CHAPTER 1

INTRODUCTION

1.1 CATALYST

Catalyst is the substances which change the reaction speed both positive or negative side and it can be recovered at the end of the reaction without any changes in original. In other words, the chemical reaction speed always measured in terms of reaction rate, in which some catalyst can increase the reaction rate whereas some of them may decrease. Both types of catalyst have been used in many industries and the question is how the catalysts increase or suppress the reaction rate without consuming the catalyst. To answer this question, we should consider about activation energy. Every chemical reaction needs some amount of energy to complete the reaction from precursor to product formation, that's required energy is called as activation energy. The catalyst finds out the new pathway of reaction which consumes less or high activation energy compared with original reaction pathway, so that the catalyst materials never consumed in the reaction. Catalyst has been used in many fields of applied science and industry, due to which discovery of new and effective catalyst is an important concern at this moment. Catalysts are classified in many types such as metal catalyst, electro-catalysts, organo-catalysis, enzymes and biocatalysts, semiconductor photocatalyst and so on.

1.2 SEMICONDUCTOR PHOTOCATALYST

Semiconductor photocatalyst is a solid material and it will act as a catalyst in the presence of super-band light irradiation. Photocatalyst are classified in two types with respect to phase of the material i) homogenous i.e. The reactant and catalysts which are in same phase (H_2O_2+liquid reactant) and ii) heterogeneous photocatalyst i.e. the reactant and catalysts which are in different phase (TiO_2+liquid reactant). On the other hand, based on semiconductor property (band gap) of the photocatalyst, it categories in two branches such as UV and visible light photocatalyst. The photocatalyst applications majorly covered two areas i) energy production (artificial photosynthesis) and environmental remediation sectors (water purification & CO_2 reduction). Photo-induced chemical reactions have huge impact at this moment to meet the urgent necessary to protect the environment and produced solar energy to storable energy in the form of fuel. Photocatalytic is the paramount and sensible approach because it's non-toxic, low-cost and zero waste chemical reactions. For, example a semiconductor exposed with super-band irradiation, the loosely bonded electrons in the valence band travel to reach the conduction band by utilizing the adsorbed energy. Simultaneously the equal number positive holes will be generated in their valance band. The charge carriers migrates on the surface of the semiconductor, consequently the reduction and oxidation reactions takes place with oxygen and water molecules. Thus results in strong free radical generation such as $OH^{\cdot}$ and $O_2^{\cdot}$.The produced free radicals can accelerate the reactions with target chemicals or some other substances. On the other hand, electron-hole back recombination also possible via non-radiative transition before the production of free radicals. There are few important factors directly influenced on the overall catalytic efficiency such as, ability of visible light absorbance, quantum efficiency (turn over number) and electron-hole recombination is a critical factor in semiconductor photocatalyst. In above mentioned issues, electron-hole recombination is key factor in semiconductor photocatalyst. The above described reactions are collectively called as photocatalytic reactions. Still, now approximately more than 190 various semiconductor's photocatalytic activities were studied. Even some are commercialized, unfortunately the efficiency of the semiconductor catalyst not matched as expected level. Scientists are intensively working to improve the semiconductor photocatalyst efficiency. Specifically reduce the charge carrier recombination before free radical production. To address this issue some modification was made on pure semiconductor such as single and double metal doping, designing a heterojunction semiconductor with suitable band gap material, ferroelectric material heterojunction and so on.

1.3 NANOMATERIALS IN PHOTOCATALYST

Nanomaterials open up a new avenue in semiconductor photocatalyst compared with conventional materials where nanomaterials provides attracting features. For instance, when the size of semiconductor photocatalyst is reduced from bulk to nano-scale, the properties such as high aspect ratio, improved active sites, band-gap modulation, and light harvesting are changed. Due to the improved properties, the efficiency of the nanostructured semiconductor photocatalyst is higher than bulk semiconductor photocatalyst. We can grow the nanomaterials with different structured, morphology and orientation. The photocatalytic efficiency highly depends on the catalyst morphology, band gap, band potential, surface area and active sites. Undoubtedly, the nanostructured semiconductor efficiency is higher than bulk semiconductor however; the required efficiency is too far away from current semiconductor photocatalyst efficiency. In this scenario, carbon nanomaterials turn out to be the most attractive candidate. For instance, carbon nanotubes, carbon dots, graphene and graphene oxide (GO) are used in many applications including water purification, energy storage and environmental sectors. Among this, two dimensional carbon nano materials is a new and attractive candidate as the semiconductor photocatalytic nanohybrid. Two dimensional carbon nano materials possess some striking features such as high surface area, high charge carrier mobility, electron accepting nature and able to hold the semiconductor nanoparticles on their surface and promising one dimensional confinement. Above said exciting properties of the two dimensional nano sheets, makes them a good supporting material for semiconductor photocatalysis. Thus, the efficiency can be enhanced and charge carrier recombination can be curtailed very significantly.

1.4 AIM AND OBJECTIVE

The efficiency of semiconductor photocatalyst is highly suffered from "photo-induced electron hole recombination" process. This issue has not been solved effectively. The aim of this work is that using various two dimensional nanostructured carbon materials, the photocatalytic efficiency can be enhanced via reducing electron hole recombination. The main objectives are:

1. Systematic preparation and studying the intrinsic physical properties of GO, GR and GD nanostructured layered materials.
2. Understanding the adsorption property of graphene-oxide with different degrees of oxidation levels.
3. Graphene-oxide (GO)–Fe^{3+} hybrid nanosheets with effective sonocatalytic degradation of Reactive Red 120 and study of their kinetics mechanism.
4. Study the enhanced photocatalytic efficacy of organic dye using various semiconductor-graphene nanohybrid systems.
5. Demonstrate the semiconductor-graphdiyne nanohybrid system for photocatalytic degradation of organic dye.

1.5 THE OUTLINE OF THE THESIS

Chapter 1 introduces the thesis main contents such as catalyst, semiconductor photocatalyst and nanomaterials in photocatalytic research field. Thesis structure is also given in this chapter.

Chapter 2 delivers the literature review, which describes about the discovery, mechanism and updated development in the field of semiconductor photocatalysis and two dimensional layered nanomaterials.

Chapter 3 describes the materials, methods used in this work and preparation of GO, GR and GD and their characterizations.

Chapter 4 defines the adsorption properties of various degree of oxidized graphene-oxide and their mechanism.

Chapter 5 provides the sonocatalytic degradation of RR120 in the presence of (GO)–Fe^{3+} hybrid nanosheets and their kinetics mechanism.

Chapter 6 explains the various metal oxide, metal sulphide semiconductor-graphene nano-hybrid catalyst for enhanced photocatalytic degradation of organic dye.

Chapter 7 investigates the semiconductor-graphdiyne heterojunction for enhanced photocatalytic degradation with phenolic and organic dyes. The enhancement was intensively examined by photoluminescence spectra.

Chapter 8 gives the summary, conclusion and the future outlook/scope.