This chapter discuss overall summary of the thesis based on the four main objectives. The future plan of this work is also discussed.
7.1. Overall Summary

In conclusion, in the thesis entitled ‘Design and Studies on Graphene – Metal Oxide Nanocomposites for Photocatalysis’, we successfully investigated and implemented the applicability of graphene as a critical component in the design of efficient photocatalyst. Since the properties of graphene and graphene-based nanocomposites heavily influenced by its synthesis method, we successfully synthesized various compounds using following two synthesis strategies.

1. RGO/BiVO₄/TiO₂ ternary nanocomposites
2. RGO/Tin Oxide heterovalent heterojunction Nanocomposites
3. Graphene/ZnO nanocomposite
4. Graphene/Copper oxide nanocomposite
5. Graphene/Tin oxide nanocomposite

The XRD and Raman spectroscopy studies identified and confirmed the structural composition of graphene-metal oxide nanocomposites. Morphology analysis using FE-SEM, HR-TEM images revealed the dispersion of desired metal oxide nanoparticles on graphene sheets.

The need for a low-cost and efficient method for synthesis of graphene based nanocomposites as to utilize in real world applications like water purification, Hydrogen generation, etc. were identified and we proposed a new method. In the thesis work, we developed and introduced a facile, speedy, low cost and environmentally friendly synthesis strategy ‘Two Step Electrochemical Method’ for the fabrication of graphene-metal oxide nanocomposites. To introduce and investigate the reliability of the ‘Two Step Electrochemical Method’, we successfully synthesized Graphene-ZnO nanocomposites. Identified and confirmed the phase pure composition using XRD and Raman spectroscopy. An enhanced photocatalytic activity is
obtained for Graphene-ZnO nanocomposite (annealed at 500°C) over bare ZnO (annealed at 500°C, synthesized by electrolysis) nanoparticles under UV light. The reaction rate constant was found to be, \( k = 5.39 \times 10^{-2} \text{ min}^{-1} \). The photocatalytic activity of Graphene-ZnO (annealed at 500°C) got comparable to that of the standard Degussa P-25 TiO₂. Moreover, to test the industrial scalability of the ‘Two-Step Electrochemical Method’, we made an attempt to verify the possibility of the method for the fabrication of any other graphene–metal oxide nanocomposites. The Graphene-Copper oxide, Graphene/Tin oxide nanocomposites were successfully synthesized by the two-step electrochemical method. The XRD and Raman spectroscopy characterizations identified and confirmed the composition of graphene/copper oxide and graphene/tin oxide nanocomposites. The photocatalytic activities of the composites under visible light were also explored. The photocatalytic degradation reaction rate constant of graphene/copper oxide was obtained as \( k = 2.43 \times 10^{-2} \text{ min}^{-1} \). It was found that graphene/tin oxide nanocomposite act as a good photocatalyst under visible light with a degradation rate constant, \( k = 1.39 \times 10^{-1} \text{ min}^{-1} \). The mechanism behind the photocatalysis was explored and graphene was identified as to play the role of an electron trapper.

In this thesis, a successful effort was made to fabricate nanocomposites with tunable band gap energies useful for enhancement of photocatalytic efficiency. We successfully designed and fabricated an efficient photocatalyst RGO/BiVO₄/TiO₂ ternary nanocomposite by tuning the band gap energy of both BiVO₄ and TiO₂ metal oxides. By varying the weight percentage of RGO and TiO₂, the band gap energies of BiVO₄ (monoclinic BiVO₄) and TiO₂ is tuned respectively and obtained an efficient photocatalyst in visible light with a degradation reaction rate constant, \( k = 4.59 \times 10^{-1} \text{ min}^{-1} \). The mechanism behind the activity suggests RGO acting as an electron trapper and TiO₂ behaving as an efficient mediating co-catalyst.
In this thesis, another successful effort was made to design various metal oxides on graphene sheets in such a way that the rate of recombination of photogenerated electron – hole pairs is possibly reduced, resulting in enhancement of the efficiency. By designing suitable combination of tin oxide heterovalent heterojunctions on graphene sheets, we successfully developed an excellent photocatalyst with a degradation rate constant, \( k = 4.37 \times 10^{-1} \text{ min}^{-1} \) under visible light. The mechanism behind the enhanced activity driven by the heterojunction was resolved. Moreover, the possibility of introducing pH during synthesis as a modulating variable to develop different combinations of heterovalent cum heterojunction tin oxides on 2D scaffold graphene material is also explored. Different combinations of tin oxide heterojunctions are identified and confirmed using XRD and Raman spectroscopy as RGO/SnO_2/Sn_3O_4, RGO/SnO_2/Sn_3O_4/Sn_2O_3, and RGO/SnO_2/SnO (negligible presence).

Throughout the thesis, graphene plays key role in the properties of the graphene based metal oxide nanocomposites. Graphene basically take the role of a matrix phase on which different metal oxides were arranged, aimed at photocatalytic application. Graphene projected as a critical component in the band gap energy tuning of the metal oxides. Graphene acted as a highly influencing component in the determination of metal oxide composition in the graphene based nanocomposites. Graphene, by acting as an electron trapper offered enhancement in the photocatalysis in all graphene based composites discussed in this thesis. The Graphene acted as a potential interface to connect the component metal oxides and facilitated electronic transition between the metal oxides in the graphene based nanocomposite system, which favored photocatalytic activity. In summary, graphene act as a multifunctional critical component in its two forms, firstly as GO during the synthesis, for indirectly controlling the metal oxide compositions and influencing the band gap energy of metal oxides on graphene sheets; and secondly as RGO or graphene by
acting as a 2D interface between the different metal oxides and promoting the charge separation between photogenerated electrons and holes in photocatalysis.

The discussed work in physical sciences and the interdisciplinary areas of material science is aimed to be beneficial to the society. The outcomes of this thesis could help the progress in frontier research on graphene nanocomposites and for the real world applicability of graphene.

### 7.2. Future Plan

It is very clear that graphene act as a critical component for enhancing the efficiency of photocatalyst and therefore it should be extended to more nanocomposite systems.

The RGO/BiVO$_4$/TiO$_2$ and graphene-tin oxide heterovalent heterojunction nanocomposites can be explored deeper by using XPS and measuring the lifetime of excited electrons with photoluminescence. The XPS data analysis will be helpful to uncover the key role of graphene (as GO, especially influence of oxygen during synthesis) in the determination of compositions and band gap energies of metal oxides in the graphene based systems. By this way it could be possible to obtain a better control on structure and composition of the metal oxides on graphene sheets. It is reported that the surface morphology can affect the band edges of metal oxides. Significantly surface to volume ratio has a considerable role in the efficiency of a photocatalyst. So by taking weight percentage of RGO, morphology variations, and surface to volume ratio as variables, it could be possible to tune the band gap energy of different combination of metal oxides on graphene sheet, such that a highly efficient photocatalyst can be achieved. The analysis of life time measurements with photoluminescence will be effective to study the life time of electrons in different conduction band levels.
of metal oxides on graphene sheets, and hence to understand the electron-hole recombination capability of the composite system. This sort of PL analysis is very suitable to design various compositions of metal oxide junctions and hence to introduce intermediate energy level between the band gap, and also to tune their band gap energies, such that an overall control on photocatalysis mechanism could be obtained. By implementing all the above mentioned ideas, our plan in future to develop a variety of graphene based metal oxide ternary nanocomposites for photocatalysis seems quite feasible. Moreover the possibility of absorptive removal of organic dye using the RGO/BiVO₄/TiO₂ by introducing optimum weight percentage of RGO is also under investigation.

It is important to improve the ‘Two-Step Electrochemical Method’ to achieve its applicability to synthesise the graphene- metal oxide composite system. It is to introduce more refinement on the synthesis method to get a very few layer graphene sheets on which the nanoparticles are dispersed effectively in a uniform manner. It could be achieved by obtaining optimum conditions for the variables like molar concentration of the electrolyte, applied dc voltage, amount of defects introduced in as synthesized graphene sheets, time of electrolysis and pH of the electrolytic solution. The optimum parameters could be extended to fabricate different graphene based transition metal oxide nanocomposites in more reliable and controlled level. The optimization is needed to control the oxidation state of metals in metal oxides, and to prevent the agglomeration of nanoparticles on the graphene. Trial and error methods could be followed to reach at this optimum level of the variables. After implementing better refinement on the method, comparative studies between graphene based metal oxide synthesised via two step electrochemical method and other available method, especially hydrothermal method also comes under the future plan. The size variations and morphological designing on graphene based metal oxides are also to be
Overall summary and future plan

studied to highlight the two-step electrochemical method as a predominant method for real world application graphene nanocomposites.

The scope of the work discussed in this thesis can scale new heights with the successful implementation of the said future plans. The proposed future plan can open new vistas for graphene based technology aimed at solutions for the society, especially photocatalysis.