

2.1 Semiconductor electrolyte interface[34, 35]

This subsection deals with aspects related to electron transfer at semiconductor electrolyte interfaces. The electrochemical potential of the solution is determined by the redox potential of the electrolyte solution, and the redox potential of the semiconductor is determined by the Fermi level. When a semiconductor is immersed in this redox electrolyte, the electrochemical potential (Fermi level) is different across the interface. Equilibrium of this interface thus necessitates the flow of charges from one phase to others and a “band bending” ensues within the semiconductor phase. Band bending phenomenon is shown in Fig 2.1 for n – type and p – type semiconductor. The excess charges that are now located on the semiconductor do not lie on the surface, but extend to a significant distance.

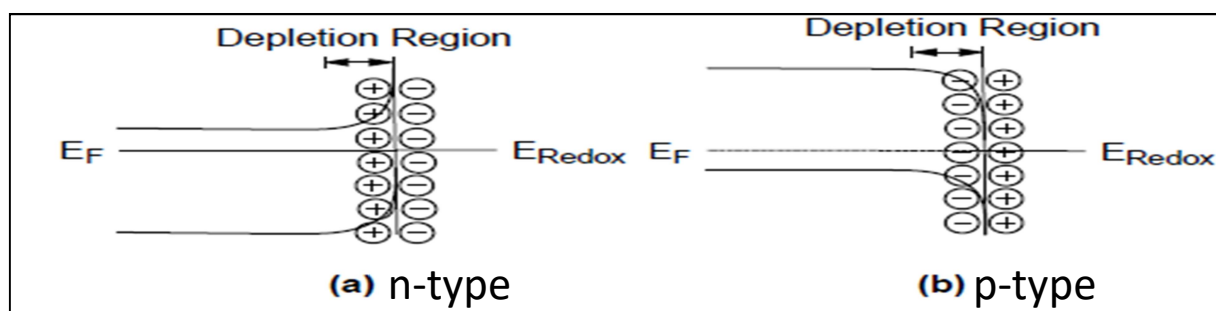


Fig 2.1 Band Bending of semiconductors

This region is referred to as the space charge region and has an associated electric field.

Hence, there are two layers to be considered:

- (i) Interfacial (semiconductor - electrolyte) layer
- (ii) Space charge layer

The situation before and after contact of the two phase are illustrated in Fig 2.2 (a & b). After contact, the net result of equilibrium is that $E_F = E_{F, \text{redox}}$ and a “built – in” voltage, V_{SC} develops within the semiconductor phase, as illustrated in the right hand frames of Fig 2.2 (a) and (b). For an n-type semiconductor electrode at open circuit, the Fermi level is typically higher than the redox potential of the electrolyte, and hence electrons will be transferred from the electrode into the solution.

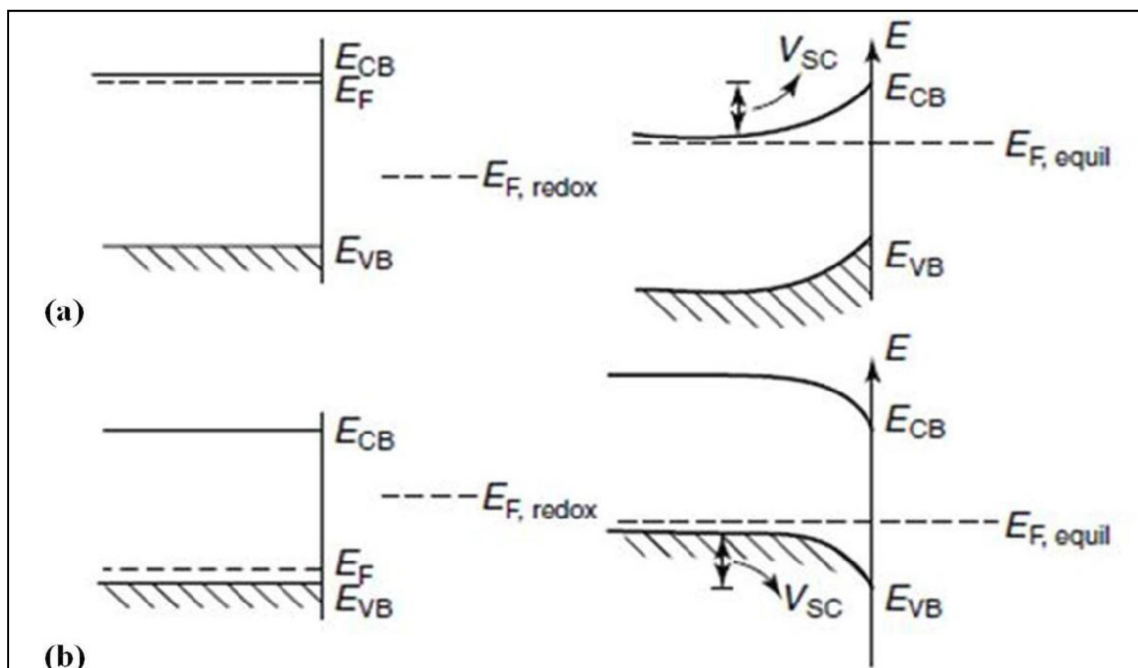


Fig 2.2: The semiconductor – electrolyte interface before (LHS) after (RHS) for (a) n-type semiconductor (b) p – type semiconductor

Therefore, there is a positive charge associated with the space charge region which is also referred to as a depletion layer. For a p-type semiconductor, the Fermi level is generally lower than the redox potential, and hence electrons must transfer from the solution to the electrode to attain equilibrium. This generates a negative charge in the space charge region, which cause a downward bending in the band edge [Fig 2.2 (b)]. Since the holes in the

space charge region are removed by this process, this region is again a depletion layer. There are only a few charge carriers available for charge transfer, and electron transfer reaction occurs slowly, if there is a depletion layer at the interface.

2.1.2 Effect of bias potential on semiconductor – electrolyte interface

When potential applied to the interface electrode shifts the Fermi level, the band edges in the interior of the semiconductor (i.e., away from the depletion region) also vary with the applied potential in the same way as the Fermi level. However, the energies of the band edges at the interface are not affected by changes in the applied potential. Therefore, the change in the energies of the band edges on going from the interior of the semiconductor to the interface, and hence the magnitude and direction of band bending, varies with the applied potential. Mainly there are three situations which are affected by bias potential as shown in Fig 2.3

(I) If applied potential is equal to the flat band potential then no net charge will flow through semiconductor – electrolyte interface, this situation is shown in left side of Fig 2.3

(a)

(II) When applied potential is greater than flat band potential in positive direction for n-type direction and negative direction for p-type semiconductor then depletion layer increases. Electron generated by light will pass through external circuit. This situation is shown in middle of Fig 2.3 (b)

(III) When applied potential is less than flat band potential negative direction for n-type semiconductor and positive direction for p-type semiconductor then accumulation layer

increases. Semiconductor – electrolyte interface behave like metal semiconductor, electron will flow easily and not affected by light. This situation is shown in right of Fig 2.3 (c)

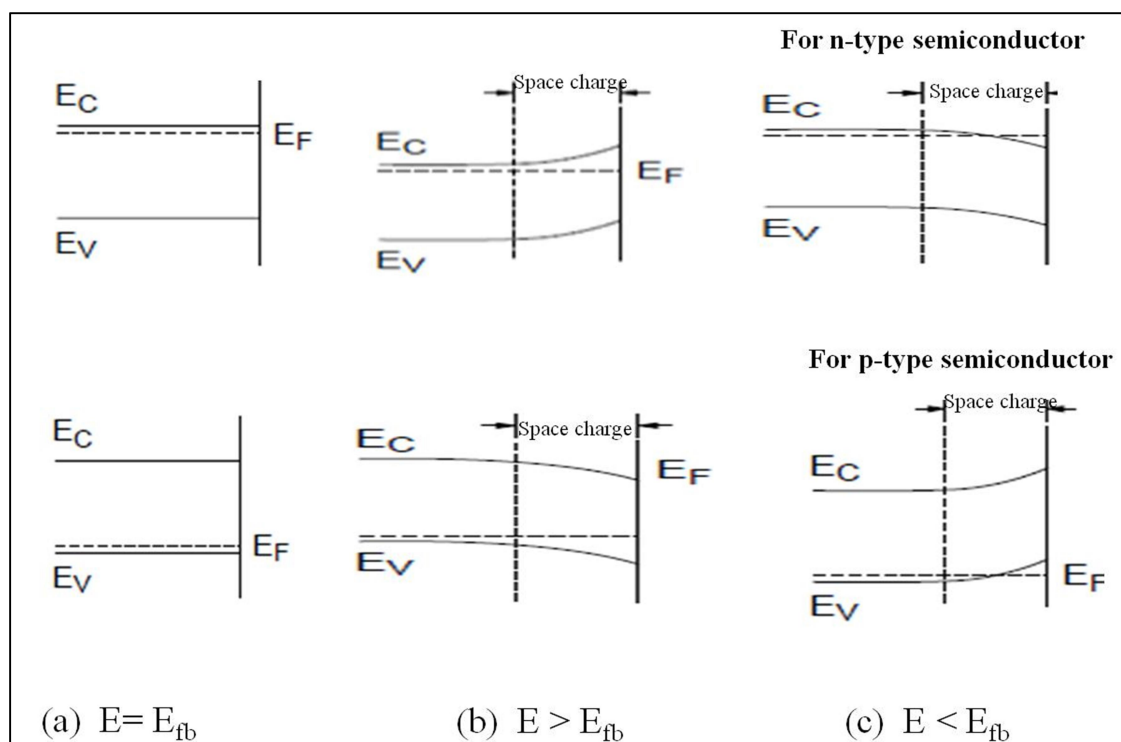


Fig 2.3 Effect of bias potential on semiconductor – electrolyte interface

For an *n*-type semiconductor at positive potentials, the band edges curve upwards, and hence the hole moves towards the interface, and the electron moves to the interior of the semiconductor. The hole is a high energy species that can extract an electron from a solution species; that is, the *n*-type semiconductor electrode acts as a photoanode [situation II and Fig 2.3(b)]. On the other hand for *p*-type semiconductor, the band edge curve downward, and hence the electron moves towards the interface, and the hole moves to the interior of the semiconductor. The electron passes through external circuit participate in the reaction to produce hydrogen. So, *p*-type semiconductor electrode will act as a photocathode.

2.2 Fabrication of electrode

Performance of electrode material is influenced by electrode fabrication method and substrate. Electrode is an important component of a photo-electrochemical process for water splitting. At room temperature, typical electrode consists of supported or unsupported catalyst particles with polymer-based binder loaded on electrode substrate or diffusion layer. There is a current effort towards the development of high utilization and low-loading electrode for PEC performance. Such development strongly depends on the electrode fabrication method and the substrate material.

Electrode fabrication technology has wide range of applications in various areas. It is a base of outstanding developments in the various fields of science and technology such as solid-state electronics, optics, magnetism, coatings, supercapacitor, photovoltaic (PV) cells and photoelectrochemical cell. It is well known that the properties of electrode are dependent on the method of deposition. The required properties and flexibility can be achieved by choosing the appropriate deposition method for electrode. Electrode fabrication methods can be broadly classified into physical and chemical methods. In physical methods, vacuum evaporation and sputtering are enclosed, in which material to be deposited is transferred to a gaseous state either by evaporation or an impact process and deposited on the substrate. The chemical methods include the usually liquid phase chemical processes such as conventional Spin coating, Successive ionic layer adsorption and reaction (SILAR) and chemical bath deposition method.

There are many techniques by which electrode can be fabricated:

(i) Spin Coating

Uniform thin films on flat substrates are deposited via the spin coating method, which encompasses products such as thin and ultrathin films. Procedures on spin coating include deposition, spinup, spinoff, and evaporation. The overloaded solution is deposited onto the substrate, rotated at high speeds, and finally, the solution coats the substrate via centrifugal force. The desired thickness is obtained by continuous rotation. The solvent, being volatile, simultaneously evaporates. The film's thickness is dependent on the solution's concentration, solvent, and spin speeds [36]. The thin film is deposited by the high angular spin speed. The thickness of the films is less than 10 nm, which is useful in photoelectrochemical process.

Spin coating method is widely used for the fabrication of photoanode. Recently, Selvaraj et al [37] fabrication TiO_2 thin film by spin coating method. They optimized the layer of TiO_2 and observed the effect of light in photoelectrochemical process. Shinde et al [38] synthesized MoS_2 single layer photoelectrode by spin coating method on fluorine doped tin oxide (FTO) substrate. They observed that MoS_2 exhibit p-type semiconductivity and very efficient photoelectrode for water splitting. Ramli et al [39] also fabricated TiO_2 film on FTO glass substrate by spin coating method followed by sintering at 465°C for 45 mins and used for PEC application.

However, cost may be a limiting factor in its use in electrode fabrication.

(ii) Successive ionic layer adsorption and reaction (SILAR) method

SILAR method is operated at low temperature. Therefore, a variety of substrates such as insulators, semiconductors, metals and temperature sensitive substrates (like polyester) can be used [40]. As a low temperature process, it also avoids oxidation and corrosion of the

substrate. In this method, substrate can be dipped in cations followed by anions solution and the process may be repeated several times as required.

In various application, thin film electrode can be prepared by SILAR method. Pathan et al [41] reported first time the deposition of CdTe by SILAR method and characterized by different tools. Yin et al [42] fabricated CdS nanoparticle-modified α -Fe₂O₃/TiO₂ by SILAR method for efficient photoelectrochemical (PEC) water oxidation. By integrating CdS/ α -Fe₂O₃/TiO₂ ternary system. They reported that light absorption ability of the photoanode can be effectively improved with an obviously broadened optical-response to visible light region, and separation of photo generated carriers, giving rise to the enhancement of PEC water oxidation performance.

(iii) Chemical Bath Deposition (CBD) method

In this technique it is possible to control the film thickness and chemical composition by varying the deposition parameters such as temperature, precursor concentration, complexing agents used and the pH of the solution. In CBD process, thin films are deposited on a solid substrate when it is immersed into a dilute solutions of one or more metal salts (MP⁺), a source of chalcogenide, X (X=S, Se, Te) ion and a suitable complexing agent in an aqueous solution[43]. The deposition of the film occurs on the substrate when the value of ionic product exceeds the solubility product, otherwise it is precipitated out

Thin film thickness and concentration of catalyst is difficult to determine by chemical bath deposition method. However, chalcogenide based catalysts are widely used as thin film which are prepared by chemical bath deposition method. This method of fabrication is not suitable for composite or heterostructure material. Nair et al [44] synthesized various

chalcogenides (CdS, CdSe, ZnS, ZnSe, PbS, SnS, Bi₂S₃, Bi₂Se₃, Sb₂S₃, CuS, CuSe, etc.) by chemical bath deposition method. They observed that typical growth curves, and optical and electrical properties of these films were improved remarkably. Liu et al [45] et fabricated MoS₂/CdS p – n heterojunction film with high photoelectrochemical activity for H₂ evolution under visible light were successfully prepared by electrodeposition followed by chemical bath deposition method. The MoS₂/CdS heterostructure showed much higher visible-light photoelectrocatalytic activity and higher stability toward the water splitting than pure CdS film. The MoS₂/CdS film with an optimal ratio of 0.14% exhibited the highest photocurrent of 28 mA/cm² and the highest IPCE of ca. 28% at 420 nm at 0 V vs Ag/ AgCl. The critical role of MoS₂ in the MoS₂/CdS film was investigated. The improved photoelectrochemical performance of the MoS₂/CdS heterojunction film was attributed to the visible light absorption enhanced by MoS₂ and the formation of a p-n junction between CdS and MoS₂, which accelerated the effective separation of photogenerated carriers by the internal electrostatic field in the junction region.

(iv) Drop casting method

It is a process in which concentration and thickness of the material can be controlled by amount of catalyst drop cast on the substrate. It is also operated at room temperature. It requires one binder and one volatile liquid in which catalyst is deposited. Volatile liquid is used as a dispersing material, so that catalyst is easily dispersed in solution and uniform thickness will form. This method is not limited to any particular catalyst. This is widely used for every single semiconductor as well as composite. Commonly, nafion solution and

Teflon solution are used as binder and ethanol and N, N –dimethylformamide (DMF) are used as dispersing agent.

Xie et al [46] synthesized electrode of MoS₂ with controllable disorder engineering by drop cast method. They were used Nafion solution as a binder N, N –dimethylformamide (DMF) as a dispersing solution and applied for hydrogen production. Zhang et al [47] also fabricated MoS₂ and carbon aerogel composite electrode by drop cast method. They observed that electrode is highly stable for 2,000 cycle used for hydrogen production.

There are various substrate based on glass are used in electrode fabrication like FTO, ITO and Glassy carbon. These substrates are very costly and difficult to cut into small pieces as required. However, their resistance is low as compared to carbon based substrate [48-51]. Carbon materials, including graphene, carbon nanofibers (CNFs), carbon nanotubes (CNTs), activated carbon, carbon papers, and so on, are ideal substrates for material loading subsequently used as photoelectrode for hydrogen production [52].

2.3 Photoelectrocatalyst

The word catalyst was first time used by Berzalius in 1836 after that Oswald defined catalysis as a substance that changes the rate of reaction without being consumed in the reaction [53]. In general, catalyst speeds up a reaction by decreasing the value of the activation energy by changing the reaction mechanism. The development of electrocatalysis is connected to research on fuel cells and an explicit definition of an electrocatalyst has been given by Grubb in 1963 [54]. Trostwijk and Deimel was the researcher which observed the phenomenon of water splitting [55]. In this way catalysis,

electrocatalysis, photoelectrocatalysis term came into circulation. Photoelectrocatalysis is the photo reaction in presence of electrode on which a catalyst is present.

The efficiency of photoelectrocatalytic devices depends on the material's efficiency to carry out the photoelectrochemical reaction in order to create and transport charge carriers which enhance the activity towards water splitting. Material properties and performance are very important for the overall operation of a photoelectrocatalytic water splitting device. The band edge position of semiconductors relative to water splitting is the important parameter. The flat band potential (E_{fb}) of each material determines the onset potential of water oxidation or reduction for the photoanode and photocathode respectively. Although, recombination in the space charge layer, hole trapping sites on the surface, and hole accumulation due to slow oxygen kinetics may delay this onset, resulting in lower photocurrents at lower potentials. Materials with: ideal band positions for water splitting kinetics, appropriate band gaps for light absorption, strong chemical bonding for stability, and good semiconducting qualities for charge separation are the main aspirations for photoelectrocatalytic materials.

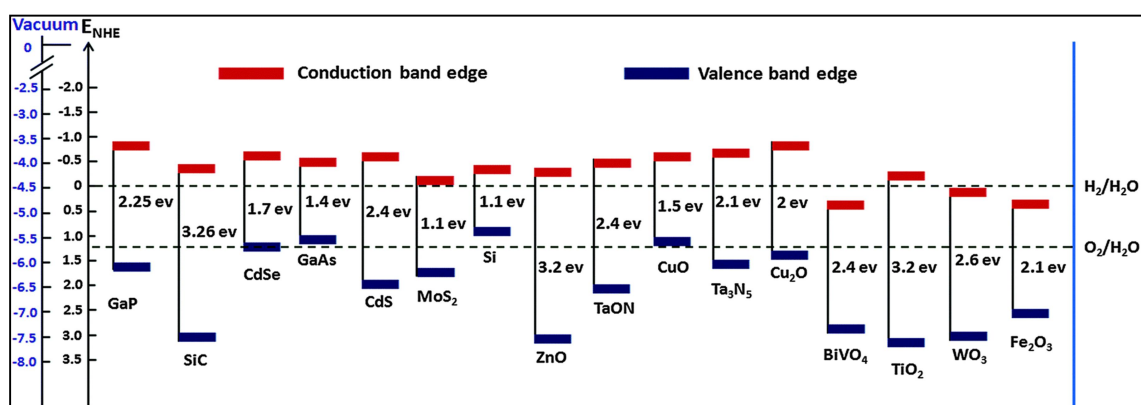


Fig 2.4 Conduction and valance band edge position of semiconductor

As shown in Figure 2.4[56], the bottom level of the conduction band (CB) has to be more negative than the redox potential of H^+/H_2 [0 V vs. Reversible Hydrogen Electrode (RHE)], and the top level of the valence band (VB) has to be more positive than the redox potential of O_2/H_2O (1.23V vs. RHE) for effective water splitting reaction. Therefore, the primary condition for choosing any semiconductor as photoelectrocatalyst is that it should have a minimum band gap of 1.23eV, with suitable edges of CB and VB for water splitting reaction [57].

These sought materials, in theory, should be inexpensive, non-toxic, easily processed/fabricated, and abundant. Finding these characteristics qualities in materials are not obvious, thus much research has been completed in order to adhere to these requirements and find new materials which possess these desired characteristics.

There are mainly three type of photoelectrocatalyst which fulfill all characteristic feature for water splitting

- ✓ Oxide based photoelectrocatalyst,
- ✓ Nitride based photoelectrocatalyst and,
- ✓ Chalcogenide based photoelectrocatalyst

2.3.1 Oxide based photoelectrocatalyst

To further understand the fundamental properties of metal oxides for water splitting, it is necessary to understand their electronic properties and therefore chemical bonds which form electronic properties. Metal oxides are generally ionic in nature due to the fact that oxygen is much more electronegative than any metal. Therefore, valence electrons are either fully or partially transferred from oxygen to the metal ions [58]. This makes metal

oxides more uncertain due to their localized electron movement, as opposed to delocalized electron movement in covalently bonded materials. Thus the distinction between a direct and indirect metal oxide semiconductor is more obscure than with typical electrode material [59]. This is major drawback of oxide based photoelectrocatalysts. However, many researcher works on oxide based photoelectrocatalysts.

Fusishima and Honda first time observed water splitting reaction in oxide based catalyst (TiO_2) in 1972 [60]. Another drawback of oxide based semiconductor is the high recombination of charge carriers. Mohapatra et al [61] reported electron – hole (e – h) recombination loss is major practical problem in using TiO_2 as photocatalyst. They describe the use of the additive to reduce e – h recombination losses which significantly improved the photo current density of the integrated TiO_2 . Hamid et al [62] observed that various modification strategies have been proposed to enhance the activity of ZnO (and semiconductor metal oxides in general) towards photocatalytic water oxidation. Nevertheless, the challenge remains to identify affordable synthesis techniques that can provide fine control over the morphology, carrier concentration and bonding between ZnO and extrinsic modifiers. Sekizawa et al [63] also reported Fe_2O_3 based photocathode with aid of TiO_2 layer, and form multi- heterojunction. They observed that inserted layer of TiO_2 exhibited a defect on surface of p-type photocathode and enhances efficiencies towards water splitting.

2.3.2 Nitride based photoelectrocatalysts

Metal nitrides are the family of interstitial compounds containing the parent metals with nitrogen atoms integrated into the interstitial sites. The parent metal structure could be

modified by intercalation of the nitrogen atoms. The metal lattice expands and the distance between metal atoms increase after the formation of interstitial metal nitrides, broadening the metal d-band. The d-band contraction would cause a greater density of states (DOS) near the Fermi level in comparison with the parent metal[64].The redistributions of the DOS are helpful to improve the properties of parent metals. In addition, the metal nitrides also possess a wide variety of interesting properties such as high hardness, melting temperature, and electronic conductivity[65]. Therefore, metal nitrides have wide applications in several fields of semiconductor and catalyst [66].In particular, metal nitrides have promising applications in electro-, photo- or photoelectrocatalytic reactions due to their unique electronic structures, high electrical conductivity and good corrosion resistance[67].

However, synthesis route of metal nitride is relatively complex. For example, Mo_2N can be directly synthesized through heat treatment of molybdenum oxide under NH_3 flow of 100 mL min^{-1} at 700°C for 2 h [68]. In the synthesis of TiN and Fe_xN , ammonia is frequently used as nitrogen source with heating temperature between $400 - 1000^\circ\text{C}$ [69]. However, high efficacy towards water splitting required aqueous or acidic electrolyte, but nitride based photoelectrocatalysts is not stable in this medium of electrolyte [70].

However, Li et al [71] reported TiN as a plasmonic booster to enhancing the PEC water splitting of TiO_2 photocatalyst. The TiN improve plasmon resonance on the N-TiO_2 to enable high photoactivity in a broadband UV–vis light region, and assists in the charge generation-separation efficiency of TiO_2 for enhanced water oxidation kinetics. Song et al [72] reported that Mo_2N nano composite catalysts. Mo_2N was synthesized by

polymerizing *p*-phenylenediamine (*p*-PDA) with ammonium heptamolybdate and following calcination under N₂ atmosphere. It showed excellent HER performance in 0.5 M H₂SO₄ solution, allowing a low overpotential of 217 mV to produce H₂ with 10 mA cm⁻² current density, catalyst loading of 0.5 mg cm⁻². After 1000 cycles of acceleration degradation tests, Mo₂N remains negligible overpotential loss.

2.3.3 Chalcogenides based photoelectrocatalyst

Chalcogenides are chemical compounds consisting of at least one chalcogen anion and at least one electropositive element. It is well known that semiconductors including metal chalcogenides are remarkably important photoelectrocatalyst for hydrogen production. Among the various metal chalcogenides, CdS and MoS₂ has received considerable attraction as active photoelectrocatalyst for hydrogen production under visible light due to its desirable properties such as band gap, suitable band position. However, it has serious problems such as rapid recombination and photocorrosion.

Qutub et al [73] observed that CdS is attractive chalcogenides due its appropriate band edge position and suitable band gap (2.42). Band gap lies in the range of visible light and effective for water splitting. Yang et al. [74] reported if a different chalcogenide (PbS) is combined with CdS - TiO₂ and applied as photoelectrochemical protection of 304 stainless steels. Composite exhibited excellent photoelectrochemical performance due to electric field formed in the TiO₂/PbS interface and the CdS/PbS interface which promotes the separation of electrons and holes in the hybrid semiconductor. These interfaces between semiconductor/electrolyte and schottky barrier boost the photogenerated electron transfer from the semiconductor to the connected metal, leading to enhancement of the

photoelectrochemical performance. Jiang et al [75] reported $\text{In}_2\text{Se}_3/\text{MoS}_2$ photoelectrocatalyst composite for water splitting. They observed that $\text{In}_2\text{Se}_3/\text{MoS}_2$ heterojunction exhibited excellent photoelectrochemical performance toward water splitting than bare In_2Se_3 , due to numerous p-n junctions formed at the interfaces of composite. Zhou et al. [76] synthesized few layer MoS_2 on Ti foil by hydrothermal method. They observed that MoS_2 nanoflake photocathode grown in water exhibited excellent photoelectrochemical performance. Chalcogenides was modified in the form of nanorod[77], nanowire [78], and flower [79] like structure to avoid recombination.

Basically, charge recombination, as discussed below, is the measure issue for oxide, nitride or chalcogenides based photoelectrocatalyst for hydrogen production. However, band edge position and stability of chalcogenides based photoelectrocatalyst is more appropriate so chalcogenides is more suitable than other catalyst.

2.4 Charge recombination and its prevention

Whenever semiconductor is irradiated by visible light and generated charges are not used to reduce/oxidized to split water, simply they recombine with hole generated an efficiency of whole system decreased.

There are three ways to avoid recombination of charge carriers and enhanced the efficiency towards water splitting.

- ❖ Doping of noble metal
- ❖ Combination of two semiconductors and
- ❖ Providing support to the semiconductor

2.4.1 Doping of noble metal

Noble metals such as Pt, Pd, Ru, Ir possess the function for trapping light-induced electrons, and act as the active sites for H₂ production as well[80, 81]. Thus they have been widely used as co-catalyst cooperated with each other in water splitting, especially the reduction reaction of hydrogen protons. The possible addition of noble metal can capture electrons and sent for possible reaction. Since, Fermi level of Noble metal is lower than conduction band of semiconductor, it is possible that generated charge carriers transfer to the Fermi level of the noble from conduction band of semiconductor and avoid the recombination[82, 83].

Recently, Chang et al [84] synthesized CdS/Pt/SrTiO₃ composite. They observed that composite exhibited excellent hydrogen production rate (57.9 mmol g⁻¹h⁻¹) under visible light irradiation. Pt can serve as e⁻ trapping and reaction sites, by which the recombination of photoinduced charge carriers can be suppressed and photoelectrocatalytic reaction can be promoted. Zhang et al [85] reported that ternary photoelectrocatalyst WO₃/Au/CdS showed efficient photoelectrochemical performance due to presence of Noble metal. The pristine WO₃ and CdS displayed a weak anodic photocurrent of 0.4 and 1.0 μA at 0 V with visible light illumination, respectively. The photocurrent of WO₃/Au was 1.5 μA, which was 3.75 times of that of WO₃. The increased photocurrent reflected the high separation efficiency of photogenerated carriers, suggesting that to couple the Au nanoparticles with WO₃ was an effective method to overcome the drawback of high recombination rate of photogenerated charge carriers. Wang et al [86] observed that photoelectrocatalyst CdS/CuInS₂/Au/TiO₂. With a high Au loading may benefit the high photoelectrical

efficiency. However, size of noble metal is also important parameter for photoelectrical efficiency. Zhao et [87] reported that urchin-like ZnO-Au@CdS microspheres were obtained by depositing Au nanoparticles (NPs) and CdS NPs on the surface of urchin-like ZnO microspheres. They also observed that the introduction of intermediate electron transfer of Au nanoparticles to isolated ZnO and CdS systems significantly enhances the PEC property.

2.4.2 Combination of two semiconductors

Combination of two semiconductors or more, are the most exciting and recent strategy to achieve absorption of large part of the solar radiation for increasing the efficiency of the water splitting process. In a combination of two or more semiconductor system, the small band gap semiconductor is primarily responsible for visible light absorption and sensitizing the large band gap semiconductor through electron and/or hole injection. Efficient electron injection requires that the bottom of the CB of the small band gap semiconductor be above the bottom of the CB of the large band gap semiconductor [88]. The electron transfer between the two semiconductors could also enhance the charge separation and inhibit the recombination rate by forming a potential gradient at the interface. These composite heterostructures combine the properties of two semiconductors in unique architecture to address the shortcomings of individual semiconductors as photoanode, representing a new and promising approach for PEC and other applications. Whenever two semiconductors (or more) possessing different energy levels for their corresponding conduction and valence bands then excited charge from one semiconductor passes to other semiconductor and avoid recombination. Phenomenon of charge transfer is shown in figure 2.5.

Recently, various studies with respect to water splitting have shown improved visible-light photoelectroactivity with combined semiconductors, viz, Zhang et al [89] was synthesis ZnS-CdS semiconductors and observed improved PEC performance due to formation of heterojunction between ZnS-CdS. Chagueta et al [90] also observed improved activity towards water splitting in ZnS and CdS – TiO₂ nanostructure photoelectrocatalyst.

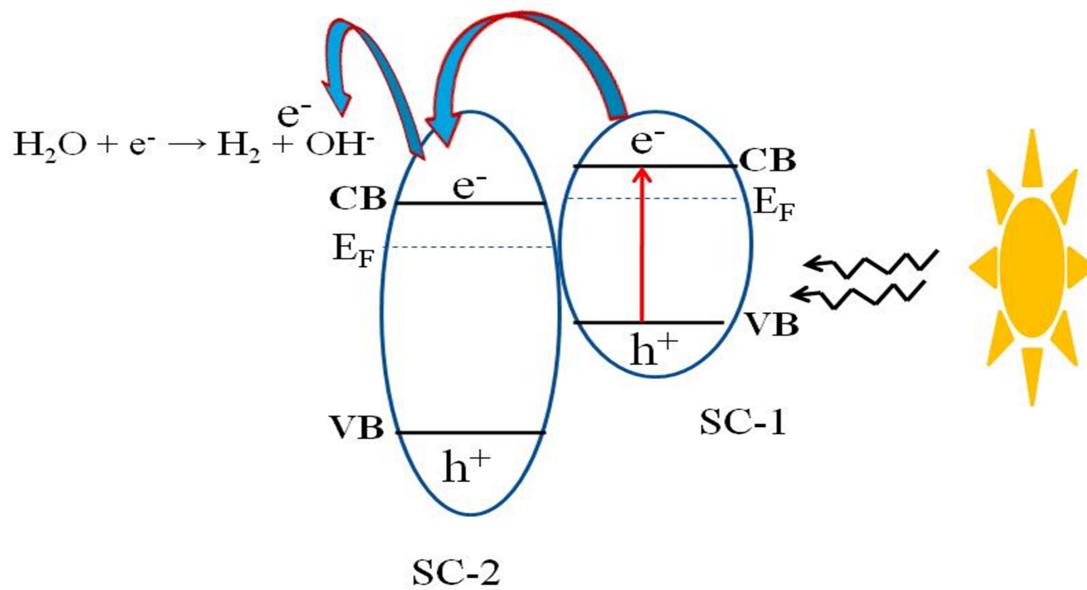


Fig 2.5 Schematic diagram for charge transfer between two semiconductors

Ji et al [91] synthesized leaf-like CdS/MoS₂ hybrids. The interactive influences between MoS₂ and CdS on the photoelectrocatalytic activity for catalyst of CdS/MoS₂ were characterized by analyzing the current density (J)–potential (V) curves of cathodic and anodic polarization. The CdS/MoS₂ hybrid showed the improved photoelectrochemical performance which was attributed to the visible light absorption enhanced by MoS₂ and the formation of p–n junction between CdS and MoS₂. Diby et al [92] synthesized TiO₂ nanorod with CdS by hydrothermal method and they observed that improved

photoelectrochemical performance due to formation of heterojunction between two semiconductors. Zhong et al [93] also synthesized first time a novel rods-on-rods CdS branched TiO₂ nanoarrays by in-situ growth strategy. The controllable surface-to-volume ratios of CdS nanorods, combining with their original intimate connection with TiO₂ nanorods, not only enhance both the solar light scattering and absorption performance, but also effectively promote the separation and transportation of photogenerated charges. Liu et al [94] fabricated MoS₂ nanosheets composited with TiO₂ nanorods to obtain a heterostructure with improved photoelectrochemical (PEC) performance. TiO₂ nanorods were initially prepared using a hydrothermal method, and then MoS₂ nanosheets were synthesized using TiO₂ nanorods as the substrates. Jiang et al [95] worked on MoS₂/WS₂ heterostructures with decoration of Bi₂S₃ nanorods through different stacking sequences (MoS₂/WS₂ (bottom layer) + Bi₂S₃ (top layer) and Bi₂S₃ (bottom layer) + MoS₂/WS₂ (top layer), respectively). They found that the composite catalysts of both stacking sequences can promote visible-light utilization and accelerate the electron transportation. Linear Sweep voltammetry towards PEC performance indicated that MoS₂/WS₂+Bi₂S₃ possessed higher photoelectrocatalytic activity than that of Bi₂S₃+MoS₂/WS₂ due to its proper energy band alignment that facilitates the effective carrier separation, the lower charge transfer resistance, higher electrochemically active surface area as well as the fast electron transfer kinetics.

2.4.3 Providing support to the semiconductor

Graphene/rGO as co catalyst and their preparation

Graphite is an allotrope of carbon and present in the form of multilayered. The single layer called “graphene” considered as the first two-dimensional (2D) crystal [96]. It consists of carbon atoms arranged in a hexagonal lattice, which is only one atom thick, graphene lattice with two carbon atoms per unit cell denoted by A and B shown in Fig 2.6. Basically, the CB (π^* -state) and the VB (π -state) of graphene meet at six points and these are also called Dirac points [97], as shown in Fig 2.7. The band structure of graphene is symmetric about the Dirac point with the Fermi level located between VB and CB. As a result, graphene behaves as zero-band gap material or semi-metal. With this exclusive band, structure graphene shows high conductivity that is essential for high electron mobility. Furthermore, the band structure of graphene tailored by heteroatom doping can result in the shift of Fermi level and shift in Dirac point. Subsequently, graphene shows n-type or p-type semi conductivity with a small band gap [98, 99].

Prior to the focus on graphene, there was extensive research on the preparations and properties of graphite oxide and later graphene oxide. The difference between graphene and graphene oxide (GO) is the addition of oxygen atoms bound with the carbon scaffold as shown in Fig 2.8 As a result, graphene is hydrophobic in nature whereas GO is hydrophilic, that is, easily dispersible in water. In addition, GO contains both aromatic (sp^2) and aliphatic (sp^3) domains, which further expands the types of interactions that can occur with the surface [100]. GO is easily reduced to reduced GO at high yields; however, the quality of the produced graphene is not suitable for electronic applications or mechanical reinforcement of polymers due to structural defects created during the synthesis of GO.

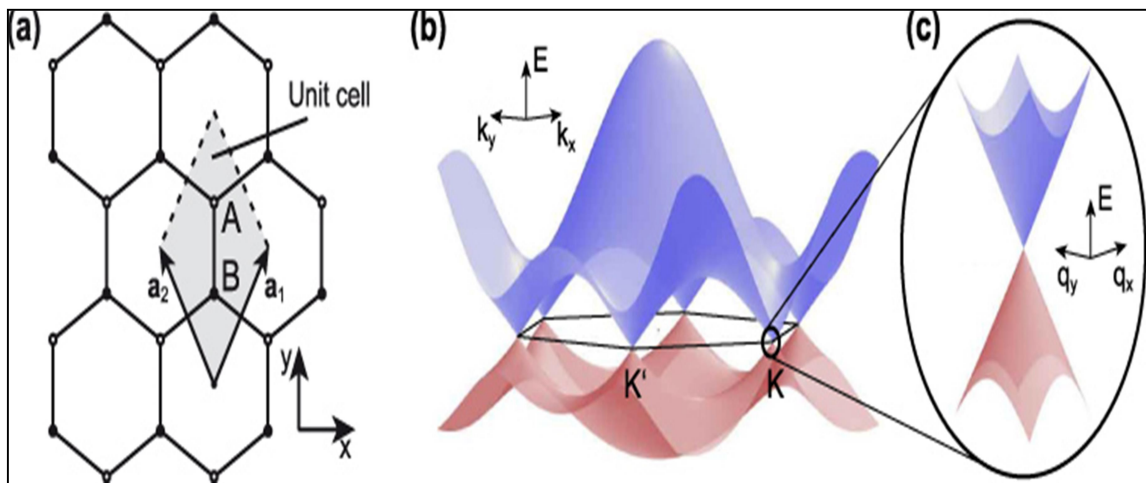


Fig 2.6: Electronic structure of Graphene Lattice

In most cases, functionalization is the best way to achieve the best performance out of graphene or GO. In this respect, the literature is massive for the growing applications of graphene and GO modified through both noncovalent interactions and covalent bonds. Generally, covalent functionalization compromises of the sp^2 structure of graphene lattices [101], thus resulting in defects and loss of the electronic properties

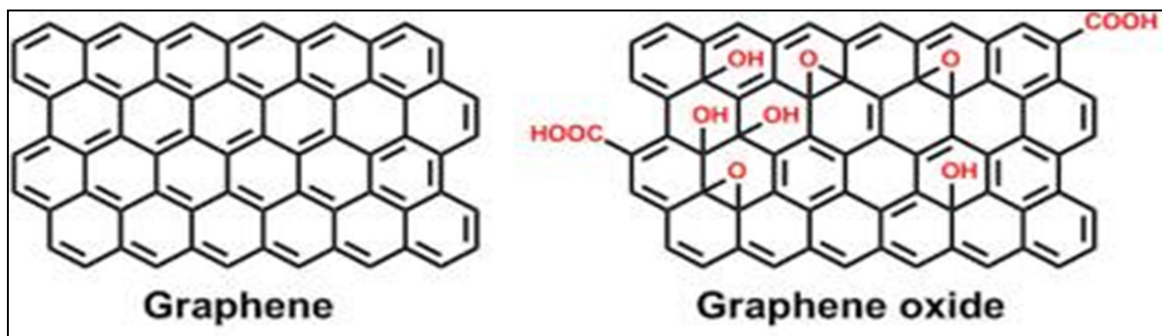


Fig 2.7 Oxidation of Graphene to produce Graphene oxide

. In contrast, noncovalent functionalization is largely preferred, as it does not alter the structure and electronic properties of graphene while it simultaneously introduces new chemical groups on the surface. Common examples of noncovalent functionalization

include polymer wrapping, π - π interactions, electron donor–acceptor complexes, hydrogen bonding, and van der Waals forces [102].

Thus, synthesis route is important protocol to improve electrical conductivity of graphene and chemical interaction with other semiconductor.

GO can reduced by following method:

- (i) Chemical method,
- (ii) Thermal method,
- (iii) Photocatalytic reduction method and
- (iv) Electrochemical method

(i) Chemical Method:

Oxidation of graphite to graphene oxide followed by the reduction process is the commonly used method for mass scale production of graphene or reduced graphene oxide (rGO). GO can react with chemical reagent to produce rGO. Generally, the reduction can realized at room temperature or by moderate heating. For the chemical reduction of GO to rGO, the requirement for equipment and surrounding is not as critical as that of other reduction method which makes reduction for the mass production of graphene compared with other reduction method. Zn powder, Hydrazine, Sodium Citrate and ascorbic acid etc are used as reducing agent for reduction of graphene oxide [103-105]. Recently, Sarkar et al [106] reduced graphene oxide by chemical method using Zn powder as the reducing agent and forming a composite of rGO-ZnO. This composite can use as photocatalyst for hydrogen production. Park et al [107] and Chua et al [108] also produced reduced graphene

oxide by chemical method and they used hydrazine as reducing agents to reduce GO to rGO.

Kanishka et al [109] synthesized reduced graphene oxide by using green reducing agent (Ascorbic Acid) at different time. They observed that the oxidation of graphite has given highly oxidized GO with a 9.30 Å interlayer space and about 33% of oxygen atomic percentage. Until 50 min of the reduction, both GO and RGO coexist. The reduction rate is fast within the first 30 min.

(ii) Thermal Method

GO can be reduced solely by heat treatment and the process is named as thermal annealing reduction. In the initial stages of graphene research, rapid heating (>200 °C/min) was usually used to exfoliate graphite oxide to achieve graphene [110]. The mechanism of exfoliation is mainly the sudden expansion of CO or CO₂ gases evolved into the spaces between graphene sheets during rapid heating of the graphite oxide. The rapid temperature increase makes the oxygen-containing functional groups attached on carbon plane decompose into gases that create huge pressure between the stacked layers. Based on state equation, a pressure of 40 MPa generates at 300 °C [111]. However, for the exfoliation of GO, 2.5 MPa is required [112]. The exfoliated sheets can be directly named graphene (or chemically derived graphene) rather than GO, which means that the rapid heating process not only exfoliates graphite oxide but also reduces the functionalized graphene sheets by decomposing oxygen-containing groups at elevated temperature. Ji et al [113] synthesized reduced graphene oxide incorporated with cobalt oxide nano-composites. GO was reduced to rGO at different annealing temperature 300 °C, 400 °C and 500 °C.

(iii) Photocatalytic reduction method

GO can also be reduced by photochemical reaction with the assistance of a photocatalyst like TiO_2 . Recently, Williams et al [114] reported the reduction of GO in a colloid state with the support of TiO_2 particles under ultraviolet (UV) irradiation. Initially, TiO_2 absorbs UV light and generates electron hole pair. In the presence of ethanol, the holes scavenged to produce ethoxy radicals, thus leaving the electrons to accumulate within the TiO_2 particles. The accumulated electrons interact with GO sheets to reduce functional groups. Color of GO changed during the reaction from light brown to dark brown.

(iv) Electrochemical reduction method

Electrochemical reduction method promises the reduction of GO to rGO by removing oxygen functionalities [115]. This method is carried out by forming GO sheets or films in a electrochemical cell using an aqueous buffer solution at room temperature. The reduction usually needs no special chemical agent, and is mainly caused by the electron exchange between GO and electrodes. This method avoids the use of toxic reducing agent like hydrazine and eliminates the byproduct.

After depositing a thin film of GO on a substrate (glass, plastic, ITO, etc.), an inert electrode is placed opposite to the film in an electrochemical cell and reduction occurs during charging of the cell. By cyclic voltammetric scanning in the range of 0 to -0.1 V (respect to a saturated calomel electrode) to a GO-modified electrode in a 0.1 M KNO_3 solution, Pumera et al [116] found that the reduction of GO began at -0.6 V and reached a maximum at -0.87 V. The reduction can be achieve by only one scan and is an electrochemically irreversible process in this scanning voltage range.

Zhou et al.[117] reported the best reduction effect using an electrochemical method. Elemental analysis of the resultant rGO revealed a C/O ratio of 23.9, and the conductivity of the rGO film was measured to be approximately 85 S/cm. They found that the potential needed to realize the reduction is controlled by the pH value of the buffer solution. A low pH value is favorable to the reduction of GO, so the authors proposed that H⁺ ions participate in the reaction.

An et al. [117] used electrophoretic deposition (EPD) to make GO films. They found that GO sheets can also be reduced on the anode surface during EPD, which seems counter-intuitive to the general belief that oxidation occurs at the anode in an electrolysis cell. Though the reduction mechanism is not clear, the simultaneous film assembly and reduction might be favorable to some electrochemical applications. Based on the above results, reduction of GO by these method are highly effective. However, oxygen containing functional group have not removed by this method, which will affect the chemical interaction with other semiconductor and consequently photoelectrocatalytic activity towards water splitting [118].

In situ photoelectrochemical approach is another important method by which GO is reduced to rGO, and also chemically interacted so that photoelectrochemical activity towards water splitting is increased.

Recently, Tang et al [119], Cobos et al [120], Yu et al [121], Chen et al [122]etc applied this method to reduce GO to rGO and used in different application. In the field of photoelectrochemical process Chang et al [123] reported that quantum dots Graphene can be prepared by in situ growth and showed enhanced photocurrent generation capability and

incident photon-to-electron conversion efficiency (IPCE) at visible light, and could also be an efficient platform for other optoelectronic applications. Hong et al [124][140] synthesized CdS supported on in situ reduced graphene oxide. They reported improved photocatalyst performance of CdS/rGO attributed to enhancement of the connection between CdS and rGO sheets, which accelerates the effect of the separation of photoinduced electrons and holes by transferring the photoinduced electron to rGO sheets. Zhang et al [125] reported ternary CdS–Graphene–TiO₂ Hybrids. Graphene oxide reduced in situ and they reported that catalyst is able to tune the energy band, increase the surface area, and facilitate the electron transfer thus avoiding the recombination of charges (electron hole pair). The improved photoelectrocatalytic performance attributed to the combined interaction of rGO with other semiconductor. Wu et al [126] demonstrate the realization of a WO₃–reduced graphene oxide (RGO) nanocomposite *via* hydrothermal growth of ultrathin WO₃ nanoplates directly on fluorine-doped tin oxide (FTO) substrates, followed by in situ photo-reduction to deposit rGO layers on WO₃nanoplate surface. Photoanodes made of the WO₃–rGO nanocomposites have achieved a photocurrent density of 2.0 mA cm⁻² at 1.23 V with respect to reversible hydrogen electrode (RHE), which is among the highest reported values for photoanode based on hydrothermally grown WO₃. Electrochemical impedance spectroscopy reveals that the increase of photoelectrochemical activity has attributed to the enhanced charge transfer by the incorporation of rGO. Therefore, electrode can be fabricated with catalyst and GO with in situ electrochemical reduction of GO. The process is relatively simple, fast, and affordable, likely to form intimate contact between GO and rGO.

Today, several researchers had reported that semiconductor supported by reduced graphene oxide and photoelectrochemical activity towards water splitting has remarkably improved.

Khan et al [127] synthesized the CdS-rGO nano composite, prepared by precipitation method in which CdS nanoparticles anchored successfully onto graphene sheets. A combination of CdS nanoparticles with the optimal amount of two-dimensional graphene sheets had a profound influence on the properties of the resulting hybrid nanocomposite, such as enhanced optical, photocatalytic and photo-electronic properties. They observed that CdS-Graphene nanocomposite could serve as an efficient visible-light-driven photocatalyst as well as photoelectrochemical performance for optoelectronic applications. The significantly enhanced photo catalytic and photoelectrochemical performance of the CdS-Graphene nano composite attributed to the synergistic effects of the enhanced light absorption behavior and high electron conductivity of the CdS nanoparticles and graphene sheets, which facilitates charge separation and lengthens the lifetime of photogenerated electron-hole pairs by reducing the recombination rate. The as-synthesized narrow band gap CdS-Graphene nano composite are used for wide range of visible light-induced photocatalytic and photoelectrochemical based applications. Wang et al[128] synthesized hierarchical graphene/CdS/Ag₂S (G/CdS/Ag₂S) photoelectrocatalyst, and found to have an excellent effect in the light absorption. The photocurrent density of the G/CdS/Ag₂S nanofilms for photoelectrochemical water splitting was measured to be up to 5.18 mA/cm², which could be ascribed to the minimum recombination of charge carriers due to graphene is used as a electron accelerator. Wang et al[128] prepared a photoelectrochemical sensor on FTO electrode modified with CdS quantum dots (QDs), graphene (GR) and molecularly

imprinted polypyrrole (MIP). They observed that While a MIP layer of 4-aminophenol was deposited on CDS-GR nano composite modified electrode, the photocurrent response to 4-aminophenol on the modified electrode was promoted due to the specific binding of MIP with 4-aminophenol. The photoelectrochemical response was linearly proportional to the concentration of 4-aminophenol in the range of $5.0 \times 10^{-8} \text{ mol L}^{-1}$ to $3.5 \times 10^{-6} \text{ mol L}^{-1}$, with a detection limit (3S/N) of $2.3 \times 10^{-8} \text{ mol L}^{-1}$. Moreover, the MIP/CdS-GR modified FTO electrode showed excellent selectivity. Han et al [129] synthesized a graphene based ternary composite of Graphene – CdS – ZnO by simple hydrothermal method. They observed that ternary composite exhibited superior photoelectroactivity toward water splitting due to better light harvesting and minimum recombination of charges. Shen et al [130] synthesized CdS:Mn supported by graphene by simple hydrothermal method. They observed that Graphene greatly enhanced and facilitated visible light absorption as well as electron transport and CdS:Mn/rGO shows better photoelectrochemical performance than bare CdS. Xiao et al [131] prepared a layer by layer self-assembly of CdS supported on graphene sheets. They attributed that alternating graphene/CdS multilayer films showed enhanced photoelectrochemical activity under visible light as compared to bare CdS due to structural advantage of graphene in graphene/CdS composite film. Xie et al [132] also reported that, ZnTe modified with reduced graphene oxide has been widely used effectively in the field of solar energy conversion. They also observed that synergetic effect between rGO and ZnTe composite enhance the photoelectrocatalytic performance towards water splitting.

Amongst all metalChalcogenides are the most common photoelectrocatalyst for water splitting that produces hydrogen under visible light due to its properties such as narrower band gaps (visible light adsorption) and suitable band positions. However, recombination and photo corrosion are there two drawbacks, which may affect the photoelectrocatalytic activity of hydrogen production. These can be avoid, by using graphene as a supporting material preferentially to avoid recombination, which decreases electron-hole recombination rate and increases long time stability, charge separation efficiency and separation rate. Recently, researcher are showing great interest in carbon based materials and especially in graphene -based semiconducting materials because of their positive synergic effects in photo electrochemical hydrogen production. Various properties of these materials for PEC hydrogen production can be enhance by the using suitable techniques and modifications. For an instance, strategies for tailoring the properties of carbon-based materials, such as liquid solid surface, doping effect and interface engineering have been proposed to change the structure of graphene and to improve its semiconducting properties. Reduced graphene oxide (rGO) is also a semiconductor covalently surrounded by hydrophilic oxygen-containing functional groups, such as carbonyl, hydroxyl, epoxy, carboxyl groups depending on reduction degree of graphene oxide (GO), has a large surface area and wide band gap. By adjusting its reduction degree, the band gap of this material can modify so that it can use in visible light photoelectrocatalysts region.

2.5 Future scope of work based on the literature review

Hydrogen has all the potential to be considered as the future source of energy. It becomes more attractive when hydrogen is produced by dissociation of water utilizing the solar radiation. To this effect photoelectrocatalytic decomposition is a promising technology. The main objective is the fabrication of electrode and major cost is only due to reactor. Therefore, extensive work has been reported in the literature on the development of photoelectrocatalysts.

There are three classes of catalysts, i.e. oxides, nitrides and chalcogenides. Chalcogenides are inherently more active and have narrow band gap suitable for harvesting of solar radiation. Conduction band edges of these compounds are more negative compared to the reduction potential of water and thus making reduction of water feasible. Cadmium sulphide and Molybdenum disulfide are such photoelectrocatalyst. However, CdS and MoS₂ suffer from photocorrosion. Literature reports that the photocorrosion may be suppressed by using appropriate sacrificial agents.

However, the recombination of charge (recombination of photogenerated electrons and holes) has no easy solution. Two approaches have been reported in the literature. In the first approach a noble metal, especially platinum is incorporated in the semiconductor and the metal acts as a sink for electron. In the second approach, a composite is made of two semiconductors where photogenerated electrons in semiconductor of narrow band gap are transferred to the conduction band of the large band gap semiconductor. In addition the catalysts should exhibit high conductivity for the transfer of electron to solid liquid interface. Owing to the high cost of noble metals and second approach is being

investigated. The composites made from chalcogenides and rGO are promising catalyst because it offers a fast electron transfer kinetics both at the solid – solid interface as well as solid – liquid interface.

The transfer of electron from one semiconductor to another depends on the nature of interface between the two semiconductors. A chemical interaction which leads to an intimate contact between the two is essential. Therefore, development of catalyst preparation techniques and in situ reduction of GO, was increases the appropriate interaction, which results into high activity in area of research. There are many semiconductors which have been attempted with CdS. However, recently there is a focus on the use of GO/rGO as co-catalyst with CdS or MoS₂. GO/rGO has many positive attributes. Its semiconductor property can be tailored by doping, these have excellent electron mobility property and they can also chemically interact with CdS and MoS₂ at the interface to promote efficient charge separation.

2.6 Objective of present work

The present work was carried out with the following objectives:

- ❑ Develop techniques to prepare Chalcogenides (CdS and MoS₂) supported on rGO Photo electrocatalysts with formation of heterojunction at interface with high electrical Conductivity
- ❑ Characterize catalysts by XRD, FTIR, DRS, PL, HRSEM, TEM/HRTEM, XPS, EIS and Mott-Schottky
- ❑ Develop inter relations between preparation technique microstructure and activities of catalyst

The work reported in the thesis has been presented in three sections as given below.

- ❑ Section I: Development of CdS supported on photoelectrocatalyst on electrochemically reduced rGO
- ❑ Section II: Optimization of rGO supported CdS photoelectrocatalyst
- ❑ Section III: Development of rGO supported CdS-MoS₂ photoelectrocatalyst