STUDIES ON SURFACE MORPHOLOGY, MECHANICAL PROPERTIES AND EXCITON DYNAMICS OF NANOSCALE TUNGSTEN DICHALCOGENIDES EMPHASIZING RADIATION EFFECTS

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Chapter 7.
Conclusion and future directions

7.1 Conclusions

This thesis aims to explore the characteristics of few-layer tungsten disulfide (WS_2) and tungsten diselenide (WSe_2) materials under various radiation environments. A broad and diverse range of irradiation techniques were employed, incorporating energetic particle exposure, diverse ion species, ion beams, and varying ion fluences to examine their effects on these materials from eV to near GeV energy scale. The results reveal a range of intriguing phenomena that depend on both the type of radiation exposure and the fluence/doses chosen. Consequently, several investigations were conducted to understand the radiation-induced phenomena in these systems. In particular, the impact of UV- and β-irradiation was studied with an emphasis on changes in material porosity and the resulting influence on photocatalytic efficiency, especially in the case of WS_2. Moreover, WS_2 was subjected to energetic γ-ray exposure to examine the mechanical properties, specifically in terms of strength and load-bearing capacity. In addition, to inspect the radiation-induced effects, ion beams such as He^{2+}, C^{2+}, and U^{28+} ions were employed to irradiate the WS_2 system across a varied energy range, from low-energy (keV scale) to high-energy (GeV-scale) irradiation. The resulting structural, vibrational, morphological, luminescence and excitonic emission-related manifestations are discussed. Furthermore, an interesting feature observed in the WS_2 system was the formation of ion tracks upon high-energy 0.85 GeV U^{28+} impact. Besides, the WSe_2 system was also investigated to study its structural and morphological modification with different ions, as well as rheological responses explicitly under γ-irradiation. Lastly, first-principles calculations were conducted to complement the experimental results, specifically focusing on the formation of single-vacancy (chalcogen-based) defects, defect clusters, dopant incorporation, and migration barrier energy. These calculations supported correlating radiation-induced phenomena, such as defect formations, with variations in the electronic band structures of WS_2 and WSe_2 systems independently. This chapter summarizes the key results and findings inferred from the studies conducted on the aforementioned systems.

In Chapter 2, various synthesis processes as regards exfoliated WS_2 and WSe_2 materials, and basic characterization techniques are detailed. Development of fractal-like patterns formed in WS_2/NaCMC composites via a solvent-evaporation method has been discussed. Morphological analysis through FE-SEM and AFM revealed the evolution of fractal structures, with NaCMC serving both as a host matrix and a percolating agent crucial to pattern formation in the 2D WS_2 system. Fractal dimension analysis using the box counting method showed bi- and tri-modal fractal features, with dimensions varying from 1.98 to 1.60 as WS_2 content in NaCMC host was increased from 1 to 4 wt.%.

In Chapter 3, the structural and mechanical effects of γ-irradiation on WS_2 and its nanocomposites are highlighted. XRD confirms the hexagonal crystal structure of WS_2 with *c*-axis orientation, while Raman spectroscopy identifies in-plane, E^{1}_{2g} mode at ~352 cm^{-1} and out-of-plane, A_{1g} mode at ~418 cm^{-1}, along with defect-related *LA* modes near ~178 cm^{-1}, prominent at 35 kGy γ-dose. XPS reveals W^{4+} and S^{2-} oxidation states, with slight shifting of binding energy and peak broadening after irradiation, indicating deviations from the stoichiometric ratio of 1:2 in WS_2 system through the formation of sulfur vacancies. Further, the tensile measurements reveal enhancement in tensile strength, ductility, and flexibility, particularly at 1 wt.% WS_2 loading and 10 kGy dose, due to an improved interfacial bonding with the NaCMC host matrix after γ-irradiation. The nanocomposites show up to an 83% increase in strength, with higher energy absorption and elongation at break. However, higher filler loadings and doses cause microcracks, stress concentration, and void formation, reducing their mechanical strength.

In Chapter 4, a comprehensive analysis of the structural modifications in WS_2 resulting from exfoliation and UV- and *β*-radiation exposure are presented. FE-SEM imaging revealed a distinct layered morphology with clear separation of sheets from the bulk WS_2, whereas elemental analysis confirmed the presence of sulfur vacancies. Exfoliated WS_2 nanosheets exhibited an enrichment of meso- and macropores, likely influenced by defect formation and further enhanced by UV- and *β*-radiation exposure. N_2 adsorption-desorption isotherms reveal type IV characteristics, and BJH pore-size distribution confirms the presence of a wide range of pore sizes. Raman spectroscopy showed redshifted and broadened E^{1}_{2g} (~352 cm^{-1}) and A_{1g} (~421 cm^{-1}) vibrational modes due to localized thermal effects at higher laser power. Furthermore, *β*-irradiated WS_2 demonstrated an improved photocatalytic performance, particularly under UV-light exposure, achieving approximately 59.4% degradation of congo red dye within ~45 min.

In Chapter 5, the effect of ion irradiation on the structural, morphological, optical and electronic properties of WS_2 are discussed. 15 keV He^{2+} ions induce the formation of helium bubbles, nanovoids, and surface corrugation. Moreover, oblique ion incidence at 55° causes exfoliation and slipping of layers, while normal incidence leads to the formation of inorganic fullerene (IF)-like structures at a critical fluence of 5×10^{15} ions/cm^2, as confirmed by HR-TEM imaging. With 15 keV C^{2+} ion irradiation, the development of localized WC phase above ion fluence 1×10^{15} ions/cm^2 and graphitic carbon dots were observed, along with a disproportionate augment in carbon content at higher fluences. The DFT calculations reveal that carbon as a dopant and sulfur vacancies shift the conduction band minimum to the *M*-point in the Brillouin zone, enabling bandgap tuning and a transition from semiconducting to semi-metallic behaviour. Furthermore, swift heavy ion (SHI) irradiation using 0.85 GeV U^{28+} ions results in sulfur vacancies, ion track formation of track diameter, ~6-7 nm in both bulk and exfoliated WS_2 systems. Temperature-dependent PL measurements of exfoliated WS_2 display that direct exciton emission becomes predominant, whereas emission from defect-related trap states drops beyond ~240 K. The integrated PL intensity plot reveals a substantial enhancement in defect-bound emission after irradiation, with 4.6 times increase at 10 K, attributed to the higher defect concentration in exfoliated WS_2, while the exciton emission displays a 1.6-fold decline in intensity. From the temperature-dependence of emission intensity plots, the first-order temperature coefficients (α), obtained through linear fits to the defect emission intensities of exfoliated WS_2, both pristine and irradiated at a fluence of 1×10^{11} ions/cm^2, were found to be negative, with values of 2.2×10^{-3} K^{-1} and 3.0×10^{-3} K^{-1}, respectively. In the case of irradiated bulk WS_2, the direct exciton and defect-bound emissions also exhibited negative α values of 3.0×10^{-3} K^{-1} and 2.5×10^{-3} K^{-1}, respectively. However, for exfoliated WS_2, the direct excitonic emission displayed a nonlinear temperature dependence, described by a third-order polynomial fit. Furthermore, the average exciton lifetimes (τ_{av}) decrease by 32 % in the bulk WS_2 and by 21 % in the exfoliated system after irradiation, exhibiting the presence of non-radiative defect states induced after irradiation. Notably, the overall quantum yield, calculated from time-resolved photoluminescence (TR-PL) decay dynamics, was markedly higher in irradiated exfoliated WS_2, reaching 92.4 %. This suggests that the defect states introduced in the exfoliated system act as efficient radiative centers, thereby enhancing radiative recombination pathways.

In Chapter 6, the role of ion irradiation in precisely tailoring the properties of the WSe_2 system is investigated. The study investigates the effects of γ-rays, 15 keV He^{2+} and C^{2+} ions, and high-energy 60 MeV N^{5+} ions, revealing that the phase structure and crystallinity of WSe_2 remain largely intact, as confirmed by XRD patterns retaining the hexagonal crystal structure. When γ-irradiated WSe_2 was incorporated into a NaCMC polymer solution, the resulting nanocomposite exhibited a non-Newtonian, shear-thinning behaviour, with a power-law index between 0.84 and 0.86 when considered in the moderate shear rate range of 0-1000 s^{-1}. The fitted plots across various shear rate ranges reveal a transition from Newtonian behaviour ($m \approx 1$) to non-Newtonian behaviour ($m < 1$), as depicted in the bar graphs, with increasing shear rate from low to moderate values. The derivative curve of viscosity indicates that the glass transition temperature of the WSe_2/NaCMC nanocomposites lies within the range of 55-65 °C. With 15 keV He^{2+} ions, notable changes were observed in morphology and microstructure. The He^{2+} ion exposure leads to the development of IF-like features of spherical shape at a fluence of 5×10^{15} ions/cm^2 under normal incidence. Raman spectroscopy further confirms C implantation with 15 keV C^{2+} ions on WSe_2, with the appearance of D and G bands. After 60 MeV N^{5+} irradiation, HR-TEM images showed layered sheets with void regions, and AFM analysis revealed an increase in surface roughness, reaching an RMS roughness value of ~146 nm at the highest fluence. Moreover, DFT calculations reveal that Se atoms are more susceptible to dislodgment than W atoms, leading to the formation of vacancy clusters. These defects introduce localized states near the Fermi level, primarily involving Se 4p and W 5d orbitals, and demonstrate the potential to modify the bandgap of WSe_2.

Here are the major highlights based on the primary findings presented in the chapter summaries:

- Fractal-like patterns were developed in WS_2/NaCMC composites, with fractal dimensions ranging from ~1.98 to 1.60 with an increase in WS_2 content.

- γ-irradiation of WS_2 exhibited improved tensile strength up to 83%, along with ductility and flexibility, at a dose of 10 kGy in the nanocomposite system.

- β-irradiation on WS_2 system revealed an increase in the number of mesopores, boosting its photocatalytic efficiency to ~59.4% of congo red dye degradation till ~45 min exposure to UV light.

- 15 keV He^{2+} irradiation caused structural modification in WS_2, such as developing IF-like structures and slipping sheets, while C^{2+} ion irradiation created sulfur vacancies and implanted carbon atoms, leading to localized WC phase formation.

- 0.85 GeV U^{28+} ions introduced ion tracks and manifested excitonic properties, with a non-linear temperature-dependent direct excitonic transition being observed in exfoliated systems. After irradiation, the average exciton lifetimes (τ_{av}) decreased by 32%, from 3.64 ns to 2.49 ns in the bulk WS_2, and by 21%, from 3.81 ns to 3.01 ns in the exfoliated system. Notably, despite the reduction in lifetime, the exfoliated WS_2 exhibited a significant increase in quantum yield (QY), reaching 92.4 % post-irradiation.

- WSe_2/NaCMC nanocomposites exhibited shear-thinning behaviour with a power law index varying from 0.84-0.86 and revealed glass transition temperatures of the nanocomposites ranging from 55–65 °C.

7.2 Future outlook and directions

The ability to precisely control and modify the properties and structures of 2D TMDCs is crucial for strengthening our understanding and advancing their practical applications. Ion beam irradiation techniques, with their highly tunable parameters, specific manufacturing of materials, and advanced equipment evolved, are particularly promising in this regard. Gaining insights into the mechanisms and control principles underlying irradiation-induced effects is essential for effectively tailoring the structure and performance of 2D materials, thereby unlocking their full potential across a range of applications.

- Studying the effects of ion beam irradiation on WS_2/WSe_2-based van der Waals heterostructures and alloyed 2D systems such as WS_xSe_{1-x}, particularly those doped with rare-earth or metal atoms, in a controlled manner, could tailor the properties of the material.
- WS_2 and WSe_2 show strong potential for advancing quantum technologies, particularly when integrated with 2D topological insulators. This combination enables access to the quantum spin Hall phase and its helical edge states, topologically protected by time-reversal symmetry and capable of dissipation-less transport, making them ideal for spintronic applications.
- Irradiated WS_2 and WSe_2 present exciting opportunities for next-generation junction devices. Controlled irradiation can introduce chalcogen vacancies or defect states that locally tune the electronic and optical properties of these materials. Such engineered defects can enable the formation of p-n junctions, Schottky barriers, or tunnel junctions within a single monolayer or heterostructure.
- The modification of various 2D materials, such as $MoTe_2$, $MoSe_2$, SnS_2, $SnSe_2$, ReS_2, etc., using charged particle beams and investigating their effect specifically in monolayer and bilayer form is particularly promising, as reduced dimensionality

enhances quantum confinement, excitonic effects, and valley polarization. These thin-layered 2D systems can exhibit strongly layer-dependent properties and enable tunable optoelectronic and electronic properties.

- Moreover, irradiation-induced phase transitions in TMDCs offer the potential to discover novel metastable phases with unique properties required for various device functionalities.