Chapter 6

Summary and Future Scope

“The science of today is the technology of tomorrow.”

- Edward Teller
6.1 Summary

Scientific aspirations owing to the exhilarating properties displayed by molybdenum family of materials namely, Mo, MoO$_3$, and MoS$_2$ as well as their polymer nanocomposites have acted as a beacon during the course of this dissertation. In this concluding chapter, an abridged précis of the experimental work accomplished during the course of Ph. D. highlighting the prominent achievements is presented. The consequential conclusions from this thesis work have enabled us to chalk out a roadmap for the future work.

Swelling developments in the field of nanoscience and nanotechnology has been witnessed over the last 2 decades and can be attributed to fascinating properties as well as advanced & multifunctional applications of nanomaterials. The research in this field has flourished due to the accessibility of new methods of synthesizing nanomaterials as well as tools for characterization and manipulation. Scientific ambition owing to the exciting properties displayed by molybdenum family of materials namely, Mo, MoO$_3$ and MoS$_2$ as well as their polymer nanocomposites have acted as inspiration during the course of this dissertation. As far as synthesis is concerned, the following strategy has been evolved in this dissertation work:

- Synthesis of plain and hierarchical nanostructures of Mo and MoS$_2$ by conventional solvothermal route and rapid generation of MoS$_2$ nanostructures via microwave assisted solvothermal route.
- Large scale production of nanocomposites of Mo-MoO$_3$–PPS and MoO$_3$–PPS using facile, economical and green solid-solid reaction route.
- Gram scale production of MoO$_3$ nanostructures using facile, economical conventional and ultrasonication assisted sol-gel reaction route.

The application-oriented studies of the synthesized nanostructures were carried out in:

- Exploration of antimicrobial as well as biofilm inhibition activity of MoS$_2$ nanostructures as well as nanocomposites of Mo-MoO$_3$–PPS.
- Investigation on achieving superior dielectric constant in nanocomposites of MoO$_3$–PPS as a step towards their high-temperature capacitor application.
- Examination of photocatalytic activities of MoO$_3$ nanostructures prepared by sol-gel (conventional and ultrasonic assisted) as well as solid-solid state reaction methods.
Chapter-wise summary of the desertion work is presented below:

Chapter 1 begins with a succinct introduction to nanoscale phenomena. The length scale dependent properties and applications of nanomaterials have been discussed in this chapter.

Chapter 2 provides a detailed portrayal of the philosophy behind carrying out the Ph.D. research work through an adequate literature survey. Owing to the fascinating properties and applications of nanomaterials, various synthesis techniques have been evolved. Nevertheless, the scope of the present chapter was limited to discussion on synthesis techniques which have been employed in the present work namely, solvothermal route, solid-solid reaction, and sol-gel route. Subsequently, a short yet crisp description of the selected materials (Mo, MoO$_3$, and MoS$_2$) was provided highlighting the need for conducting the research on these materials. All the discussion revolving around synthesis techniques as well as materials selection was adequately supported by the literature survey at appropriate locations. Finally, the challenges in the nanomaterials synthesis and the strategies to overcome them were presented in the Motivation and Scope section.

Chapter 3 deals with the conquest over the challenge corresponding to the synthesis of plain and hierarchical nanostructures of MoS$_2$ using the novel strategy of hydro/solvothermal reaction. It has been observed that structure and morphology of the synthesized nanomaterials can be suitably modified by varying the reaction time. Flower-like hierarchical nanostructures of MoS$_2$ with hexagonal crystal structure have been successfully obtained by employing the conventional solvothermal method. To the best of our knowledge, this is probably the first report dealing with studies pertaining to the effect reaction time on the structural and morphological properties of MoS$_2$ hierarchical nanostructures using the solvothermal route. The challenge of rapid synthesis of nanostructures has been dealt successfully using microwave assisted ‘green’ solvothermal technique for the first time. High prevalence of multidrug-resistant bacteria among bacteria-based infections decrease the effectiveness of current treatments and may culminate into contagion related deaths. In this context, it was innovatively presumed that biocompatible and non-cytotoxic molybdenum disulfide
nanostructures (MSNs) would provide an effective solution for overcoming bacterial resistance. The formulation containing MSNs demonstrated biofilm inhibition effect which enhances the versatility of its applicability. In this chapter, not only quantitative antibacterial property of our MSNs established prima-facie but also the possible mechanism of the antibacterial activity by detecting and measuring ROS, analyzing the change in enzymatic activity of redox enzymes (SOD and CAT) was ascertained. Realization of antimicrobial action by the disruption of cellular function as against rupture of the cell is an important scientific observation of this work. Our studies on MSNs have supported the belief that cyto-toxicity is not a major concern for this class of nanoparticles which makes them a promising candidate for clinical trials in small animals.

Drug formulations based on MSNs may have vital and unprecedented applications in pharmaceutical and biomedical industry, especially in combination with antibiotics as it may enhance their ability to destroy bacteria that have acquired resistance to them. Additionally, these formulations may be coated on medical devices / apparatus such as catheters and endoscopes to curtail the biofilm formation as well as can be used for external applications.

The challenge of producing the polymer nanocomposites based on engineering thermoplastic matrix has been tackled using solid-solid reaction which is solventless, ‘environmental friendly’ and economical route in Chapter 4. In this chapter, more attention has been paid to the description of the creation of polymer nanocomposites owing to their possible advance devices and system applications. The typically selected examples were Mo-MoO$_3$-PPS and MoO$_3$-PPS. The chapter has been divided into three distinguishing sections of synthesis of the said nanocomposites. Each section deals with the synthesis protocol using particular molybdenum precursors in the equimolar ratio of Mo precursor: PPS. In the first section, a preliminary account on successful synthesis of submicron/nanostructures of molybdenum oxide polymorphs in thetractable polymer matrix by facile solid-solid reaction technique using molybdenum hexacarbonyl precursor has been reported. Here, molybdenum hexacarbonyl and PPS were admixed in 1:1 molar ratio and subjected to heating (285 °C) for different time durations. Structural analysis revealed the predominant formation of orthorhombic $\alpha$-MoO$_3$, while electron microscopy examination disclosed that the morphology (from 1-D to 3-D) and structure of the resultant polymorphs depends on the reaction interval. Owing to the coupling of desired characteristics of both
Molybdenum oxides and PPS in the form of submicron/nanocomposites can be advantageously exploited in advanced solid state device fabrication such as capacitors and sensors (including biosensors). However, the scope of the present section has been limited to the exploration of synthesis of MoO$_3$-PPS nanocomposites only. In the in-situ synthesis of molybdenum oxide nanostructures in engineering, thermoplastic has been accomplished using ammonium molybdate as Mo precursor via a facile solid-solid technique at 285°C has been reported in the second section. The increase in reaction time from 6 to 48 h enhanced the tendency of forming 2-D sheet-like structures. The XRD patterns predominantly show peaks pertaining to reflections of orthorhombic $\alpha$-MoO$_3$ along with monoclinic Mo$_8$O$_{23}$ as minor phase. Nonetheless, for the reaction time of 48 h, only $\alpha$-MoO$_3$ has been obtained. The morphological investigation disclosed the formation of sheets like structures which is in concurrence with the layered nature of this material. Achieving the superior dielectric properties of the resultant nanocomposites can be considered as the outstanding contribution to the scientific quest in terms of better dielectric constant (double than pure PPS) and appreciable loss tangent values. For samples MP06, MP24 and MP48, the dielectric constant and loss tangent are found to be 7.74, 8.47, 6.30 and 0.14, 0.13, 0.089, respectively, at 1 MHz frequency. These nanocomposites may be employed as capacitors for high power, high-temperature AC field, and surface mounts circuits. The obtained nanocomposite may also be useful for various flexible radio frequency identification (RFID) tag-based applications such as access control, smart cards, and library control as well as energy storage related devices and systems.

In the third section, synthesis of nanocomposites comprising Mo-MoO$_3$-PPS has been successfully accomplished by following solid-solid reaction protocol using molybdenum (III) chloride as the precursor. Identification of the structural changes and phases indicate the predominant formation of cubic phase of metallic molybdenum and minor phase peaks of monoclinic MoO$_3$. As reaction time increases from 6 to 48 h, the tendency to convert to MoO$_3$ is found to be enhanced. The synthesized NCs demonstrated antimicrobial behavior as evinced form MBC/MFC and time kill curves. Even though the higher concentration of the NCs is required for such activity (due to the entrapment of the synthesized nanostructures within the polymer matrix), this work is significant in terms of fabricating the biomedical devices and components coated with such antimicrobial NCs films. The preliminary result of the antifungal activity is the
novelty statement of this chapter since these materials may also show anti-cancer properties as it is a thumb rule that antifungal materials are also anti-cancer.

A brief qualitative and comparative discussion on account of the results of the three sections has also been carried out at the end of Chapter 4. It may be noted that suitable choice of molybdenum precursor plays a crucial role in determining whether MoO$_3$-PPS or Mo-MoO$_3$-PPS can be generated. Along with reaction time, molybdenum precursor decides the structural and morphological aspects of the synthesized nanocomposites. These aspects, in turn, assign the application potential to these nanocomposites in different fields.

**Chapter 5** presents the studies pertaining to the large scale (few grams/batch) synthesis of MoO$_3$ nanostructures using the conventional and ultrasonication assisted sol-gel techniques. Even though sol-gel is a slow process, it easily enables grams scale production of nanostructures. One dimensional (1-D) nanorod and two-dimensional (2-D) nanobelt like MoO$_3$ nanostructures were prepared by sonochemistry assisted and conventional sol-gel method, respectively. The as-prepared MoO$_3$ nanostructures were used as a photocatalyst to degrade methylene blue (MB) solution dramatically within very short irradiation time of 30 minutes indicating that the as-prepared MoO$_3$ nanostructures were promising candidates for the photodegradation of organic dyes facilitating environmental remediation. The rate constant for nanorod-like and nanobelt like nanostructures were 0.0786 min$^{-1}$ and 0.233 min$^{-1}$, respectively. In the last section of the chapter, a comparison of photocatalytic properties of MoO$_3$ nanostructures prepared by solid-solid reaction route against those prepared by conventional and ultrasonication assisted sol-gel method is given and it has been shown that nanostructures prepared by sol-gel method exhibit better photocatalytic behavior.

In **Chapter 6**, the important findings of the work presented in this dissertation are summarized briefly to arrive at the logical end of the thesis. Additionally, the future scope of the research needed to be undertaken has been discussed in the light of the major conclusions drawn from this work.
6.2 Future Scope
In this thesis, synthesis of plain and hierarchical nanostructures of Mo and MoS₂ has been described using conventional hydro/solvothermal technique while rapid generation of MoS₂ nanostructures was carried out using microwave assisted solvothermal route. Solventless and economical solid state reaction route have been entrusted for the preparation of MoO₃-PPS and Mo-MoO₃-PPS nanocomposites. The synthesized nanostructures, as well as nanocomposites, have been explored for applications in areas like biomedical and electronics. Even though, in-depth studies and scientific outcome of this work have invoked new levels of understanding our work also can culminate into avenues for future cross-border research points, as enumerated below:

1. It is worth exploring the synthesis of plain and hierarchical nanostructures of MoS₂ using different Mo precursors as well as by varying the reaction temperature and time in conventional as well as microwave assisted solvothermal route.

2. Synthesis of mono/few layered MoS₂ has generated a lot of research interest and therefore, there is a need to apply modified strategies in all the three techniques for achieving this.

3. Solid-solid reaction technique may be pursued for the direct generation of MoO₃ and MoS₂ nanostructures.

4. The synthesized nanostructures, as well as nanocomposites, have tremendous application potential, a glimpse of which has already been seen in the present thesis. This potential has to be resourcefully tapped and used for the benefit of mankind. Myriad applications of these nontoxic nanostructures may span areas such as hydrogen generation and storage, photo-catalysis, hybrid solar cells, drug storage and delivery.

5. Finally, it is hypothesized that blending MoS₂ nanoparticles with antibiotics may not only reduce the toxicity of both agents towards human cells by decreasing the requirement for high dosages but also enhance their bactericidal properties, and such a hybrid approach can drastically reduce nanoparticle associated toxicity and offer a significant improvement in the design of antibacterial agents.