ABSTRACT

Synthesis and sensing attributes of semiconducting transition metal dichalcogenide nanostructures with special emphasis on WS_2, aided by exploitation of their antimicrobial activity

Transition metal dichalcogenides (TMDCs) are compounds composed of transition metal elements and chalcogenide elements (S, Se, Te). In TMDC materials, there exist non-bonding *d* bands. The electron occupancy of *d* bands in these materials regulate the electronic structure of these materials. As such TMDCs enclose a broad spectrum of materials such as insulating, semiconducting and metallic. There is a total of 60 TMDCs, including both natural and synthetic variants. Of 60, almost 40 TMDCs are layered in nature. In layered TMDCs there exists strong intralayer covalent bond between the chalcogenides and weak interlayer van der Waals bonds between the layers. This anisotropy in the structural arrangement facilitates the exfoliation of these materials from three-dimensional (3D) to two-dimensional (2D) structures. As such, TMDC nanostructures having different layer number can be obtained through exfoliation. Interestingly, TMDCs have layer-dependent properties. They possess a direct band gap due to breaking of spatial inversion symmetry, followed by a high excitonic binding energy at the monolayer limit. Besides, they have layer-dependent luminescence efficiency and active sites which make them efficient for photo sensing, catalysis, antipathogenic activities, etc. Again, nano enzymatic behaviour of nanostructured TMDCs assists them for efficient chemical sensing and biosensing.

Although TMDC materials are old, nanostructured form of these materials has gained attention just after the advent of graphene and its intriguing properties. As such, research on some TMDC is still at an evolving stage. To date, numerous fundamental and application-oriented investigations have been reported on MoS_2 based systems, however this is not same for WS_2 systems. For-instance, there are several reports on MoS_2 nanostructured systems regarding heavy metal ion sensing where the prime transduction mechanism is electrical. Surprisingly, there are only few reports on WS_2-based heavy metal ion sensor. The reported sensors are primarily based on optical transduction mechanism. Apart from sensing, there are a few reports on WS_2, where photo-induced effects are extensively studied. In addition to these, non-functionalized, untreated WS_2 has not been extensively studied regarding antipathogenic activities. As such, in this thesis, an attempt has been made to carry out laser-induced electrical, crystallographic, and

morphological analysis of WS_2 systems. The investigation is further extended to WS_2 nanosheet based material system coupled with noise. Then, WS_2 nanosheet/ Cu electrode based system has been fabricated towards electrical detection of heavy metal ions. In addition to these, ultrasonication time and rotation rate dependent antimicrobial analysis of these materials have been carried out against multiple pathogens. Throughout the thesis, solvo-sonication method was used for exfoliation of the TMDC materials because this technique is simple, effective, and scalable. Again, as WS_2 share the same structural arrangement and similar electrical and optical properties with MoS_2, therefore MoS_2 has been considered as a reference material to study WS_2.

Accordingly, Chapter I starts with a discussion on global inclination towards materials with multifunctional properties and the fact that most of the nanomaterials are multifunctional by nature. With the introduction of layered materials, the discussion is gradually shifted to layered transition metal dichalcogenides (TMDCs). In the beginning, different properties of TMDCs such as electronic, optical, vibrational, chemical, and enzymatic etc. are discussed. It is followed by an abridged discussion on application-dependant synthesis of TMDCs and different synthesis techniques. Then there is a brief description on different properties of the TMDCs responsible for different applications. Finally, some of the mechanisms underlying chemical sensing with TMDC materials are discussed followed by their antipathogenic application. The chapter is concluded with the objectives and outlines of the thesis.

Chapter II provides an overview of the synthesis technique (solvo-sonication method) and characterization, such as X-ray Diffraction (XRD), Raman spectroscopy, UV-vis spectroscopy, and field emission scanning electron microscopy (FESEM), of WS_2 and MoS_2 nanostructures. Then, a comprehensive Raman spectroscopic investigation involving different laser powers was performed, and subsequent morphological, chemical, and polymorphic changes in WS_2 nanosystems were discussed. It was observed that the local phase transition from *2H* to *1T* in WS_2 can be initiated by applying a minimum of 50 mJ of laser irradiation. The local phase transition is associated with local oxidation, followed by the formation of inorganic fullerene-type nanostructures. This investigation holds promise for *in situ* phase patterning on WS_2 nanostructures for different optoelectronic applications.

In *Chapter III*, a sensing technique was developed for detection of Zn^{2+} ions with the help of WS_2 nanosheets/Cu electrode system. Through a controlled liquid-phase exfoliation procedure, multi-layered WS_2 nanosheets were synthesized. The nanosheets were drop-casted on the finger-like Cu electrodes. This heterojunction scheme exhibited linear ohmic characteristics. However, with the addition of heavy metal ions, there was a drastic multifold rise in current, accompanied by a nonlinear current–voltage response. Accordingly, the electrical response of this WS_2 nanosheets/Cu electrode system was tested for several heavy metal ions. It was observed that the scheme possessed considerable selectivity towards Zn^{2+} ions. Consequently, a detection limit of 0.94 ± 0.05 ppb was obtained for the as-fabricated sensor. In this study, non-functionalized and untreated WS_2 nanostructures were used. The scheme is simplistic in design and holds promise in relevant sensing protocols.

In *Chapter IV*, a fabrication procedure has been explained with the help of which $^1/_f$ dependent noise was introduced in a WS_2 based resistive unit, and laser irradiation was used to control the amplitude of the noise. When the unit was irradiated with lasers of wavelengths 650 nm, 532 nm, and 400 nm with an output power of 5 mW, a maximum five-fold increase in the noise fluctuations was observed. Normally, noise in the electrical measurements is undesirable. However, in applications such as stochastic-resonance-based weak-signal detection, noise generators are required. Because of the bulky nature of conventional noise generators, they cannot be integrated into electronic devices. In this context, the proposed scheme may help to introduce threshold level noise in an *in situ* manner, which can help to detect weak signals in stochastic-resonance-based applications. Such resistive units can also be integrated into other electronic devices, making the sensing process more feasible.

In *chapter V*, antimicrobial activity of non-functionalized WS_2 and MoS_2 few layer nanosheets have been investigated against *M. smegmatis, S. aureus, B. cereus, P. aeruginosa, Y. pestis, C. albicans* etc implementing agar well diffusion method. Few-layered WS_2 and MoS_2 were synthesized using solvo-sonication method followed by liquid cascading. The antimicrobial performance of MoS_2 and WS_2 was observed to be better than that of standard antibiotics (Gentamicin for bacterial culture and Nystatin for fungal culture) against *P. aeruginosa. Aeruginosa* and *C. Albicans*. On the other hand, performance of standard antibiotics was found to be better than few layer WS_2 and MoS_2 against *B. Cereus*. All pathogens were susceptible to MoS_2 nanosheets; however, *M. smegmatis* showed intermediate susceptibility to WS_2 nanosheets. Here, rotation rate-dependent analysis was also performed. However no major changes were observed. The ultrasonication dependent study confirms that ultrasonication is not a determining factor for antimicrobial activity of TMDCs.

Chapter VI, summarizes all the important findings of this thesis work. It also unravels some of the prospects of the present investigations.