CHAPTER 8
SUMMARY

The goal of the project is to investigate the semiconductor photocatalytic activity with the combination of two dimensional nanostructured materials for degradation of organic dyes. Semiconductor photocatalyst is highly sensitive to electron-hole back recombination. The graphene oxide, reduced graphene and graphdiyne nanostructure has been prepared at laboratory scale and its fundamental properties has been studied.

The first stage of the project is to prepare graphene oxide from graphite by modified hummer's method. The graphene oxide was synthesized by varying the oxidation level (i.e.) different amount of $KMnO_4$ were added to oxidize graphite. The optimized amount of $KMnO_4$ is 6 g for 2 g of graphite, after the optimization the GO was reduced to graphene. On the other hand graphdiyne nanostructure was successfully prepared via cross coupling reaction. The prepared nanostructures such as GO, GR and GD were characterized by XRD, SEM, HR-TEM, EDAX, FT-IR, XPS and Raman spectroscopy.

After successful preparation of different types of two dimensional carbon nanostructures. The photocatalytic properties were examined with organic dye degradation experiments. The as prepared two dimensional nanostructured GO shows semiconductor behavior, the photocatalytic degradation of MB as modal organic dye was investigated. The result reveals unexpected adsorption which dominated the photocatalytic property due to the strong functional group on the either side of sheet and high band gap of GO. Adsorption phenomena were intensively studied using the effect of adsorbent, adsorbate, solution pH, and temperature. In addition, the Gibbs free energy, entropy and enthalpy changes were also examined for all GO products. Further, adsorption isotherm plot such as

Langmuir and Freundlich isotherm models for all GO samples were carried out. From the results, It is observed 99% dye removal is achieved using partially and fully oxidized GO.   The adsorption property was increased from G1 to G4 at ambient atmospheric condition and it was strongly influenced by pH and temperature. As the pH increased from 5 to 10, the adsorption property was increased. Similarly the adsorption efficiency increased with increase in temperature owing to the endothermic reaction.

The sonocatalytic degradation of GO–Fe^{3+} hybrid was investigated by using RR120 dye. The degradation rate was increased, when electron scavengers like PMS, PDS, H_2O_2 and KIO_4 were added. The degradation rate of RR120 was decreased by the addition of the inorganic ions like SO_4^{2-} Cl^{-}, H_2PO_4 and HCO_3^{-}. It is observed that the electron scavengers reacts with Fe^{2+} to promote the degradation reaction via a generation of free radical species. Since the inorganic ions cover the surface of the GO–Fe^{3+} hybrid system due to the electrostatic interaction, the dye adsorption process was reduced. Further, the inorganic ions reacts with Fe^{2+}–Fe^{4+} to produce the less reactive species other than OH radical. Comparatively the PMS showed the superior efficiency towards degradation. TEM, XPS and EDAX analysis were confirmed the formation of Fe^{3+} ions in GO nano sheet and UV spectra revealed the transfer of conduction band electrons from GO to Fe^{3+} ions. Our studies shows a potential pathway in understanding the trap and transfer mechanism of GO– Fe^{3+} hybrid nanosystem and their sonocatalytic degradation of dye RR120.

In the next section we investigated the enhanced photocatalytic property of graphene based semiconductor as photocatalyst. Different nanohybrids such as GR-WO_3, GR-$SnWO_4$ and GR-ZnS has been prepared via microwave assisted synthesis by varying the concentration of GR. The GR semiconductor nanohybrids exhibited enhanced photocatalytic efficiency in comparison with the pure semiconductor. The photocatalytic activity was examined via degradation efficiency and pseudo first order rate constant. The mechanism of enhanced photocatalysis was proposed and it was proven through photoluminescence spectroscopy. The same behavior was observed for various semiconductor photocatalyst such metal oxides and metal sulfides (GR-WO_3, GR-$SnWO_4$ and GR-ZnS). Further, the amount of GR in nanohybrid was optimised. The decrease in photocatalytic activity was observed on raising amount of GR beyond the optimized level

Table 8.1 Rate constant of different semiconductor- two dimensional carbon nano hybrids

S. NO	**Name of the Catalyst**	**Amount of catalyst (mgL^{-1})**	**Name of pollutant**	**Catalyst (Pure) K_{app}(min^{-1})**	**GR-1 K_{app} (min^{-1})**	**GR-2 K_{app} (min^{-1})**
1	WO_3	50	MO	0.0321	0.0521	0.501
2	β-$SnWO_4$	50	MO	0.0317	0.0425	0.0481
		50	RhB	0.5787	0.8333	0.8723
3	ZnS	50	MB	0.00198	0.00293	0.00261
		50	RhB	0.00298	0.00872	0.00812
4	ZnO	50	MB	0.00426	0.00181	0.00191
		50	RhB	0.0029	0.00166	0.00176

In the final section of the thesis, we proposed a novel two dimensional materials such as graphdiyne nanostructure. The GD structure was successfully grown on copper substrate. Later the GD-semiconductor has been prepared via hydrothermal method in Teflon-coated autoclave. The physical and chemical properties of as prepared material were systematically studied with highly sophisticated instrument techniques. The effect of GD on the semiconductor photocatalyst was studied by the degradation of MB and RhB dyes. The experimental results ensured that the incorporation of GD into ZnO, positive enhancement was observed in terms of degradation efficiency and pseudo first order rate constant. We examined the improved photocatalytic property of GD-ZnO nanohybrid via photoluminescence spectroscopy. From this we understood that, the GD will decrease the number of electron-hole pair recombination in ZnO.

8.1 FUTURE WORK

The following are future work which will be carried out to deeply understand about the two dimensional nanomaterial in photocatalytic sector.

In this entire project we prepared particulate photocatalyst and same has been studied for its properties and photocatalytic activity as well, which helps in further investigation of graphene semiconductor thin film for photocatalytic application. Thin films provides some features which aids in studying the photo-electrochemical properties, e.g. photocurrent, flat band potential etc. However, the particulate photocatalyst exhibits high surface area in comparison with the thin film photocatalyst. The TiO_2 based commercial products are available in market like photocatalytic tiles, paints, ceramics and etc. However, the efficiency of the product is less compared to the expectation. We are planning to commercialize GR-semiconductor photocatalytic product. Water splitting and CO_2 reduction is our next target: Water splitting is a potential area because energy consumption is increasing every day, we need to discover alternative energy source. Water splitting is an environmental friendly approach to meet the energy demand. We are planning to utilize the GR-semiconductor nano hybrids for water splitting experimental. However, in this whole project we haven't carried out this experiment due to time restrictions and instrument unavailability