

4.1 Conclusions

Photoelectrocatalytic dissociation of water utilizing solar radiation is a promising technology for hydrogen production which is considered a future source of energy carrier. Chalcogenides is an active photoelectrocatalyst for the reaction as it has a narrow band gap and also the conduction band edge is suitable placed with respect to the reduction potential of water. However, for high activity the recombination rate of electrons and holes should be contained. Making composite of Chalcogenides with noble metals or other semiconductors are established techniques to reduce charge recombination rate. Composite of chalcogenides with GO/rGO are particularly promising because it may affect charge separation as well as owing to high electron conductivity of GO/rGO, transfer of electron to the solid-liquid interface becomes fast and hence the activity. However, synthesis route of reduction of GO is important protocol to improve activity as well as interaction between Chalcogenides and surface of graphene.

However, the activity is reported to be highly dependent on the microstructure in particular the nature of the interface between CdS and GO/rGO. Microstructure in turn depends on the details of preparation variables.

Present work carried has been presented into three sections.

In the first section, rGO supported CdS catalysts for photoelectrochemical reaction of water to hydrogen were synthesized by different routes. The catalyst which was prepared by precipitating CdS on GO and subsequently carrying out electrochemical reduction of GO to rGO showed a better activity. This catalyst showed p type semiconductivity and M-S analysis also showed that it had high charge carrier density and a greater flat band potential. The EIS revealed that this catalyst also offered least

resistance to charge transfer to the solid-liquid interface and subsequently lower electron-hole recombination rate. The DRS showed that, it had superior optical properties. The improved photo response of catalyst has been attributed to the above mentioned factors. The FTIR and XPS results confirm chemical interaction at the interface of the CdS and rGO. The interaction is supported to be through π^* orbital of C and 'n' orbital of S. This interaction is found to be high when GO was reduced to rGO in situ electrochemically. Thus, the synthesis route which promotes chemical interactions at the interface of CdS and rGO leading formation of a heterojunction is key to a better activity for photoelectrochemical reduction of water to hydrogen.

In second section, Electrodes with CdS supported on rGO catalysts were prepared by in situ electrochemical reduction of GO to rGO. The in situ electrochemical reduction led to formation of heterojunction at the interface due to intimate contact between CdS and rGO leading to a chemical interaction. It leads to lowering of charge transfer resistance and recombination rate of photo generated electrons and holes, which provide a better activity to electrodes. A 10 wt% r GO was found to be the optimum loading. A lower loading of rGO does not result into uniform distribution and intimate contact between rGO and CdS consequently insignificant interaction between the two. On the other hand, a higher loading or r GO (beyond 10 wt %) results into shielding of CdS from radiation by rGO to have an adverse effect on the activity.

In third section, we have reported preparation of MoS₂-CdS-rGO photoelectrocatalysts by hydrothermal technique. Activity of MoS₂ was seen to enhance significantly when CdS and rGO were incorporated to MoS₂. Results confirm electronic interactions at the solid-solid inter faces of the three components. In presence of MoS₂& rGO the CdS was largely in the cubic phase. Similarly trigonal (metallic) phase of MoS₂ was also observed at the interface in addition to the hexagonal phase. The morphological studies

revealed that both rGO and MoS₂ had formed plate like structures and these plates were in intimate contact to each other. CdS is seen to form particles which were on the surface of rGO and MoS₂ and also imbedded between the layers of MoS₂. The XPS and FTIR analysis have revealed formation of heterojunction at the interfaces. Since there exists number of residual groups on the surface of rGO, it is concluded that chemical interaction has taken place between 'S' of CdS/MoS₂ and 'C' of rGO through π^* orbital of C and n orbital of S. Similarly Mo being more electronegative than Cd the electronic interaction between MoS₂ and CdS has taken place due to an intimate contact between them. These electronic interactions have resulted into formation of heterojunction. The formation of heterojunction has facilitated charge transfer at solid – solid interface and thus these results a greater charge separation. The Impedance spectroscopy results show that the conductivity of MoS₂-CdS-rGO has increased when CdS and rGO were incorporated to MoS₂. This is due to (i) formation of trigonal phase of MoS₂ which has a metallic character and also (ii) due to high conductivity of rGO. The M-S analysis has shown p-type semiconductivity. It has been also revealed that addition of CdS & rGO to MoS₂ has resulted into greater flat band potential and high charge carrier density. Thus, the greater charge separation and high electronic conductivity, high flat band potential with high carrier density have resulted in a superior activity to the MoS₂-CdS-rGO catalyst reported in the present work.

