Chapter I

Introduction

"What is now proved was once only imagined"

– William Blake

1.1 Overview

Material research is reaching new heights and dimensions each day, while ushering extreme service-induced material design, re-evaluation, and remodelling to mitigate global challenges and individual demands. Nowadays, materials and material systems with different levels of autonomy are preferred to conventional unifunctional materials by investors dealing with applications such as military, healthcare, space, automobile, and the promotion of better lifestyles [1,2]. As such, there has been a surge in the search, development, and implementation of materials or material systems with polyvalent functionality to reduce space, cost, maintenance etc. Nanomaterials are the materials undergoing different quantum confinements. They are usually multifunctional in the sense that they are characterized by low-dimensional structures and they possess a high surface-to-volume ratio, which makes them sensitive to changes in the local environment. Nevertheless, some of them enjoy structural, electronic, fabrication related, and biological advantages over others, making them one-of-a-kind. Examples of such wonder materials include layered materials. Layered materials are a family of materials with highly anisotropic crystallographic arrangements, where atoms on a plane are strongly bonded and atoms on neighbouring planes are weakly bonded. Consequently, they are persuadable to exfoliation i.e., the material can be peeled off layer by layer from the rest of the crystal and exhibit layer-dependent properties. Graphite/graphene, transition metal dichalcogenides (TMDCs), elemental atomic sheets (Xenes), metal nitrides/carbides/carbonitrides (MXenes), metal oxides/phosphides/halides, mixed oxides, etc., are some of the materials which come under the umbrella of 'layered materials'. Layer-dependent investigation was only a suggestion given by legendary physicist Richard Feynman in a futuristic lecture "There is a plenty of room in the bottom" in 1956 [3]. This was later realized by Robert Frindt while exfoliating molybdenum disulfide (MoS_2) flakes into thick, few, and single layers by implementing multiple approaches, including sticky/scotch tape [4, 5]. This legacy, which reached its zenith of popularization in 2004 with the advent of graphene and the discovery of its extraordinary properties [6], continues till date; thereby leading to varieties of fabrication or synthesis approaches, characterization techniques and application schemes.

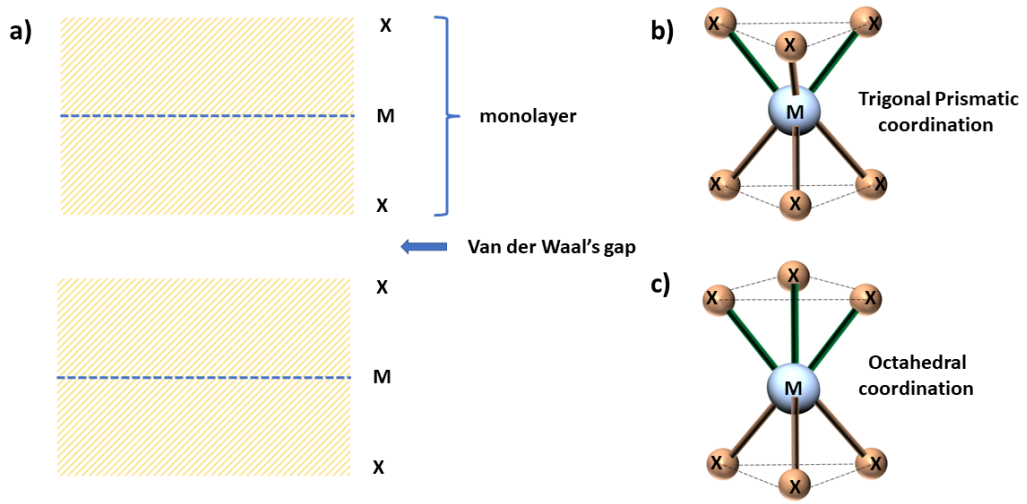

Fig. 1.1. (a) Basic atomic layer arrangement in TMDC **(b)** trigonal prismatic and octahedron coordination arrangements in TMDC. Adapted after [9].

Considering the immense potential implicit in these layered systems, this thesis investigates one of the highly anticipated layered materials namely TMDC. To be more specific, the investigations are centred around WS_2 and allied systems, while considering MoS_2 as a reference material towards multidimensional applications such as sensing, actuating, biomedical etc. As such, in the following sections some of the important properties, sensing and actuating attributes and nanoenzymatic aspects of these materials will be briefly discussed, emphasising the target materials.

1.2 Layered transition metal dichalcogenides (TMDCs)

1.2.1 Structure and polymorphism in TMDCs

Transition metals and chalcogen atoms crystallise into about 60 TMDCs including both synthetic and naturally obtained variants. Interestingly, two-third of them exhibit layered structures [7]. In TMDCs, transition metals e.g., W, Mo, Ta, Nb, V, Hf, Pt, are sandwiched between chalcogen atoms e.g., S, Se, Te. The standard formula for these types of materials is MX_2 where M represents the transition metals and X represents chalcogen atoms. **Fig 1.1(a)** illustrates the basic atomic layer arrangement in these materials. The three atomic layers X-M-X altogether termed as 'monolayers' where, transition metals are six-fold and chalcogen atoms are three-fold coordinated leading to two different possible arrangements i.e., trigonal prismatic and octahedron (**Fig 1.1(b)**). The atomic planes in a monolayer are not exactly flat [8]. Thus, the individual layer thicknesses may lie within 6-10 Å.

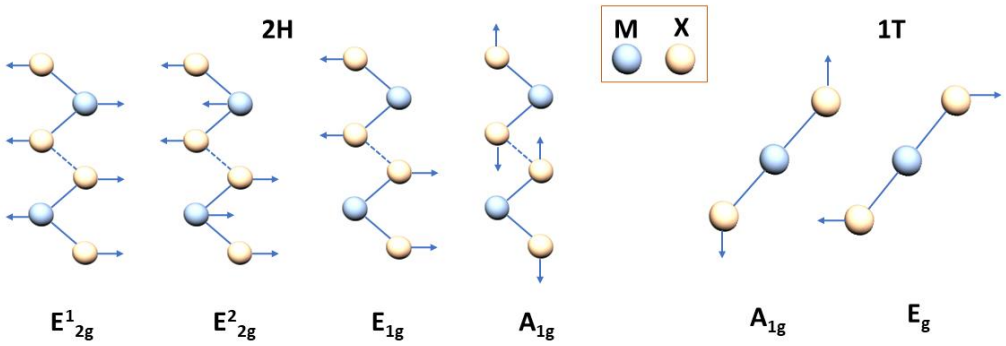

Fig.1.2. Atomic displacement vectors in TMDC.

TMDCs exhibit various polymorphs. The commonly encountered polymorphs of TMDCs are *1T*, *2H*, *3R* and, *1T'*, where, the numbers signify the number of layers present in a unit cell and the letters signifies the symmetry (*T*-tetragonal, *H*-hexagonal, *R*-rhombohedral, *T'*-monoclinic); nevertheless, there exist other polymorphs as well [7,10]. Depending upon stacking symmetries, one polymorph may have different variants, e.g., *2H* polymorph has two common variants— $2H_a$ and $2H_c$, where the former is characterized by AbA CbC stacking, while the latter is characterized by CaC AcA stacking. Niobium and Tantalum chalcogenides are found to acquire $2H_a$ polytype, while, Molybdenum dichalcogenides and Tungsten dichalcogenides are found to acquire $2H_c$ polytype. It is interesting to mention that monolayers of TMDCs have only two polymorphs— trigonal prismatic coordination with hexagonal symmetry (the D_{3h} group) and octahedral coordination with tetragonal symmetry (the D_{3d} group).

1.2.2 Properties

TMDCs exhibit extremely fascinating and diverse material properties. In this section, some of the properties of TMDCs are briefly discussed.

1.2.2.1 Electronic

Around 2009-2011, several experimentalist and theoreticians report the crossover from indirect band gap in few and bulk TMDCs structures to direct band gap in monolayers [11-15], where shift of valence-band maximum from Γ to *K* point was observed. Interestingly, valence-band maximum of single layer WS_2 at $\pm$ *K* points of hexagonal Brillouin zone was suggested by Albe *et al.* in 2002, however, they did not report it to be indirect-to-direct band transition at that time [11]. Later, this phenomenon was observed for all the

compounds of group VIB and shifts in valence-band maximum was confirmed by angle resolved photo-emission spectroscopy [16-18]. Experimentally, the crossover can be confirmed by performing photoluminescence (PL) analysis of single and multilayers. At monolayer limit, a manyfold increase in PL intensity is observed unlike multilayers. The increase in PL is associated with blueshift of PL peak position [12, 13]. Valence-band splitting due to large spin-orbit coupling is another important aspect of TMDCs. PL peaks attributed to A and B excitons give the experimental evidence of the band splitting [13].

1.2.2.2 Optical

The electronic structure of a material manifest mostly in absorption and photoluminescence results. It is already discussed that due to strong spin-orbital coupling, valence-band splits in TMDCs. The largest splitting is observed at *K* point. The conduction band minimum is also at *K* point, which make it doubly degenerate. Therefore, two transitions from valence band to conduction band take place, giving rise to two low energy peaks A and B in the absorption spectrum [19]. The difference in the electronic and optical band gap suggest that the obtained peaks are excitonic peaks. Additional excitonic peak, C is due to transition between density of states peaks [20,21]. Even in PL spectra, A, B and C peaks are observed in conformity with absorption measurements [13, 22].

1.2.2.3 Optoelectronic

Néstor Perea-López *et al.* carried out photoresponse measurement on few-layer WS_2 system to find out that laser irradiation give rise to photocurrent and it varies in non-linear fashion with the incident power [23]. Similarly, Lopez-Sanchez *et al.* made photoresponse measurement on monolayer MoS_2 to find out that photocurrent increases with increase in the frequency of excitation [24]. Similarly, several other optoelectronic phenomena such as photo-thermoelectricity [25], photovoltaic [26] etc. are observed in TMDC material-based systems. As such, TMDCs are used in different optoelectronic devices for instance photodetectors [23,27], solar cells [28] etc.

1.2.2.4 Vibrational

Symmetry in TMDC system depends on the number of layers (single, odd layers, even layers) and stacking (AB, ABC) orders in the system. Thus, irreducible phonon

representation at Γ point changes accordingly. In bulk *2H*-MX_2 (M=Mo, W, X=S, Se), there are total of six atoms in a unit cell and they belong to D_{6h}^4 point group symmetry. Theoretical calculations suggest that this *2H*-bulk structure results in 18 vibrational modes (3 × number of atoms) [29]. There are three acoustic and fifteen optical modes [30]. These modes can be further subdivided into Raman (R) active modes, infrared (IR) active modes and optically silent modes [31]. It is considered that there are four Raman active modes in bulk *2H* structure and two Raman active modes in bulk *1T* structure [29, 32]. The atomic displacements corresponding to the modes are presented in **Fig 1.2**. However, number of distinct modes changes with layer numbers [33]. It was realized that Raman technique is an interesting noninvasive technique to probe vibrational characteristics of TMDC materials and related dynamics such as intra and interlayer forces [34] or to identify the number of layers [35] or crystalline phase of a material etc. Wang has elaborately described Raman spectroscopic principles and some analysis which are specific to TMDCs and TMDC composites [36].

1.2.2.5 Chemical

In chemical terms, exfoliation loosens up the s–p_z orbital interaction between consecutive layers and change the hybridization at monolayer limit giving rise to huge photoluminescence [13, 14]. When shrunken vertically, the basal planes expose and edges terminates by either metal or chalcogen atoms. Similarly, when shrunken laterally, there appear step-edges, kinks, corner atoms. The co-ordination at these edges or sites controls the chemistry in TMDCs [37]. The vacancies, edges, kinks are the active sites of the TMDC material which offers great catalytic and sensing ability to TMDCs. Tuxen *et al.* experimentally demonstrated that due to steric hinderance, sulfur (S) vacancies also shows location specific reactivity [38]—which is an interesting aspect for vacancy dependent applications. They have also exemplified the benefits of edge-plane functionalization for enhanced reactivity; which is a proven technique for better reactivity [39, 40]. Thus, chemistry of TMDCs can be developed by different techniques and can be implemented for specific applications.

1.2.2.6 Enzymatic

Owing to structures having active sites resembling that of natural enzymes, some nanomaterials exhibit enzymatic behaviors and are termed as nanoenzymes. Nanoenzymatic

behaviors can be observed in nanomaterials having different spatial confinements i.e., zero dimension (0D), one dimensional (1D), two-dimensional (2D) etc. [41-43]. However, researchers shifted their focus from OD to 2D because the large lateral dimension of the layered materials comes with reduced toxicity, while the large surface area is loaded with abundant active sites to fill and deliver therapeutic agents [44]. Untreated, unfunctionalized nanosheets as well as composites, doped or heterostructure TMDC possess various enzymatic activities such as peroxidase (POD) [45, 46], catalase (CAT) [47], oxidase (OD), superoxide dismutase (SOD) [47] etc. Although, there exist numerous applications of TMDCs from biosensors to therapeutics based on their enzymatic activities [48], the toxicity mechanisms of TMDCs are still not fully understood [49] and clinical translation of these materials is still facing challenges [50]. However, recently, Appel *et al.* has reported low cytotoxic and genotoxic nature of two-dimensional WS_2 and MoS_2 [51].

1.2.3 Synthesis of transition metal dichalcogenides

The synthesis techniques of TMDCs are mostly application dependent. The synthesis processes are customized for a precision-made output. In electronic and optoelectronic applications, methods such as chemical vapor deposition (CVD), physical vapor deposition (PVD), molecular beam epitaxy (MBE), and laser-irradiated synthesis etc. are usually preferred, and substrate engineering, doping engineering, and contact engineering are incorporated [52]. In photocatalytic water splitting applications, solution-based synthesis methods or dry micromechanical methods are preferred to CVD, PVD, because freestanding few, and monolayer TMDCs in solution perform better as co-catalysts [53, 54]. Similarly, in biomedical applications, such as cancer treatment and biosensing, chemical exfoliation is widely used for synthesis of TMDC nanostructures [50].

Different synthesis techniques exist, and new methods are being developed to meet demands like precision, cost, sustainability, scalability, and biocompatibility. However, based on the integration and disintegration of atoms and molecules, the synthesis approaches of TMDC can be broadly categorized into two types: top-down and bottom-up. In the top-down method, bulk TMDCs are broken down into smaller particles, whereas in the bottom-up method, materials are fabricated atom-by-atom or molecule-by-molecule into larger particles. Under top-down methods, micromechanical exfoliation, liquid-mediated exfoliation, exfoliation followed by intercalation are some of the most popular approaches, whereas, gas-phase synthesis, liquid-phase reactions, solventless reactions, etc.,

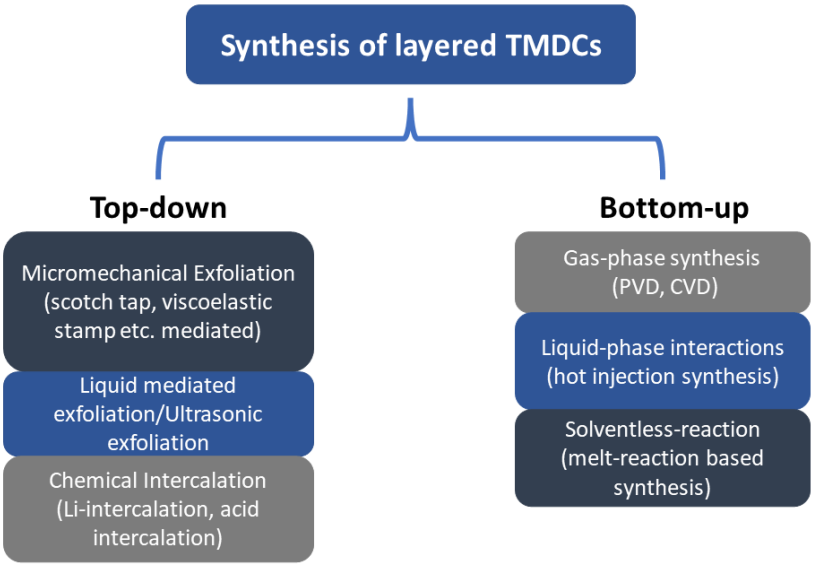

Fig.1.3. Different synthesis processes of TMDCs

are some of the bottom-up approaches [55]. Gas-phase synthesis techniques such as Low Pressure–Physical Vapor Deposition (LP–PVD) [56, 57], Chemical Vapor Deposition (CVD) [58-63] are high-precession methods that require bulk TMDC or metal and chalcogen precursors and typically involve high vacuum and temperature setups— therefore, have scalability issues. Liquid-phase reactions involve the decomposition of precursors in a heated environment [63]. In solventless reactions, precursors are deposited on a suitable substrate and heat is applied to melt them. It is then followed by the formation of TMDC nanostructures in the molten mixture [64]. These methods are quite tedious, and only non-monolayer nanostructure synthesis is possible. Among micromechanical processes, the ground-breaking method uses sticky tape, which was first implemented by Frindt and co-workers [4,5], and was famous after its implementation in the discovery of graphene [6]. However, most of these methods are not scalable [65-67]. Later, the wet grinding method was designed to offer scalability to micromechanical processes; however, it failed to produce monolayers [68]. Similar to the sticky tape method, intercalation is an old method for the synthesis of TMDC nanosheets [69]. Intercalation processes are scalable however, these processes are associated with changes in the phase of the TMDC material. In addition to other recent hybrid methods, direct liquid-mediated exfoliation is one of the most popular scalable synthesis processes. It involves ultrasonication of TMDC in a suitable solvent. This method is also known as solvo-sonication method. Interestingly, the same solvent could be used to exfoliate different TMDC materials. Generally, this exfoliation process is not associated with a change in the phase of a material [70]. Some of the synthesis processes of TMDCs are shown in **Fig 1.3**.

1.2.4 Applications

Various properties discussed in *section 1.2.2***.** make TMDCs multifaceted in terms of their applicability. In search of an inexpensive, electrochemically stable eco-friendly material to replace costly metals like Pt, Rh, Re, Ir in hydrogen evolution reactions (HER), Norskov and others predicted high reactivity in edge sites of thin sheets of MoS_2 [71-73]. Later, it was experimentally demonstrated that sulfur terminated Mo-edge sites in MoS_2 nanostructures are the active sites for HER [74]. The basal plane of TMDCs is inactive in comparison to edge-sites. Therefore, it reduces the surface trapping of Li ions in Li-ion batteries when used as an anodic material. Thus, it proves itself to be a potential candidate for battery applications [75]. Due to high coulombic efficiency and rapid oxidation-reduction reactions at the surface, TMDCs finds its application in superconductors as well [76]. However, it was observed that composites perform better than the unfunctionalized, untreated TMDCs. Similarly, they are suitable candidates for different electronic and optoelectronic applications [52]. Thus, there are limitless application of TMDCs. The next sections are dedicated to some of the applications of TMDCs which are relevant to this thesis.

1.2.4.1 Chemical sensing

Scientific society is always in search of better sensing materials and techniques for effective and swift detection of harmful gases, compounds, ions etc. Layered TMDCs are rich in chemistry [37]. They have high surface area and low cytotoxicity [51]. They also have well-developed synthesis techniques as discussed in the earlier sections. As such, several chemical sensors have been devised based on these materials. The chemicals which are often targeted by TMDC based sensors are harmful gases for-instance NO, NO_2, NH_3, H_2, volatile organic compounds (VOC) such as toluene, acetone, ethanol, and toxic heavy metal ions like Hg, As, Cd, Pb etc. In this section, some of the chemical sensors based on TMDC materials are discussed highlighting their sensing and transduction processes and mechanisms.

Chemical sensors based on TMDCs convert the changes in the environment to some detectable signals like current, voltage, inductance, resistance, and color etc. The correlation between the analyte and the signals facilitates the measurements of the concentrations of target analytes. In general, gas sensing with TMDC is attributed to the charge transfer between gas molecules and reactive sites present in the TMDC material [77-79].

During the charge transfer process, if the sensing material loses an electron, it increases the resistance in the system and vice versa [80]. The charge transfer mechanism was further experimentally elucidated by Cho *et al.* [81] via *in situ* photoluminescence characterization of NO_2 and NH_3 treated atomically thin MoS_2. In TMDC transistor-based gas sensors, modulation of Schottky barrier plays an important role in analyte sensing. This is because, the analyte extract or add electron to the sensing material, thereby changing the Schottky barrier height. The change in the Schottky barrier height eventually manifest itself in the change in the conductivity of the sensing unit [82]. Similarly, in heavy metal ion sensor based on TMDC field effect transistors, the sensing can be explained through fundamental mechanism like doping level and Schottky barrier inflections; dipole and interfacial layer formation etc. [83, 84]. In TMDC-based fluorometric sensors, sensing happens through two processes. In the first type, interaction of analyte and sensing material results in a fluorescent material and in the second type, either sensing material or the analyte act as a fluorescence quencher [85, 86]. In TMDC-based colorimetric sensors, material-analyte results in colored products. In such sensors, the response of the sensor depends on the catalytic property of the sensing material [87].

1.2.4.2 Antipathogenic activity

It was warned by UN Ad hoc Interagency Coordinating Group on 'antimicrobial resistance' that if no measure is taken the world is going to face extreme poverty and health crisis by 2030. At present, nanomaterials are considered as new-generation antibacterial

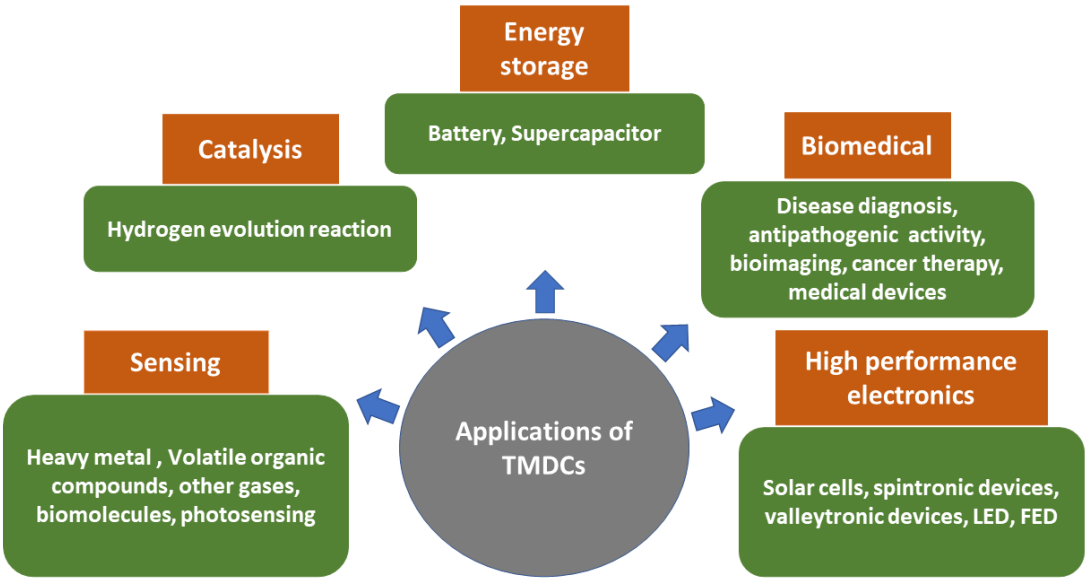

Fig.1.4. Various application of TMDCs

agents to combat such future crises because they have the capacity to physically damage the cell membrane or kill the cell by generating reactive oxygen species and free radicals. Although investigations regarding nanomaterial-based strategies for drug-resistant pathogens have been initiated, it is extremely important to conduct simultaneous investigations to determine the ultimate strength of nanomaterials against common pathogens. In this regard, transition metal dichalcogenides (TMDCs) are worthy of use as next-generation antibiotics against common and multidrug-resistant pathogens. It was already discussed that TMDCs can mimic enzymatic properties; which is also the reason for its antimicrobial/antipathogenic property [88,89]. There are several antimicrobial assays available for implementation such as diffusion methods (agar disk diffusion method, agar well diffusion method, antimicrobial gradient method, agar plug diffusion methods), dilution methods (agar dilution method, broth dilution method), thin layer chromatography etc. [90]. Generally, in the investigations related to TMDCs, colony counting techniques and agar diffusion methods are used to determine antimicrobial activity [91,92]. Although, structural details of both MoS_2 and WS_2 are similar, their antimicrobial mechanisms are different [91, 93]. It was observed that the antimicrobial activity of MoS_2 is due to membrane destruction and oxidative stress, whereas, in case of WS_2, it is mainly due to membrane destruction. Interestingly, under ultraviolet irradiation, both these materials could generate reactive oxygen species including hydroxyl radical (-OH) superoxide radical (·O2−) and singlet oxygen ($^1O_2$) [94]. Antimicrobial properties of these TMDCs can be extended to even antimicrobial therapy or wound healing applications as demonstrated by several groups [95-97]. **Fig.1.4**. presents various application of TMDCs.

From the above discussions, it is comprehensible that layered TMDC are materials with limitless possibilities. Interestingly, except a few members of this family, most of them are still at their evolving stage. Therefore, it is an opportunity to carry out investigation on such fascinating materials in order to explore more of their exotic properties and proper utilization of the same. In this context, WS_2 is a promising material to start with. For-instance, there is a number of reports where photoinduced effects in this material have been studied; however, few characterizations and conventional optoelectronics-oriented study place a limit on proper understanding of the extent of the effects as well as their futuristic implementations. Apart from photoinduced effects, there is a large research gap in WS_2 based chemical sensing applications despite their rich chemical properties. Again, it is evident from the literature that antipathogenic investigation of TMDCs is limited to

few pathogens in spite of their considerable nanoenzymatic properties. Accordingly, there is a need to fill these research gap. Thus, motivation of our research involves synthesis and characterization of untreated and photoirradiated TMDC nanostructures and development of analytical techniques for application of TMDC materials towards chemical sensing and antipathogenic activity.

1.3 Objectives of the present study

The prime objectives of the thesis work are enlisted below:

a) To exfoliate bulk TMDCs using solvent (N-methyl-2-pyrrolidone) and co-solvent (isopropanol/acetone mixture, isopropanol/water mixture) in order to synthesize multilayer and few-layer nanostructures and fabricate nanostructured TMDC based system.

b) To investigate photoinduced effect on crystallographic, morphological, vibrational, and electrical features of the synthesized nanostructures and nanostructure based systems with the help of different characterization techniques like XRD, TEM, Raman spectroscopy etc.

c) To investigate the heavy metal ion sensing attributes of the nanostructured TMDC -based systems by analysing current-voltage characteristics of the untreated and heavy metal ion treated resistive system using source-meter.

d) To investigate the antipathogenic activity of synthesized nanostructures towards multiple bacterial cultures such as *Mycobacterium smegmatis (MS), Staphylococcus aureus (SA), Bacillus cereus (BC), Pseudomonas aeruginosa (PA), Yersinia pestis (YP), Escherichia. coli (EC)* and fungal culture – *Candida albicans (CA)* using agar well diffusion method.

1.4 Outline of this thesis

Inspired by the exquisite and exigent characteristics of TMDC and TMDC based systems, in this thesis, an attempt has been made to exfoliate TMDC materials and to perform various investigation towards different applications. Accordingly, the structure of the thesis has been constructed as described below.

In *chapter I*, different physio-chemical properties of TMDC materials are discussed along with their synthesis techniques and applications. It also highlights the importance of layered materials in today's world.

In *chapter II*, two forms of WS_2 nanostructures—nanosheets and fullerenes are discussed along with their synthesis techniques. It also demonstrates the influence of laser irradiation on the WS_2 nanostructures and incorporates a discussion on polymorphisms in WS_2. Along with other standard characterizations, a detailed Raman spectroscopic study has been included in this chapter.

In *chapter III*, development of a heavy metal ion sensor based on WS_2 nanosheets is discussed in detail. The detection of heavy metal ion is based on electrical characteristics of the as-fabricated WS_2 nanosheet/Cu electrode system. The sensing parameters of the sensing unit is evaluated using source-meter. This chapter also incorporates extensive discussion on detailed sensing protocol and mechanism of this sensing unit.

In *chapter IV*, a detailed description of fabrication of nanostructured WS_2 nanosheets/Cu electrode system is given. It also includes an extensive electrical characterization of the same. From the electrical characterizations, it was evident that WS_2 nanosheet/Cu electrode-based system was coupled with current fluctuation (noise). The power spectral density vs. frequency graph of the electrical system confirms that the current fluctuation is a $1/f$ dependent noise. The noise-coupled system is found to be sensitive to different laser wavelengths in the visible range.

In *chapter V*, a detailed description of synthesis of few-layer WS_2 and MoS_2 nanosheets is given. Then investigations have been performed to examine the antimicrobial activity of these nanosheets against *M. smegmatis, S. aureus, B. cereus, P. aeruginosa, Y. pestis, E. coli and C. albicans.* The chapter also gives a plausible explanation for the antimicrobial activity of TMDC nanosheets against multiple pathogens.

Chapter VI summarizes the principal conclusion drawn from the present research activities and straighten out some future research directions.

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