Preface

Hydrogen energy is seen to be the most appropriate substitute to the current energy supply. Hydrogen generation without involving carbon can be obtained by using solar energy. Solar radiation can dissociate water to hydrogen. A promising method to harvest solar energy and convert it to hydrogen energy is by using semiconductor photocatalyst. A semiconductor utilizes the energy of photon and dissociates water. This reaction is possible in near-ambient conditions. The properties of the semiconductor used as photocatalyst strongly affect the energy conversion efficiency of water splitting process. Any photocatalytic system will consist of photoreactors which shall be the major contributors of the fixed cost. The size and consequently the cost of photoreactor shall drastically come down if efficient photocatalysts are developed. Therefore, development of efficient photocatalyst is key to the success of this promising technology of photocatalytic dissociation of water utilizing solar radiation. In order to use a greater fraction of solar radiation i.e., visible spectrum and to improve the photocatalytic hydrogen generation, several studies have been reported in the literature.

Metal sulphide semiconductors used as photocatalyst have been gaining wide interest due to their high photocatalytic activity for hydrogen production. Compared to their metal oxides counterpart, metal sulphides generally possess ideal conduction and valence band positions, which meet the requirements for photocatalytic hydrogen production and these also have a narrow band gap for the utilization of visible light. CdS is one of the effective metal sulphides for hydrogen production due to its high conduction band edge and a narrow band gap. However, CdS suffers from low activity during photocatalytic reaction due to recombination of photogenerated electrons and holes also it suffers photocorrosion. The photocorrosion can be restricted by providing suitable sacrificial agents. However, restriction of the charge recombination phenomena is a difficult task.

The literature reports that some modifications were applied strategically for CdS photocatalyst to overcome the recombination, specially formation of heterojunction with noble metal and semiconductors. Satisfactory photocatalytic efficiency has been achieved with very costly noble metal Platinum. But there is a necessity to develop non-noble metal based photocatalysts. Currently, graphene oxide and reduced graphene oxide have been investigated widely as co-catalyst due to their ability to form heterojunction with CdS which facilitates transfer of electrons and restrict charge recombination. In addition GO/rGO has high electron mobility for quick transfer of electrons to solid-liquid interface where these mediate reduction of reaction. The charge transfer can take place only when an appropriate heterojunction is formed at the interface. The nature of interface i.e., microstructure will in turn depend on details of preparation.

First time we have reported preparation of GO/rGO CdS by a gas-solid reaction. This catalyst was found to be more active. To understand the effect of preparation variables on catalyst microstructure and consequently on activity, catalysts were characterized exhaustively. Further, to be used, the catalyst in addition to being active must also be durable. In addition, kinetics of the reaction should also be known. In the present work, a detailed activation, deactivation and kinetic studies were also carried out.

Frequently, ultrasounds are used for process intensification. The literature reports use of ultrasound for photocatalytic degradation of pollutants. Only a few reports are there on ultrasound assisted photocatalysis for hydrogen production. In the present work, such studies were carried out and the mechanism of interaction of ultrasound with photocatalysis has been discussed. The complete work has been presented in five chapters.

In chapter one, the subject has been introduced. It includes the worldwide energy demand, environmental issues, description on hydrogen as a future energy carrier and hydrogen production techniques. The literature review, in particular, the advancement in visible active photocatalyst especially CdS based photocatalysts for photocatalytic water dissociation has been discussed in chapter two. The review on development of heterogeneous photocatalysts based on graphene has also been included in this chapter. In this chapter, we have also included review on kinetic study and the effect of ultrasound in photocatalysis. At the end of this chapter, scope of further work based on the literature review and objectives of the present work are given.

The details of catalyst preparation and experimental set-up for hydrogen production and characterization techniques and details of experiments carried out in present study for photocatalysis with ultrasound have been elaborated in the third chapter. The fourth chapter presents the results and discussion on the activity and characterization studies. In this chapter we also made correlation amongstpreparation techniques with activity and microstructures of catalysts. Intensification in hydrogen production rate by ultrasound, and deactivation, re-activation & kinetics of catalyst are also discussed. Conclusions of the present work are presented in chapter five. References are given in the end of the thesis.