ABSTRACT

Nanomaterials are known to have excellent properties which make them useful in diverse applications in the fields of health, energy and environment [1]. In recent decades, owing to their tremendous impact in our day to day life, activities related to research and development (R&D) in this field is highly demanding and efforts of both public and Government agencies across the globe are quite encouraging and rewarding. Among nanomaterials, two-dimensional (2D) nanomaterials hold a special place, because they exhibit much improved electrical, optical and mechanical properties due to their unusually flat geometry, anisotropic bonding environment and one-dimensional carrier confinement [2]. Soon after the discovery of graphene, the study of 2D materials has gained more interest among the physicists and material science researchers [3]. It is known that, graphene is a 2D material having significantly high carrier mobility, transparency, low density, high specific area and high stretchability [4-9]. But graphene cannot be used in energy storage device applications and other optoelectronic components due to lack of a well defined bandgap in ambient environment. [2]. Therefore, researchers around the world were in search of some other suitable candidates which, to a great extent, are analogous to graphene but come with a sizable bandgap. In this regard, a special class of materials, known as transition metal dichalcogenides (TMDC) offered the right choice for right reason. TMDCs can be divided into two categories, namely, layered structures with van der Waal's gap and non layered structures [10]. Layered TMDCs consist of a transition metal (Ti, V, W, Mo) and chalcogen (S, Se, Te) elements. All TMDCs generally form layered structures where in-plane bonds are strong (covalent) and the out-of-plane bonds are weak (van der Waals) [3]. The structures also lead to the formation of single atom thick 2D layer on exfoliation. Due to different types of inter layer and intra layer bonding, these materials are highly anisotropic in nature. As a result, the in-plane properties, like mechanical, thermal and electrical properties are significantly altered as compared to that of the out of plane response [11]. TMDCs offer a unique opportunity to tunable band gap, with addition or removal of monolayers. For

instance, the most studied MoS_2 has an indirect band gap of 1.2 eV in the bulk form, which turns into a direct band gap of 1.9 eV in the monolayer form [12]. Due to the layered structure, the 2D TMDCs can offer more surface active sites and can increase the adsorption of substrates [2]. The 2D planer structure and large surface area along with thinness could be beneficial to reduce the recombination of photogenerated electron-hole pairs. Undoubtedly these materials are capable of displaying excellent optoelectronic and photocatalytic properties.

Tungsten disulphide (WS_2) is a technologically important material which comes with numerous S-W-S layers stuck together by van der Waal bonding. WS_2 has drawn attention owing to its tremendous application in the field of hydrogen storage, microelectrode material, solid lubrication, photocatalysis etc [13]. Likewise, all other TMDCs, WS_2 also undergoes a transformation from indirect to direct band gap type on decreasing the number of layers. This transition from indirect to direct bandgap and increase in bandgap energy are quite evident as a consequence of respective changes in photoconductivity, absorption spectra and photoluminescence response [2]. Being an important member of TMDC family, WS_2 could absorb light over a wide range of electromagnetic spectrum: visible, infrared, ultraviolet and near infrared, allowing it for self-excitation under light irradiation [6]. Visible light responsive photocatalyst based on nanostructured WS_2 have found a broader range of applications, while comparing with the traditional photocatalyst, such as, wide band gap TiO_2 and ZnO and SnO_2 gap, which are mostly active only under UV light illumination [14].

Apart from having a wide range of optical and optoelectronic properties, WS_2 also show high mechanical strength. In particular, WS_2 nanotubes and inorganic fullerene (IF) type WS_2 nanoparticles have demonstrated specific mechanical properties, associated with their unique structure [15]. WS_2 can also serve as an excellent solid lubricant, in the form of additives to lubrication fluids, greases and for self lubricating coatings [16].

Over the years, researchers have extensively investigated WS_2 and related systems emphasizing their electronic, photocatalytic and mechanical properties. Nevertheless, only a little information exists as regards irradiation induced effects on such systems, especially at low energy (keV) where nuclear energy loss (S_n) is dominant over the electronic energy loss (S_e). Wang *et. al.* have irradiated WS_2 nanosheets with 100 keV electron beam and have invariably observed the formation of holes and shrinking of lattice due to gradual decrease of S atoms. [17]. Similarly, the disruption of WS_2 nanotubes from the outer layer to the inside has been witnessed under 200 keV electron irradiation [18]. Conversely, Rai and co-workers have witnessed a substantial enhancement in the wear life of the WS_2 coating on steel, even up to several folds when irradiated with 2.5 MeV Ag ions [19]. In contrast, the work of Chen *et. al.* on 60 keV Ar^+ ion irradiation on the atomically thin WS_2 sheets has resulted in tailored optical properties of the WS_2 monolayer via creation and manipulation sulphur vacancies [20]. Recently, 600 keV and 6 MeV O ion irradiation effect on the WS_2 nanosheets was shown to alter the number of layers, thickness and optical band gap of the WS_2 nanosheets [21]. Thus, post irradiation effect of these layered systems, have seemingly large opportunity to exploit modified structural, optical and mechanical properties at large.

In this thesis, an attempt has been made to synthesize WS_2 nanosystems with different morphologies and study photoluminescene, photocatalytic, and mechanical properties of WS_2 nano-dimensional systems of diverse morphologies. Also, the effect of low energy ion irradiation on stack of WS_2 has been studied. We have first synthesized inorganic fullerene (IF)-type WS_2 nanoparticles and nanosheets by suitable hydrothermal processes and then, characterized as regards, their structural, optical and morphological features by employing desired tools/techniques. We have also synthesized carbon (C-) dot decorated WS_2 nanosheets and studied how the C-dots would affect the optoelctronic responses of the WS_2 nanosheets. Moreover, we have investigated the photocatalytic efficiencies of the synthesized IF-WS_2 nanoparticles, nanosheets and WS_2/C-dot nanohybrids systems using different target dyes under ultraviolet and visible light illumination. Finally, we have studied the mechanical, tribological and wetting properties of IF-type WS_2 nanoparticles were evaluated while dispersing them in a polymer matrix. We have studied the impact of 80 keV Xe^+ ions on multilayer WS_2 nanosheets.

Chapter I is the introductory chapter, where the fundamentals of nanomaterials, 2D materials with special emphasis in TMDC systems are discussed. We have also discussed different synthesis processes the researchers around the world have adopted to synthesise WS_2 materials of different morphologies. We have given a brief introduction about different characterization and analyzing tools used to characterize the synthesized samples. Here, we have also discussed the steps involved in ion-material interactions.

In *chapter II*, we discuss different synthesis processes involved in the production of IF-type WS_2 nanoparticles and WS_2 nanosheets. The IF-type WS_2 nanoparticles have been synthesized using a two-step hydrothermal process, whereas WS_2 nanosheets are derived through a one step hydrothermal route, followed by repeated ultrasonication and filtration. The as-derived systems were characterized by using different tools for exploring structural, morphological and optoelectronic features. The XRD analysis of the WS_2 systems confirms the formation of hexagonal phase of WS_2. The morphologies of IF type WS_2 nanoparticles and nanosheets were confirmed from the TEM imaging. The EDX micrographs offered the means of elemental analysis signifying the presence of the elements W and S in the prepared samples. The Raman spectra of the samples showed two characteristics modes E_{2g}^1 and A_{1g} in both the nano-WS_2 samples. A blue shift of the Raman modes in the WS_2 nano-sheets as compared to WS_2 powder gives certain clue of exfoliation. Moreover, the BET analysis exhibits the increase in specific surface area in the exfoliated nanosheets than the WS_2 powder.

In *chapter III*, we highlight optoelectronic responses of WS_2/C-dot nanohybrid systems. At first, the 2D WS_2 nanosheets were synthesized via a facile hydrothermal process followed by adequate ultrasonication. Next, Carbon dots were extracted from orange juice and subsequently, decorated over the WS_2 nanosheets employing progressive hydrothermal route. TEM images revealed the formation of 2 5 nm sized C-dots which were seen to spread over the WS_2 nanosheets. The synthesized WS_2/C-dot nanohybrids were found to exhibit excellent fluorescence property, which is eventually tunable with the excitation wavelength. The PL spectra of the WS_2/C-dot hybrid system, infact, displayed an overall rise, because of the presence of the fluorophore like C-dots. The underlying mechanism for exhibition of excitation dependent PL and red-shifting response has been attributed to models related to surface traps and electronegativity of heteroatoms [22]. Moreover, as compared to the WS_2 nanosheets, the Raman spectrum of the WS_2/C-dot hybrid nanosystem offered a marginal shifting of both the in-plane and out-of-plane vibronic modes. The two modes, E^1_{2g} and A_{1g}; shifted towards lower frequency side along with the evolution of two additional peaks, are assigned to the D and G bands of the graphitic system. The shifting of the Raman modes is ascribed to the strong interaction between the C-dots and WS_2 nanosheets, which is likely to strengthen both in-plane and out-of-plane restoring forces acting on them.

In *chapter IV*, we have studied the photocatalytic features of the three systems viz. IF-type WS_2 nanoparticles, WS_2 nanosheets and WS_2/C-dot nanohybrid systems. As, for the first two systems, we chose malachite green (MG) as the target dye, and evaluated the photocatalytic activity under both UV and visible light illumination, while for the later system we used MG and methyl orange (MO) as the target dyes and consequently, assessed the photocatalytic features under visible light illumination. Among the IF-type WS_2 nanoparticles and nanosheets, the nanosheets showed better photocatlytic response under both UV and visible light. It may be noted that under visible light illumination, the photocatalytic efficiency is found to be more effective than that under UV light in both the cases. The enhanced photocatalytic efficiency in case of WS_2 nanosheets is because of the higher surface area of the sheets than that of the IF-type nanoparticles. Thus the nanosheets provide more active sites for the photocatalytic reaction to occur. On the other hand, in case of WS_2/C-dot nanohybrid system, the degradation of MG dye is substantially higher than the MO dye. It is because the absorbance peak of MG dye falls in the red part of the visible spectrum. On comparison of all the three systems, one could find that WS_2/C-dot nanohybrid system offers excellent photodegradation efficiency, with a maximum degradation of 91% in 60 min under visible light illumination, when using MG as the target dye. Using similar conditions, the degradation values are found to be 86% and 71% as for the nanosheets and IF type WS_2 nanoparticles. The substantially high photocatalytic degradation is due to the presence of numerous C-dots in the hybrid system. The C-dots play an important role in enhancing the photoactivity of the 2D WS_2, which can be explained by the physisorption process of the dye onto the WS_2 flakes or sheets.

In *chapter V*, we have demonstrated structural, mechanical and wettability characteristics of hydrothermally processed IF-type WS_2 nanoparticles, homogeneously dispersed in a polymer host. The polyhedral, fullerene like nanostructures of WS_2 with a hollow core inside are quite evident from the TEM imaging. It may be noted that, the range of elastic and plastic regions, to a great extent, depends upon the amount of nanoparticle loading into a matrix. For nanocomposite films, elongation and consequently, Young's modulus of elasticity generally offers an increasing trend but maximal value is observed for the 6wt% nano-WS_2 loading. Breaking stress also gives an enhanced value from 2.7 to 9.7 MPa without and with 6wt% loading of nano-WS_2 at large. Moreover, tribological studies have revealed a significantly lowered coefficient of friction (COF) with inclusion of nano-WS_2. Thermally and mechanically stable nanocomposite films also presented excellent hydrophobic response by displaying high water contact angle (CA) but reduced contact angle hysteresis (CAH). Surface energies of the composite films have been calculated by considering contributions from polar and dispersive parts separately, for two reference liquids. The net surface energy was found to vary in the range of 24.7 to 37.5 mJ/m^2.

In *chapter VI*, we discuss the effect of low energy ion irradiation on the multilayered WS_2 nanosheets. The impact of 80 keV Xe^+ ions was seen to bring out structural and optoelectronic modifications in the nano-WS_2 systems. In this regard, morphology of the virgin and post irradiated samples are analyzed using TEM and AFM imaging techniques. Both the images showed fragmentation of stack of bigger sheets into smaller sheets. The AFM images revealed the formation of nanoscale hillock type structure and also increasing surface roughness. Moreover, the shifting of Raman modes towards lower energy side signified the exfoliation of the nanosheets as a result of irradiation. From the EDX micrographs a decrease in the S: W ratio can be observed, impact. Finally, the wetting properties of the pre and post irradiated samples were studied using a static water contact angle method. A trend from hydrophilic to hydrophobic nature is observed with increase in ion fluence in the irradiated samples.

In *chapter VII*, We have discussed the key conclusions drawn from our study, technical limitations, future scope and challenges in certain specific applications.

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