	Schematic representation of the impact of irradiation on the WS ₂ sheets	112
6.6 (A)	2D and 3D AFM images of the (a) un-irradiated (F0) and irradiated nano-WS ₂ systems subjected to a fluence variation of (b) 1×10^{15} (F1), (c) 5×10^{15} (F2), (d) 1×10^{16} (F3), (e) 5×10^{16} (F4) ions/cm ² . The magnified 2D images of pristine (F0) and irradiated (F4) nano-WS ₂ are also shown on the right hand side	113
6.6 (B)	The variation in % S loss, % Xe content and surface roughness with increasing ion fluence	113
6.7	PL spectra of (a) un-irradiated (F0), and irradiated nano-WS ₂ systems subjected to a fluence variation of 1×10^{15} (F1), 5×10^{15} (F2), 1×10^{16} (F3), 5×10^{16} (F4) ions/cm ² . The schematic of an asymmetric PL response with symmetry factors is shown in (b)	114

6.7	(c) Stokes shift shown for the un-irradiated and irradiated nano-WS ₂ samples (F0-F4).	125
6.8	Raman spectra of (a) un-irradiated (F0), and irradiated nano-WS ₂ systems: (b) 1×10^{15} (F1), (c) 5×10^{15} (F2), (d) 1×10^{16} (F3), (e) 5×10^{16} (F4) ions/cm ²	117
6.9	Static water contact angle (CA) values measured at the surfaces of un-irradiated and irradiated nano-WS ₂ systems. Note the progressive increase in CA with increasing ion fluence from F1 to F4: F1= 1×10^{15} , F2= 5×10^{15} , F3= 1×10^{16} , F4= 5×10^{16}	118
6.10	Variation of the CA and roughness with increasing ion fluence, (b) variation of contact line and CA with surface roughness.	119

List of abbreviations

Abbreviations	Names
TMDC	Transition metal dichalcogenides
nm	Nanometer
eV	Electron volt
0D	Zero dimensional
1D	One dimensional
2D	Two dimensional
3D	Three dimensional
IF	Inorganic fullerene
JCPDS	Joint Committee on Powder Diffraction Standards
DI	Deionized
SEM	Scanning Electron Microscope
EDX	Energy dispersive X-ray spectroscopy
TEM	Transmission Electron Microscope
FTIR	Fourier transform infrared spectroscopy
FWHM	Full width at half maxima
HRTEM	High resolution transmission electron microscopy
AFM	Atomic force microscopy
KeV	Kilo electron volt
MeV	Mega electron volt
BET	Bruner-Emmett-Teller
BJH	Barrett-Joyner-Halenda

μm	Micrometer
SAED	Selected area electron diffraction
TGA	Thermogravimetric
UV	Ultra-violet
SRIM	Stopping and range of ions in matter
TRIM	Transport of ions in matter
XRD	X-ray diffraction
Å	Angstrom
NMP	1-methyl-2-pyrrolidone
C-dot	Carbon dot
PVA	Polyvinyl alcohol
MG	Malachite green
MO	Methyl orange
COF	Coefficient of friction
CA	Contact angle
CAH	Contact angle hysteresis

List of Symbols

Symbols	Meanings
β	Full width half maxima
ε	Microstrain
E_{12g}^{12g}	In-plane Raman vibrational mode
A_{1g}	Out-of-plane Raman vibrational mode
λ_{ex}	Excitation wavelength
λ_{em}	Emission wavelength
C_0	Initial concentration of the dye before irradiation
C_t	Concentration of the dye after irradiation
k_a	Rate constant
θ_{adv}	Advancing angle
θ_{rec}	Receding angle
γ_s^d	Dispersive component of surface energy
γ_s^p	Polar component of surface energy
S_e	Electronic energy loss
S_n	Nuclear energy loss
R_q	Root mean square roughness
σ_L	Left symmetry factor
σ_R	Right symmetry factor
Δ	Stoke's shift
S_p	Electron phonon coupling constant
ω_{LO}	Longitudinal optical phonon frequency
\hbar	Planck's constant