Preface

Most appropriate substitute to the current energy supply is hydrogen energy. Hydrogen generation without involving green house gases 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 photoelectrocatalyst. A semiconductor photoelectrode utilizes the energy of photon and dissociates water. This reaction is possible in near-ambient conditions. The properties of the semiconductor used as photoelectrode strongly affect the energy conversion efficiency of water splitting process. Therefore, development of efficient photoelectrocatalyst is key to the success of this promising technology of photoelectrocatalytic dissociation of water utilizing solar radiation. In order to use a greater fraction of solar radiation i.e., visible spectrum and to improve the photoelectrocatalytic hydrogen generation, several studies have been reported in the literature.

Chalcogenide semiconductors used as photoelectrode have been gaining wide interest due to their high photoelectrocatalytic 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 photoelectrochemical hydrogen production and these also have a narrow band gap for the utilization of visible light. CdS and MoS_2 are one of the effective metal sulphides for hydrogen production due to its high conduction band edge and a narrow band gap. However, CdS and MoS_2 suffers from low activity during photoelectrochemical 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 chalogenides photoelectrocatalyst to overcome the recombination, especially formation of heterojunction with noble metal and semiconductors. Satisfactory photoelectrocatalytic efficiency has been achieved with very costly noble metal Platinum. But there is a necessity to develop non-noble metal based photoelectrocatalysts. Currently, graphene oxide and reduced graphene oxide have been investigated widely as co-catalyst due to their ability to form heterojunction with chalcogenides 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.
First time we have reported preparation of GO/rGO CdS by a precipitation method and graphene oxide is reduced in situ by electrochemical process. In situ reduction of graphene oxide to reduce graphene oxide improved the chemical interaction between metal sulfide with layer of graphene sheets. To understand the effect of preparation variables on catalyst microstructure and consequently on activity, catalysts were characterized exhaustively. Mainly, work has been divided into three sections. The complete work has been presented in four 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 photoelectrocatalyst especially chalcogenide based photoelectrocatalysts for photoelectrochemical water dissociation has been discussed in chapter two. The review

focus on development of heterogeneous photoelectrocatalysts based on graphene has also been included in this chapter.

In this chapter, we have also included review on different techniques used for reduction of graphene with different method. At the end of this chapter, scope of further work based on the literature review and objectives of the present work are given.

The third chapter presents the catalyst preparation and the details of experimental set-up for hydrogen production and characterization techniques carried out in present study for photoelectrocatalysis have been also elaborated. On the basis of catalyst preparation, third chapter has been divided into three sections. Each section carried out results and discussion on the activity characterization and mechanism are studies. Conclusions of the present work are presented in chapter four. References are given in the end of the thesis.