Abstract

The focus on two-dimensional (2D) materials began soon after the successful isolation of a single atomic layer of carbon, graphene, from graphite using the scotch-tape exfoliation technique in 2004. This breakthrough sparked a surge of interest in the development of other 2D materials composed of two or more non-carbon-based elements. Owing to their exceptional electronic, optical, and mechanical properties, 2D materials have attracted considerable research attention and are seen as highly promising for a wide range of practical applications. These materials exhibit diverse structural configurations with both direct and indirect band gaps, covering a broad spectral range from ultraviolet to infrared, including the visible region. Such characteristics are pivotal in the design and fabrication of next-generation flexible, ultrathin devices for optoelectronic, photonic, and nano-electronic applications. In addition, 2D materials possess remarkable features, such as high thermal and electrical conductivity, enhanced catalytic activity, chemical stability, and optical tunability, which make them highly advantageous for various advanced applications.

Defect engineering has emerged as a widely adopted approach for tailoring the properties of materials, playing a pivotal role in tuning the optical, mechanical, electronic, and optoelectronic properties of 2D layered materials. Defects can act as traps, recombination centers, carrier donors, or scattering sites, depending on various conditions. Among the various techniques available, ion beam irradiation stands out as a powerful physical method for introducing controlled defects and impurities to modify the microstructure and properties of materials. In particular, low-energy ion irradiation is effective for altering surface properties, often resulting in pattern formation, changes in geometry, modifications in crystal structure, and alterations in chemical composition. In contrast, high-energy ion irradiation in the MeV to GeV range can bring about significant changes in structural and physicochemical properties through intense electronic excitations caused by inelastic energy transfer. These modifications are highly dependent on the type of ion used for irradiation. In the ion irradiation process, key parameters, such as ion type, energy, fluence, charge state, atomic mass, and projectile range, play crucial roles in precisely tuning material properties. Therefore, a deep understanding of the interplay between material structure, defect formation, and advanced processing techniques is essential for the development of next-generation devices and technologies.

According to the objectives formulated, the thesis has been organized into seven chapters as follows:

Chapter 1:

This chapter gives extensive literature reviews highlighting the significance of 2D materials, emphasizing their unique properties, and applications across diverse functionalities. Particular attention is given to 2D transition metal dichalcogenides (TMDCs) due to their tuneable bandgap, high surface-to-volume ratio, and other remarkable, intriguing characteristics. Additionally, the chapter focuses on modifying the properties of 2D layered materials through methods such as particle irradiation, γ-photons, and charged ion beams. Key features like doping, point defect generation, and patterning through irradiation techniques are also reviewed in detail.

Chapter 2:

This chapter details the experimental procedure used in the study to synthesize the WS_2 and WSe_2 material. Furthermore, the various characterization techniques used throughout the thesis work are thoroughly explained. It also describes the preparation methods for WS_2 and WSe_2 based polymeric composite systems for subsequent experimentation. Additionally, the morphological modifications of the composite films featuring fractal-like structures within the layered 2D WS_2 systems are extensively discussed.

Chapter 3:

This chapter examines the mechanical properties through the stress-strain curve of WS_2 systems dispersed in a NaCMC polymeric solution at varied concentrations. The strain range of the elastic region obtained from the stress-strain curve is roughly 40-80% and depends on the amount of WS_2 loading and γ-doses. Beyond this, the plastic deformation was observed with strain-hardening features before failure. Thus, the tensile properties of γ-irradiated WS_2/NaCMC nanocomposites reveal an increase in ultimate tensile strength, accompanied by higher breaking stress. Notably, the WS_2/NaCMC nanocomposites showed nearly 83% enhancement at 1 wt.% and ~45% enhancement at 5 wt.%. loading of WS_2 irradiated at a lower γ-dose of 10 kGy.

Chapter 4:

In this chapter, the distribution of mesopores in the WS_2 system under independent UV- and β-ray exposures were analysed. The N_2 adsorption-desorption isotherm curve at

~77 K exhibited a type-IV characteristic, confirming the presence of mesopores. Remarkably, the irradiated systems showed a higher density and greater size variation of mesopores. In addition, the photocatalytic performance of these nanosystems was evaluated through congo red dye degradation, revealing an enhanced degradation efficiency of approximately 59.38% in the β-irradiated WS_2 system after 45 minutes of UV illumination.

Chapter 5:

This chapter focuses on the effect of low energy (15 keV) and high energy (0.85 GeV) ion irradiation on WS_2 systems using He^{2+}, C^{2+}, and U^{28+} as projectile ions. In the WS_2 system, irradiation with He^{2+} ions led to the formation of helium bubbles, resulting in corrugated surface structures. Moreover, the bombardment of 15 keV He^{2+} ions in the WS_2 system facilitated the development of inorganic fullerene (IF)-like structures with polyhedral morphology. In the case of 15 keV C^{2+} ion irradiation, the implantation of C atoms in these systems induced the formation of localized tungsten carbide (WC) phases. In addition to the experimental observations, the low migration barrier energy of C atoms in WS_2, calculated using density functional theory (DFT), also indicates possible substitution of C atoms in the vacant sites of the material, potentially leading to localized WC phase formation. Furthermore, the electronic band structure calculations reveal that the semiconducting state of WS_2 transitions to a gapless semi-metallic behaviour when C dopants are present in equal or more than the number of S vacancies. Next, the impact of high-energy 0.85 GeV U^{28+} ions was also studied in both bulk and exfoliated WS_2, showing the formation of ion tracks with track diameters varying from 6-7 nm. In addition, the emission properties of the WS_2 systems after irradiation with U^{28+} ions were analysed using temperature-dependent photoluminescence (PL) studies. Time-resolved PL measurements revealed a reduction in exciton decay lifetimes, from 3.64 ns to 2.49 ns in the bulk WS_2 and from 3.81 ns to 3.01 ns in the exfoliated system, attributed to enhanced non-radiative transitions.

Chapter 6:

This chapter explores the effects of various types of irradiations, γ-irradiation, low-energy (15 keV), and 60 MeV swift heavy ion (SHI) irradiation on WSe_2 systems. In particular, the γ-irradiated WSe_2 was dispersed in a NaCMC polymeric solution to investigate its rheological behaviour, with a focus on the 1 wt.% nanocomposite system. The flow behaviour of these WSe_2/NaCMC nanocomposites is characterized by the correlation between shear stress (τ), power index (m), and shear rate ($\dot{\gamma}$), represented as $\tau = K.\dot{\gamma}^m$, where K is a consistency index. The WSe_2/NaCMC nanocomposites investigated exhibit shear-thinning behaviour, as indicated by a power index (m) ranging from ~0.84 to 0.86 at a moderate shear rate range of 0-1000 s^{-1}. Besides, the WSe_2 system subjected to 15 keV H^{2+} ion irradiation shows the emergence of inorganic fullerene (IF)-like structures, forming nearly spherical morphologies at a fluence of 5×10^{15} ions/cm^2 under normal incidence (0°). Similarly, Raman analysis of WSe_2 irradiated with 15 keV C^{2+} ions reveals the presence of D and G bands, indicating adequate implantation of carbon atoms into the material. Furthermore, exposure to 60 MeV high-energy N^{5+} irradiation induces damage zones and structural disorder, resulting in the formation of vacancies in the WSe_2 system. These experimental observations are corroborated by computational studies, which demonstrate that the formation of vacancy clusters significantly reduces the indirect bandgap of WSe_2, from 1.48 eV to 0.37 eV along the *K-Γ* direction of the Brillouin zone.

Chapter 7:

This chapter discusses the concluding remarks of all the chapters and the future scope of the work.