SYNTHESIS AND SENSING ATTRIBUTES OF SEMICONDUCTING TRANSITION METAL DICHALCOGENIDE NANOSTRUCTURES WITH SPECIAL EMPHASIS ON WS_2, AIDED BY EXPLOITATION OF THEIR ANTIMICROBIAL ACTIVITY

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By

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Chapter VI

Conclusion and future directions

6.1 Conclusion

Nanostructured layered transition metal dichalcogenides (TMDCs) exhibit contrasting layer-dependent trailblazing properties. Exfoliation engenders active sites in TMDCs and thereby enhances their reactivity. Another way to tune the properties of TMDCs is to implement appropriate nano-engineering techniques (e.g., functionalization, doping, alloying etc.). The synthesis and implementation techniques of TMDCs are mostly application-induced. However, material property-driven investigations of TMDCs and their derivatives are racing in parallel because they exhibit evolving exotic properties holding futuristic promises.

The thesis entitled **“Synthesis and sensing attributes of semiconducting transition metal dichalcogenides nanostructures with special emphasis on WS_2, aided by exploitation of their antimicrobial activity”** is a blend of ‘TMDC-based sensing and biomedical applications’ and some ‘fundamentally attractive results having potential for futuristic applications’.

Chapter I briefly encompasses the overall idea of layered TMDCs— their properties, synthesis methods, and applications. Thus, it elucidates the motivation behind this thesis work. A section of this chapter also deals with the objectives of the thesis.

The takeaway from *Chapter II* — local phase transition in WS_2 could be initiated by employing a minimum of 50 mJ of laser (λ_{ex} = 514 nm) irradiation. Irradiation on nanosheets give rise to mono sulfur (S) vacancies. Presence of vacancies trigger the phase transition in the laser irradiated nanosheets. *1T* nucleation process starts when three S atoms undergo collective rotational movement. Then, they propagate through cooperative rotational-translational movement to assemble the final *1T* structure. The transition process is followed by local oxidation of the nanosheets at a specific applied energy. It happens because oxygen molecules in the environment attain sufficient energy to diffuse into the WS_2 nanosheet system and oxidize it. The oxidation and continuous laser fluence eventually give rise to inorganic fullerene (IF) like structures in the WS_2 nanosheet system. X-ray diffraction (XRD) spectra also suggest laser-induced exfoliation. Predictably, all these laser-induced effects are local. Therefore, the above-mentioned processes are recommendable only for local treatment.

In chapter III, a WS_2 nanosheet/Cu electrode system is developed by drop-casting WS_2 nanosheets on finger-like Cu electrodes. It can increase the current up to ~ thousand-fold when treated with heavy-metal ions. The unit is selective to Zn^{2+} ions with a limit of detection (LOD) of 0.94 ± 0.05 ppb and sensitivity of 0.63 ± 0.05 µA per ppb. The sensing was based on the change in *I–V* characteristics of the system when different ions were introduced to it. The system's sensing mechanism operates via charge transfer, which occurs through the formation of Lewis acid-base complexes and localized oxidation within the system.

In *Chapter IV*, the process of post-fabrication hard drying introduce current fluctuations/noise to WS_2 nanosheet/Cu electrode system. The introduction of current-fluctuation was confirmed by analysing *I–t* characteristics. The power spectral density vs. frequency spectra of the resistive system confirmed that the noise introduced was a $^1/_f$ dependent noise. The origin of $^1/_f$ noise may be attributed to generation of defects states in the system. The *I–V* and *I–t* characteristics confirmed the laser irradiation-mediated enhancement in the fluctuations in *I-V* characteristics and current noise. The effect of laser irradiation on the linear conductance of the system is of the order of 10^{-10} S. Laser intensity modulated enhancement in the current fluctuation suggested intensity-dependent characteristics of the system.

Chapter V deals with the analysis of antipathogenic activity of WS_2 and MoS_2 nanosheets against multiple pathogens *viz- M. smegmatis, S. aureus, B. cereus, P. aeruginosa, Y. pestis, C. albicans* and *E. coli*. WS_2 and MoS_2 flakes were exfoliated for several hours followed by liquid cascading centrifugation in order to obtain few-layered structures. All the pathogens were susceptible to the as-synthesized few-layered MoS_2 nanosheets. Similarly, few-layered WS_2 nanosheets also showed antimicrobial activity against all pathogens, except *M. smegmatis*, which showed intermediate susceptibility to this specimen. Comparing antipathogenic activity of different WS_2 and MoS_2 specimens, it was perceived that only mono/few-layered WS_2 and MoS_2 could manifest antimicrobial properties. Antimicrobial activity cannot be initiated simply by changing the exfoliation parameters of the material system such as duration of sonication, concentration of the material etc. Antimicrobial activity of the nanosheets starts with the embedment of TMDC nanostructures to the pathogen cell, followed by extraction of phospholipid molecule and finally membrane disruption. It is clear from the study that MoS_2 is more effective as an antipathogenic agent than WS_2 few-layered nanostructures.

It is interesting to conclude that nanosheets of different thicknesses are functional for specific applications. We used multi-layered structures for chemical sensing and to fabricate noise-modulated units, whereas we fabricated mono/few-layered WS_2 and MoS_2 nanostructures to achieve antimicrobial activity. Richard Feynman once asked during his lecture, ‘There’s plenty of room in the bottom’ that— “What could we do with layered structures with just the right layers? What would the properties of materials be if we could arrange the atoms the way we want them ...” — all the research on layered structure till date still may fall short to answer this question properly. Consequently, there is a need for diverse research work in this direction.

6.2 Future Directions

There are more than 190 k scientific papers on two-dimensional TMDCs to date. Besides, several research articles get accepted every other day. Although the reports on TMDCs are rising at this pace, the motivation towards TMDC research has not ceased. It is because every research work leaves a hint for further study, which is evident from our case as well.

While characterizing the ion treated WS_2 nanosheets/Cu electrode system, several atypical features in the *I–V* characteristics seemed to appear. For instance, some graphs seem to be characteristics of a modified Esaki diode. Although it was not discussed specifically in *chapter III* to maintain the integrity of the chapter, it is an open topic for investigation. In *chapter IV*, the study is limited to three laser sources. For a proper understanding of laser modulated characteristics, more sources can be introduced in the future. Laser-induced modulation in the system suggest that such a scheme may also be used as an *in situ* noise generator in sensing devices based on stochastic resonance. Therefore, present material system can be investigated for such futuristic applications. Again, in *chapter V*, only common pathogens were targeted; however, TMDC-based multi-drug resistant investigation is a whole new field to uncover.

The extent of this thesis is limited to unfunctionalized WS_2 and MoS_2 nanosheets. Therefore, future studies can be done on functionalized TMDCs, TMDC-based heterostructures, composites, or alloys etc. It is advisable to carry out layer-dependent studies of TMDC-based nanostructures because applications of TMDCs are extremely layer dependent. In order to have better visualization and understanding of the dynamics, one can carry out *in situ* characterizations. The author has also implemented green methods for exfoliation. However, efforts should be made to improve the current synthesis techniques to achieve products with higher quality, large lateral sizes, and better yields.