

Chapter - III

Section I: Development of CdS supported on photoelectrocatalyst on electrochemically reduced rGO

I.3.1 General

Utilization of ubiquitous solar radiation for hydrogen production by water splitting has presented a new possibility for the generation of clean, green and renewable energy[138]. However, this opportunity has presented a formidable challenge to design and develop new composite electrodes that may allow efficient solar conversion into chemical energy. In the design of such composite systems, direct band gap semiconducting materials play an important role. Such semiconductor should have not only suitable band edge positions with reference to red-ox potential of water but also a high electron-hole recombination rate must be prevented to facilitate electron –holes pair available for electrochemical reactions. This demands development of new composite materials for the production of clean and green hydrogen at a large scale by water photoelectrocatalysis. Chalcogenides, in general, have narrow band gaps which may be activated by visible light, thus suitable for harvesting solar radiation [139-141].

Cadmium sulphide has a band-gap of 2.4eV and a suitable band edge for hydrogen production [142]. Although high electron-hole recombination rates in CdS significantly reduces its water splitting activity [143]. This problem can be circumvented by introducing a co- catalyst which may provide a cascading affect i.e. photoelectron generated in CdS may get transferred to the co catalyst, whereas holes remain in the valance band of the CdS. Such an effect has been seen to be effective in charge separation [144, 145]. Incorporation of noble metals to semiconductors also results into transfer of electrons to metals from conduction band of semiconductor[146]. Pt, Au etc as co-catalysts has been confirmed to be effective, although applications of such metals are limited due to their high costs [147]. Thus, more efforts are needed to develop affordable photoelectrocatalysts having reduced bulk and surface recombination rates of electrons-holes to achieve better hydrogen generation efficiency. In this context,

supporting CdS on reduced graphene oxide (rGO) has been found to hold promise. It provides a large equi-potential surface of rGO which enhance electronic mobility as well as facilitates the charge separation[148]. Necessarily, CdS and rGO must be in intimate contact and having chemical interaction resulting in formation of a heterojunction at solid – solid interface to facilitate charge transfer from CdS to rGO[149, 150]. Literature suggests chemical interaction between π^* orbital of 'C' of rGO and n orbital of 'S' of CdS[151]. Chemical interaction is also possible through the number of functional groups on the surface of rGO [152, 153]. Hence synthesis protocol of rGO supported catalyst becomes very crucial. The process should result into interaction of CdS and rGO. Among several other routes, the hydrothermal process has been popularly used for the synthesis of photoelectrocatalyst (PEC) CdS-GO/rGO,[154-156]. CdS nanoparticles have been reported to be conveniently synthesized by precipitation method from aqueous solution at room temperature[157]. Alternatively precursors of Cd and S are mixed with GO/rGO and subjected to high temperature hydrothermally. Other investigations have reported use of different solvents, such as oleylamine [158], dimethyl sulfoxide (DMSO) [159], and 3- mercaptopropionic acid [160], besides capping agents to produce CdS nanoparticles. A common method of electrode fabrication consists of synthesis of rGO and CdS separately. Subsequently, these are mixed and put on a conducting support. The drawback of this method is that an intimate contact leading to chemical interaction of respective compounds may not be established. On the other hand, electrode can be fabricated with CdS and GO with in situ electrochemical reduction of GO[161]. The process is relatively simple, fast and affordable and likely to form intimate contact between and rGO.

Additionally, material loading, electronic mobility and electrode stability are highly substrate (support) dependent. In this regard, Indium tin oxide (ITO), fluorinated tin

oxide (FTO), glassy carbon, and Toray carbon paper (TCP) have been widely used as substrates[162].

Herein, in our work we have prepared CdS by precipitation method from aqueous solution, which was mixed with GO and made into electrode and GO was electrochemically reduced in situ. This electrode demonstrated superior PEC activity. In the current investigation CdS-rGO electrodes were prepared using TCP as substrate due to its low resistivity and ease to cut into desired dimensions.

I.3.2 Experimental

I.3.2.1 Preparation of Electrode

(a) Graphene Oxide (GO)

The modified Hummers method [163] was employed to prepare graphene oxide (GO). In brief, 2 g of graphite flakes were added to 46 mL of 98% H_2SO_4 with a constant stirring keeping temperature always below 283 K. Subsequently, 8 g of potassium permanganate powder was added to the reaction mixture and the stirring was continued for further 2h. The reaction mixture was then allowed to equilibrate to the room temperature with continuous stirring. Thereafter, the mixture was kept inside a water bath for 1h at 308 K and 100 mL of distilled water was added to the mixture. 20 mL of 30% H_2O_2 was also added to this reaction mixture to dissolve residual permanganate. Finally, coloured suspension was filtered and washed with 1 M HCl and subsequently with distilled water for three times. The residue was dried in oven at 333 K for 3 days and used as and when required.

(b) Catalyst 1

It was bare CdS prepared by precipitation method. Briefly, 0.003M aqueous solution of cadmium sulfate was prepared and taken in a 1,000 mL beaker and 0.013M aqueous solution of Na₂S was added very slowly through a burette with continuous stirring. The precipitate of CdS was filtered and washed for three times with double distilled water to remove impurities from the mixture. Finally, the precipitate was dried in an oven at 343K for 3h.

Catalyst-2

Graphene-CdS Composites were synthesized in two steps. In the first step, requisite amount of graphene oxide was suspended in double-distilled water and sonicated for 1h. Required amount of CdSO₄ was added to the suspension and dissolved. The amount was calculated so that the weight of GO was 10%. In the next step, Na₂S solution was added slowly to the suspension to precipitate CdS. Finally, the solid mass, which was a composite of CdS and GO, was washed by double distilled water for three times and dried in oven at 343K for 3h.

Catalyst -3

Graphene-CdS Composites were synthesized in three steps. In the first step, requisite amount of graphene oxide was suspended in 40 mL double-distilled water and sonicated for 1h. Required amount of CdSO₄ was added to the suspension and dissolved. Subsequently, thiourea was added slowly to the suspension. The obtained solution was placed in Teflon lined autoclave for 24 hat 493K to precipitate GO-CdS. Finally, the catalyst was washed with double distilled water for three times and dried in oven at 343K for 3h. It was anticipated that the hydrothermal process would resulted into reduction of GO to rGO. The composition of the catalyst was same as catalyst -2.

I.3.2.2 Photoelectrode Fabrication:

Electrodes were fabricated on 0.5×0.5 cm TCP paper. In a typical fabrication, 50.0 μL of nafion solution was mixed with 1.0 mL of N, N –dimethylformamide (DMF). To the above solution, 2.0 mg of catalyst was subsequently added and the mixture was sonicated for 30 min to obtain homogeneous suspension. 20.0 μL of this mixture was drop casted on the TCP paper. During the fabrication the catalyst loading was kept at 0.15 mg/cm^2 . For an ohmic contact, prior to electrode fabrication a copper wire was pasted by silver glue on the back portion of the TCP. Epoxy resin was coated on the back surface and also on all the edges of the electrode. It ensured that electrochemical reactions took place only from the surface containing catalyst. The table below summarizes the catalysts and electrodes prepared and studied in the present work.

Table I.3.1 Summary of catalyst and electrode

Catalysts/Electrodes	Remarks
Cat-1	Unsupported CdS
Cat-2	GO supported on CdS by precipitation method
Cat-3	GO supported on CdS by hydrothermal method
E ₁	Electrode prepared from Cat-1
E ₂	Electrode prepared from Cat-2
E ₃	Electrode prepared from Cat-3

I.3.3 Activity of Photoelectrodes

Study of the photoelectrocatalytic activity to dissociate water for hydrogen production was carried out in methyl methacrylate photoelectrochemical cell (900 mL) of rectangular base ($12.5 \text{ cm} \times 10 \text{ cm}$) and height 5 cm. A quartz window (dia 2.5 cm) was provided on one wall of the cell at 5 cm above of the bottom which allowed light

to fall on the electrode. Measurements were performed using a potentiostat (μ Autolab Type III) with three electrode systems. The prepared photoelectrodes served as working electrodes, whereas, Pt and Ag/AgCl electrodes were used as the counter and reference electrode respectively. Inverted burettes filled with water were placed over the working and the counter electrodes to collect evolved gases. The line diagram of the experimental set up is shown in the Fig 3.1 and 3.2. An equal volume mixture of freshly prepared 0.35M Na_2SO_3 and 0.25M Na_2S solution in double distilled water was used as the electrolyte (pH $\sim$ 10.5). Prior to each experimental run, the electrolyte solution was purged with nitrogen gas for 30 min to remove dissolved gases from the solution. A 10W white LED lamp was used as a light source to simulate solar radiation. Performance of photoelectrodes was evaluated using linear sweep voltammetry. The sweep scan rate of 5mV/S was used for all the samples and 40 scans were recorded for each run. Evolved gases on cathode and anode were analyzed by gas chromatograph (5Å carbo sieve S II column) equipped with thermal conductivity detector and compared with standard oxygen and hydrogen.

I.3.4 Characterization Techniques

Structural and morphology of the catalysts and electrodes are essential to understand the properties and also how these properties affect the activity of materials toward water splitting. Therefore following photoelectrocatalysts and electrodes were characterized using the following techniques:

I.3.4.1 Fourier transforms infrared spectroscopy (FTIR)

Nicolet 5700 (Thermo Electron) FTIR spectrophotometer was used to record FTIR spectra in mid IR range ($4000\text{--}400\text{ cm}^{-1}$). FTIR spectra in transmittance mode were recorded at room temperature at resolution of 8 cm^{-1} . KBr was used as a reference

material. Samples were prepared by thoroughly mixing with the help of pastel and mortar, About 1 mg of the catalyst powder with 100 mg of KBr powder and were taken

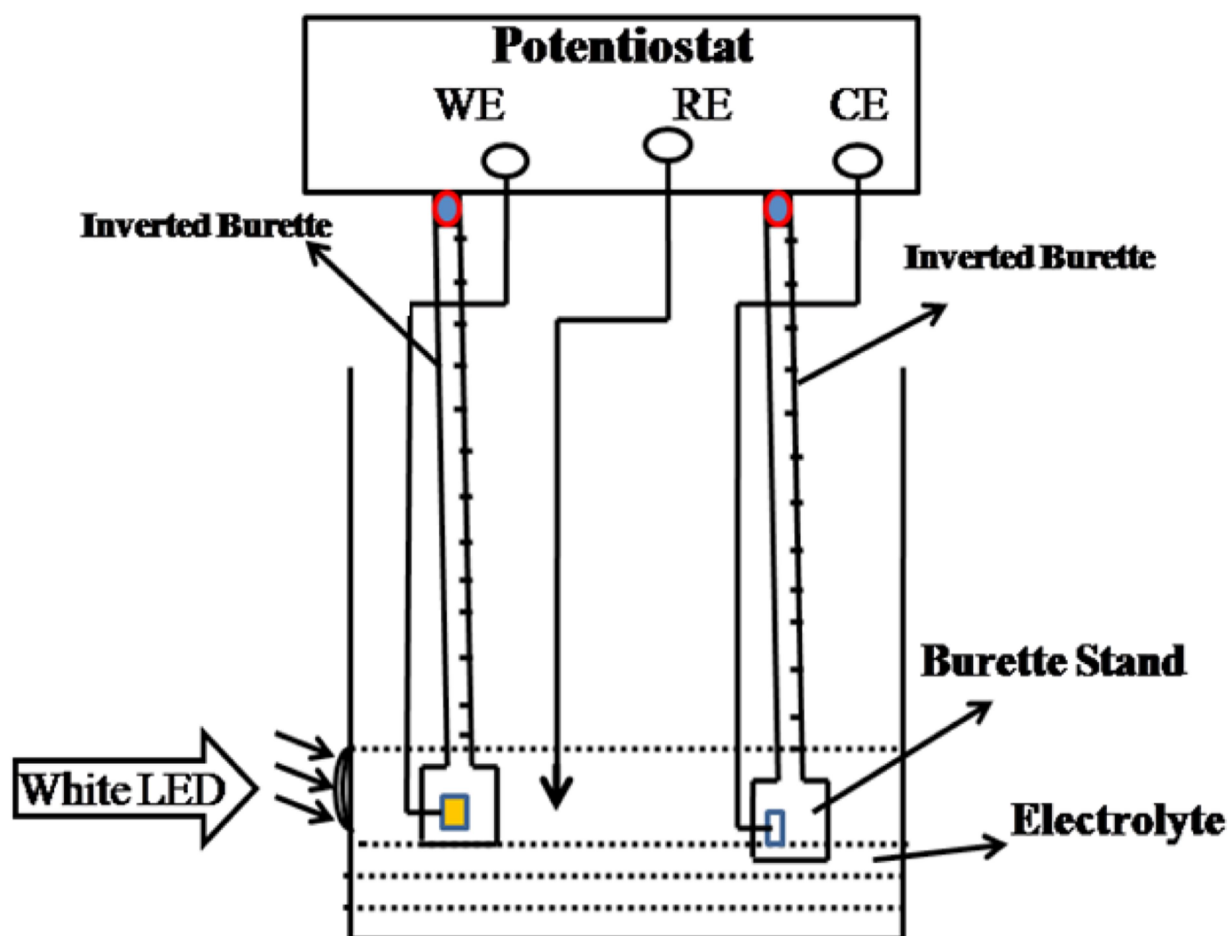


Figure 3.1: Line diagram for experimental set-up

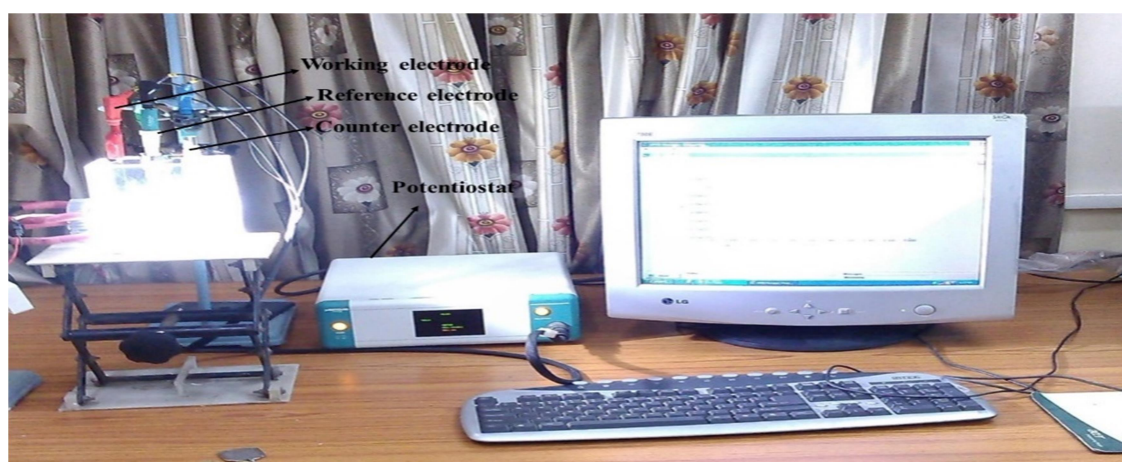


Fig 3.2 Experimental set up in operational mode

and finally made into pellet. Spectra were obtained for wave numbers in the wave number range between 400 and 3000 cm^{-1} .

I.3.4.2 X – Ray diffraction (XRD)

X-ray diffraction is used to study the structural information of materials. In this techniques the incident X-rays interact with the specimen and diffracts. Finally diffracted pattern are collected by occurrence of constructive interference according to Bragg's Law:

$$n\lambda = 2d_{hkl}\sin\theta \quad (3.1)$$

Where, n is order of reflection (any integer), value is taken 1,

λ = wavelength of the incident X- Ray

d_{hkl} = the interplanar species and

θ = is the angle where the constructive interference is maximum

Crystalline lattice sizes (D) was calculated from the Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (3.2)$$

Where, K = Scherrer Constant

β = Full width at half of the maximum (FWHM) of a reflection peak after subtracting contribution due to the instrumental broadening

Scherrer constant (K) in the formula accounts for the shape of the particle and is generally taken to have the value 0.9.

In the present study, X- ray diffraction pattern of the prepared catalysts were obtained from a Rigaku Ultima IV diffraction using Cu – $K\alpha$ irradiation. The calculated d – values were matched with standard data for identification of different phases present in various catalyst. The mean crystallite sizes of chalcogenides (CdS and MoS_2) present in catalysts were calculated by measuring the line broadening and using the Scherrer formula written below (eq 3.3).

In fact, there are three sources from which peak broadening arise:

- (a) Instrumental contributions,
- (b) Sample contributions and
- (c) Strain in the sample

Since catalysts are sulphides, which cannot bear strain, the broadening due to strain has been neglected in the present study.

The instrumental contribution needs to be subtracted from β_{total} by following equation 3.3 to get actual broadening due to sample.

$$\beta_{\text{total}}^2 = \beta_{\text{instrument}}^2 + \beta_{\text{sample}}^2 \quad (3.3)$$

The instrumental broadening is obtained from the diffraction pattern of a “standard sample” which consists of large crystallites. In our sample standard sample was ‘Si’ and the value of broadening due to instrument was 0.079.

I.3.4.3 Diffuse reflectance spectroscopy

It is an effective spectroscopic tool to estimate the band gap of semiconductor photocatalyst and the light absorption characteristics of catalysts. When the powdered sample is radiated with light, a portion of radiation is reflected at a powder surface and the remaining are either absorbed or transmitted by the powder with an integrating sphere attached to the uv- vis spectro photometer (Diffuse Reflectance spectroscopy) it is possible to again direct the reflected light to fall on the sample are obtained.

In present study, diffuse reflectance spectroscopy of catalysts was carried out on UV-vis spectrophotometer (Varian 100Bio) with a total reflection attachment. BaSO₄ was used as a reflectance standard. Absorbance data can be used for the Tauc plot using the Kubelka-Munk transformation [144,145], given by:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (3.4)$$

Where, h is the Planck constant, ν is the frequency of the light source, α is absorption coefficient, A is a proportional constant, E_g is the band gap, and n signifies the nature of the electron transition. For direct transition (in case of CdS) value of n is $1/2$, i.e. denoting an allowed direct transition [146].

According to Eqn. 3.4, once $(\alpha h\nu)^2$ is plotted against $h\nu$. The resulting graph yields a straight line that can be extrapolated to the x -axis to estimate the band gap of the material.

I.3.4.4 Photoluminescence spectroscopy (PL)

Photoluminescence (PL) spectroscopy is a non-destructive technique. In this technique, first photo excitation process is executed by absorption of the light by a sample. An electron moves to excited state due to photo-excitation which subsequently comes back to its equilibrium state. During the photo excitation, an electron may jump from the valence band and move to conduction band and subsequently come back to valence band which is called recombination. During this process, excess energy is released through emission of light. This excess energy is equal to the energy difference between the equilibrium and excited states. This emitted light is detected by photon detector through a spectrometer to give PL spectra. Thus the emission spectra corresponding to band-gap excitation may yield valuable information about recombination behaviour of photocatalysts. Recombination behaviour of catalysts was studied to establish its relation with photocatalytic activity and microstructure. In the present study, PL spectra were obtained using Fluorescence Spectrophotometer (Varian, Cary eclipse). Powder samples were placed in a sample holder. Excitation wavelength was 200 nm. Emission wavelengths were recorded from 400 to 600 nm.

I.3.4.5 Transmission electron microscope (TEM) and selected area electron diffraction (SAED)

Transmission electron microscopy was used to image and analyze the microstructure of the photocatalytic materials. Measurements were performed in a TecnaiG2 20 make TEM at 200 kV accelerating voltage. Powder samples were homogeneously dispersed in pure ethanol by means of an ultrasonic bath and then deposited on a copper grid and the solvent was allowed to evaporate under vacuum before analysis.

Selected area electron diffraction (SAED) uses diffracted electrons to elucidate crystallographic information from selected regions of the sample. This attachment was employed with TEM. The diffraction pattern was recorded from thin sample as TEM from an aperture. The spacings and orientation of the diffraction spots can be interpreted in terms of planar spacings similar to the XRD.

I.3.4.6 X-ray photoelectron spectroscopy (XPS)

XPS is a technique to analyse surface chemical property of surface of any material. XPS spectra can be obtained by irradiating a sample with X-rays beam while simultaneously measuring the kinetic energy and number of electrons that escape from sample being analyzed. Ultra-high vacuum (UHV) condition is required during analysis.

Soft X-rays (i.e. $MgK\alpha$) are used as a source. Photons are absorbed by specimen and then electrons are ejected via the photoelectric effect. The energy of the ejected electrons can be written as:

$$E_{KE} = h\nu - E_{BE} \quad (3.5)$$

Where, E_{KE} is the energy of the ejected electron,

$h\nu$ is the energy of the incident photon, and

E_{BE} is the energy of the involved bound electron state.

Binding energy is specified for individual elements. Therefore, identification of particular element will be possible by measuring the photoelectron energy. It should be

noted that for multi-component samples the intensities of the peaks are proportional to the concentration of the element within the sampled region.

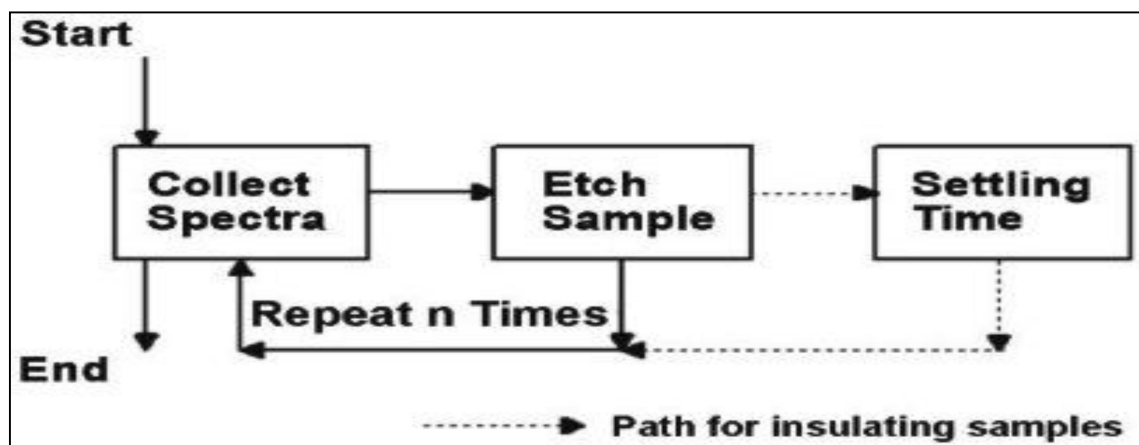


Fig 3.3: Summary of the experimental procedure for producing XPS depth profiles

XPS is a surface sensitive technique. Depth profile of a sample gives very useful information about the sample. In case of composite and co-catalyst doping, this technique is used to study the depth of surface interaction between support catalyst and doped catalyst. This depth profile of the sample can be obtained by combining a sequence of ion gun etch cycles enclosed with XPS measurements from the current surface [Fig. 3.3]. An ion gun is used to etch the material for a period of time and then XPS spectra are acquired.

In the present study, XPS studies were carried out on AMICUS, Kratos Analytical using monochromated $\text{MgK}\alpha$ (1253.6 eV) as X-ray source. A vacuum of 2×10^{-6} kPa was maintained in the analyzer chamber. For depth profiling, etching of surface was carried out by bombarding argon ions on the surface for requisite period of time. Argon gas was used with an accelerating voltage of 20 kV. The resultant beam current was 12mA. In ideal case (standard specimen), the surface of composites can be etched at about 7Å per minute under these conditions. A value of 284.6 eV for the carbon C 1s peak was used as calibration for all measurements. Raw peaks were deconvoluted accurately using XPS peaks 4.1 software.

I.3.4.7 Electrochemical Impedance Spectroscopy (EIS)

Electrical properties of material as well their interface with surface modified electrode can be evaluated by this technique.

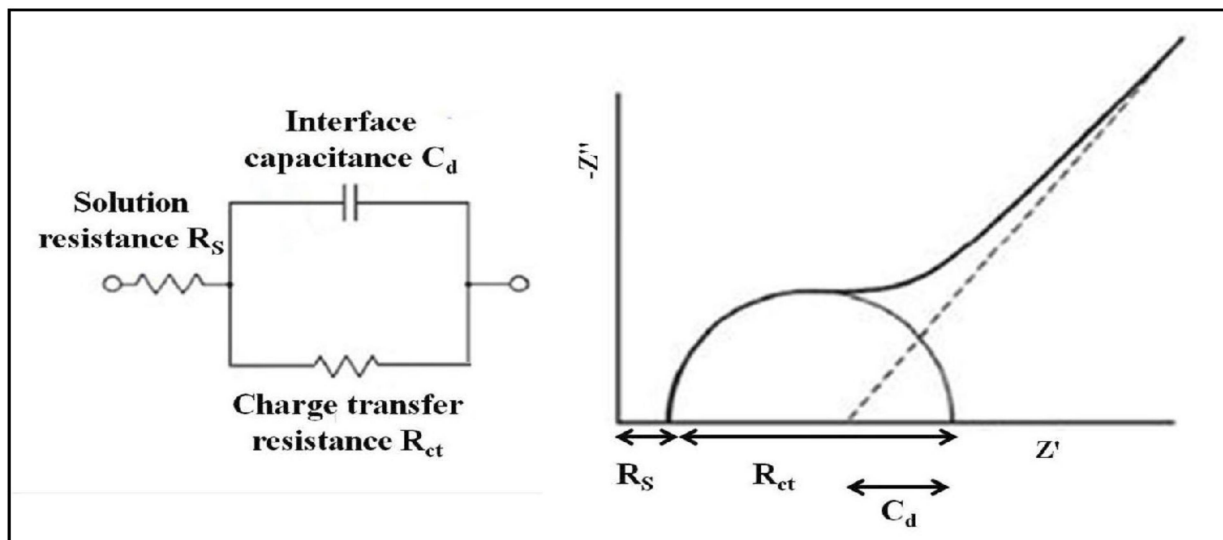


Fig 3.4 Basic component of Nyquist plot of electrochemical impedance spectroscopy [147]

The response of electrochemical system is very nonlinear. The resistance of the system is usually displayed in Nyquist plot (Fig 3.4), with the reactance inverted (since such systems are inherently capacitive). Where, Impedance (Z) is a determination of the circuit characteristics to impede the flow of electron when exposed to a periodic electrical perturbation. R_s is resistance due to solution/electrolyte. R_{ct} is the resistance associated with an electrode reaction i.e. related to generation of electron and transfer to bulk. C_d is the capacitance, created due to bulk and interface.

Impedance spectroscopy was done using an Autolab (PGSTAT 204) electrochemical work station with impedance analyzer in a two-electrode configuration. For the electrode fabrication, Toray Carbon Paper (TGP-H-60, Alfa Aesar, USA) having 0.25 cm² cross-sectional area was used. Slurry was prepared by dispersing the required quantity of photocatalyst powder in Nafion© solution with a few drops of DMF

followed by sonication in ultrasonic water bath for 1 h for better dispersion. The slurry was drop cast on the carbon paper. It was then dried in air for 6 h. Before the impedance scanning experiments, the remaining surface was polished to minimize ohmic effect.

The electrolyte was a solution of sulphite and sulphide ions which was used for photoelectrochemical activity measurement.

I.3.4.8 Mott – Schottky plot

The Mott-Schottky technique is a powerful tool for the study of electrode surfaces. Mott-Schottky plots are most often used for electrochemistry on semiconductor electrodes. They can also be used to establish type of semiconductivity of material and measure flat band potential and charge carrier density by following equation [148]

$$\frac{1}{C^2} = \frac{2}{\epsilon_0 \epsilon_r e N_A A^2} (V - V_{fb} - KT/q) \quad (3.6)$$

Where, C is the capacitance of space charge region, e is the electronic charge ($1.603 \times 10^{-19} \text{C}$), ϵ is the dielectric constant of semiconductor, ϵ_0 is the permittivity of the vacuum ($8.854 \times 10^{-12} \text{Fm}^{-1}$), N is the charge carrier density, A is the area of electrode ($25 \times 10^{-6} \text{m}^2$), V is the applied potential, V_{fb} (V) is the flat band potential which can be obtained from the Mott-Schottky plot by measuring the intercept of straight line on x-axis, K is the Boltzmann's constant ($1.38 \times 10^{-23} \text{J/K}$), T is the absolute temperature and KT/e is negligible at room temperature and 1 atmosphere pressure. Nature of the slope of the linear portion of the curve predicts the type of semiconductivity.

In the present work, Mott –Schottky analyses were performed at 1kHz with a scan rate 5mV/s under dark condition.

A summary of characterization techniques used in the present study are listed below in table I.3.2

Table I.3.2 Characterization techniques used in present study

Sr.No.	Characterization techniques	Characterization studied
1	Fourier transform infrared spectroscopy (FTIR)	Functional Group analysis
2	X- Ray diffraction (XRD)	Crystal structure – phase identification and crystallite size
3	Diffuse reflectance spectroscopy (DRS)	Visible light absorption and band gap estimation
4	Photoluminescence spectroscopy (PL)	Charge recombination and band gap estimation
5	High resolution scanning electron microscopy (HRSEM)	Morphology and particle size
6	Transmission Electron Microscopy (TEM)	Morphology, particle size and crystal structure – phase identification (from SAED)
7	X- ray photoelectron spectroscopy (XPS)	Oxidation state and surface analysis
8	Electrochemical Impedance spectroscopy (EIS)	Charge transfer mechanism
9	Mott- Schottky plot	Conductivity, valance band potential and carrier density

I.3.5 Results and discussion

I.3.5.1 Photo-electrochemical activity

At the beginning of each experiment, GO in the photo electrode was reduced electrochemically (in absence of light). Ambrosi et al[164] have reported the electrochemical reduction method of GO to rGO. Application of negative potential can eliminate most of the reducible oxygen functionalities. A cyclic voltammetry was carried out and a reduction peak at -1.2 V (SHE) was observed which was taken as reductive peak of GO to rGO. Electrodes were kept at -1.4 V for sufficient long time till the current density become negligible. Subsequent to the reduction of GO to rGO linear step voltammetry was carried out for the potential range of -0.6 to 0.6 V with

respect to SHE. The results are shown in Fig I.3.1. Experiments were carried out in dark as well as in the light. Blank experiments with electrode not containing any photo catalyst (Electrode E) were also carried out. It is seen from the figure that the dark currents (in absence of light) were negligible for all electrodes in the complete range of voltage. However, when diffuse light of LED was applied on the photo electrodes, currents were observed with negative biasing whereas negligible effect of light was observed in positive biasing. No current was observed when the same experiment was carried out with electrode where no catalyst was deposited (Electrode E). It confirms the current was due to photoelectrochemical activity. It is further noticed that photocurrent density of 296.7, 230.24, and 17.9 mA cm⁻² mg⁻¹ of CdS was obtained for E₂, E₃ and E₁ respectively at -0.6 V(w.r.t SHE). The low activity of E₁ may be understood as it was bare CdS; therefore, the charge recombination rate might be high. On the other hand E₂ and E₃ both were CdS supported on rGO of same composition, but E₂ have a better activity compare to E₃. It should be pointed out that E₂ contained rGO prepared by in situ reduction of GO electrochemical. It is also seen that photo currents are produced with negative biasing. It hints of p-type semi conductivity of the photo electrodes meaning there by that electrodes were photo cathode with positive holes (h⁺) as majority charge carriers. Further, using electrode E₂, and voltage at -1.0 V, and the run was continued for 3h and gases at the two electrodes were measured. Volume of gas evolved at the photocathode was 4.3 mL and its analysis by gas chromatography confirmed that it was pure hydrogen, whereas, only 0.3 mL of gas was produced at the counter electrode. The gas was analyzed to be oxygen; however its production was significantly less than stoichiometry. The decreased oxygen output at anode is expected due to completing reaction of oxidation of S²⁻ and SO₃²⁻ at anode. The reactions involved in

the complete process are written below. Mechanism of reaction is also discuss in section 2.1.3.

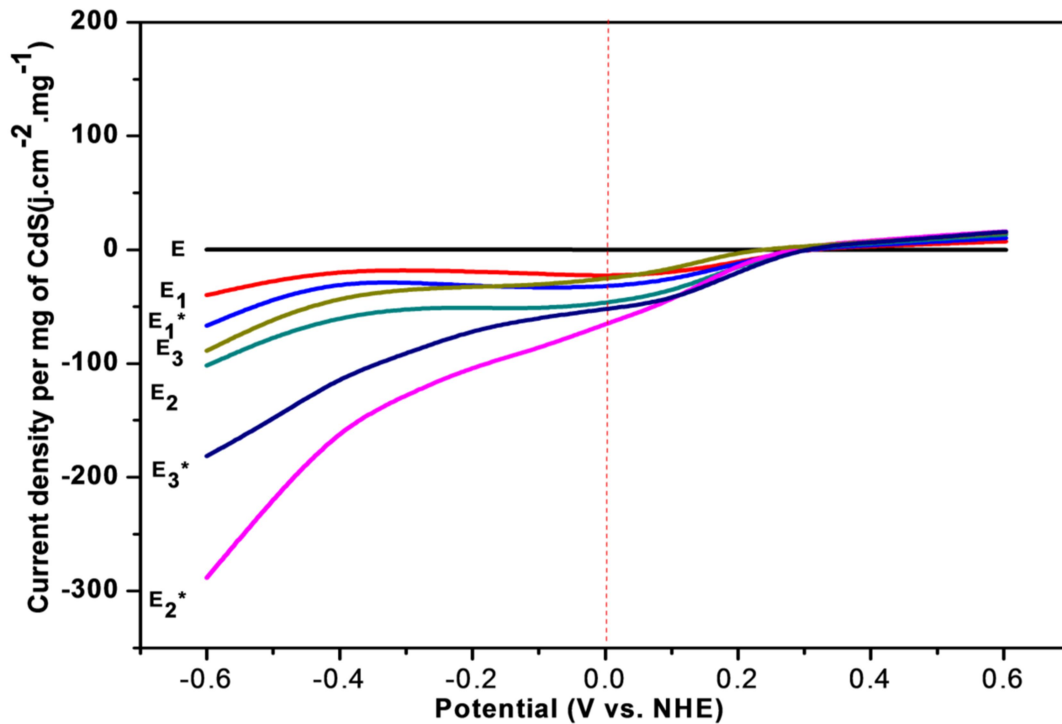
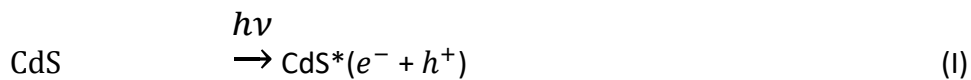


Fig I.3.1.LSV test of various catalysts in S^{2-} and $S_2O_3^{2-}$ electrolyte: E_x & E_x^* are without light and with light

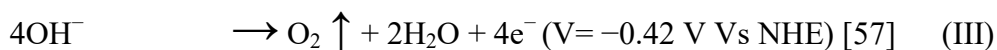
Light activation of the working electrode by light:



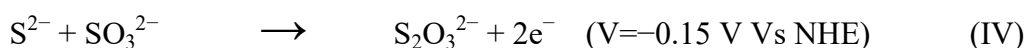
Reaction at photocathode



Reaction at anode



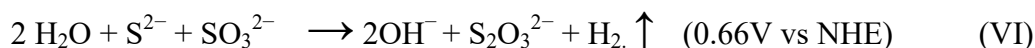
Reaction at anode in the presence of sacrificial agent (Sulfide and sulfite) ions



Electron- hole recombination:



In comparison to reaction ‘III’ the reaction IV is more favoured, therefore, the overall reaction is:



Schematic diagrams of the process occurring at electrodes are shown in Fig 3.

I.3.6 Characterization studies

I.3.6.1 FTIR studies

Functional groups and bonds formed during catalyst synthesis were investigated using infra red spectroscopy. FTIR was carried out for catalysts (Fig I.3.2) and also for electrodes E₂ and E₃(Fig 1.3.3). Analyses of these electrodes were carried out after electrochemical reduction of GO to rGO as discussed earlier. For comparison FTIR spectra of CdS and GO are also shown in Fig I.3.2. In all samples of catalyst and electrodes the characteristics peak of Cd-S stretching vibration in the range of 600-640 cm⁻¹ is observed[165, 166]. No additional peak in this region is observed in catalyst-3 which was prepared by hydrothermal reaction. However, a peak at 702 cm⁻¹ is seen in catalyst -2 which was prepared by precipitation method. We assign this peak also to the stretching vibration of Cd-S which is red shifted in comparison to the peak observed for pure CdS. Coupling of vibration is a common phenomena which causes shift in peak positions. We attribute the shift to the coupling of Cd-S and C-S vibration. Such a coupling indicates interaction between CdS and rGO. The same has been reported in the literature [151, 167]. Similarly, when electrodes prepared using cat-2 was reduced in situ, additional peaks appeared at ~540, 810, and 980 cm⁻¹. These peaks are attributed to C-S, C=S, stretching. Literature suggests C-S or C=S stretching vibration in these ranges [180]. However, these ranges are quite wide therefore, it is difficult to unequivocally assign above observed peaks to C-S or C=S stretching. However it is likely that in situ reduction, GO to rGO has resulted in an interaction between CdS and

rGO through C-S or C=S bonds. Such peaks are prominent in the electrode E₂ in comparison to electrode E₃. It is important to mention that cat-3 was subjected to a hydrothermal treatment prior to formation of electrode and subsequent electrochemical reduction. The hydrothermal treatment must have resulted in reduction of GO to rGO, therefore, effect of electrochemical reduction was less in electrode E₃ (prepared by cat-3). This observation clearly show that the electrochemical reduction of GO to rGO has resulted into a greater interaction between rGO and CdS.

I.3.6.2 X-Ray Diffraction (XRD) studies

Crystallinity and phases of the prepared catalysts were identified using X-Ray Diffraction (XRD) pattern. Results are shown in Fig I.3.4. The observed and standard values of d(inter planner spacings) and corresponding planes (hkl) are given in Table-I.3.3. The broad peaks of CdS indicate its very small crystallizes size in cat-1 and 2. It is also observed that there is no characteristic peak ($d = 2.91\text{\AA}$) of cubic phase in these catalysts.

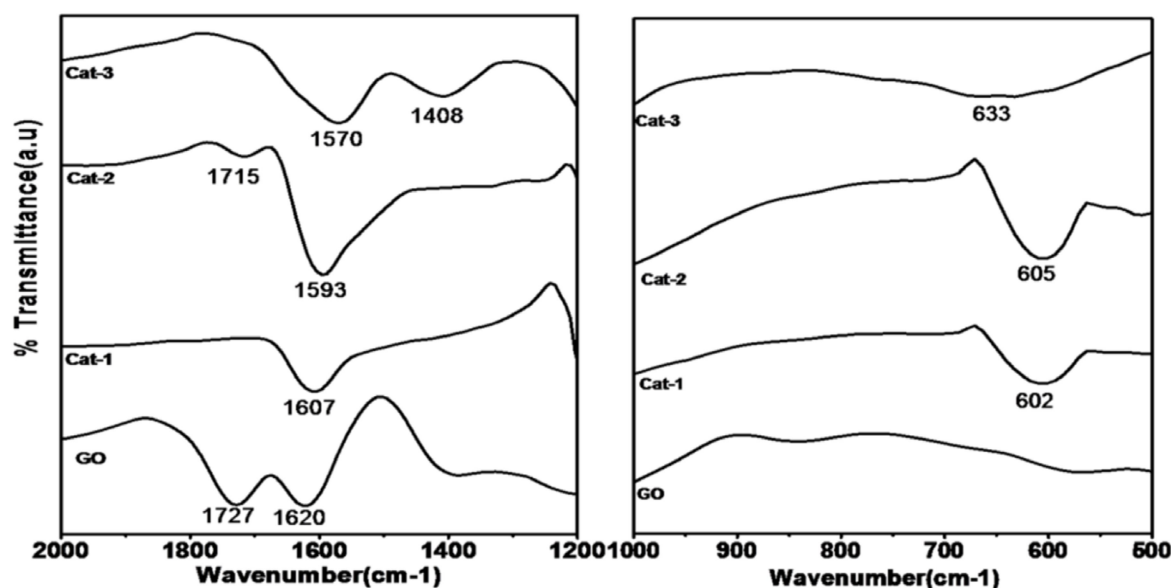


Fig I.3.2: FTIR spectra of catalyst

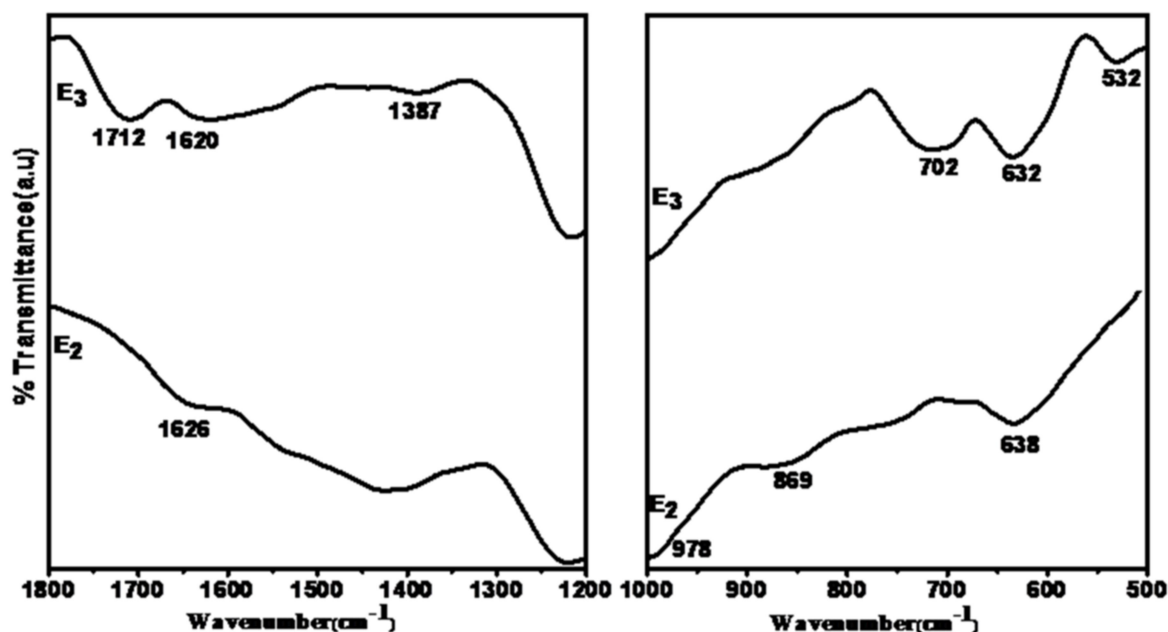


Fig I.3.3 FTIR spectra of electrode prepared by catalyst powder.

Peaks appeared at $2\theta = 26.33$, 43.59 and 51.92° corresponding to (002), (110) and (112) planes of the hexagonal phase of CdS [129, 168]. In contrast, peaks are seen to be very sharp indicating highly crystalline CdS in cat-3. Peaks mostly correspond to the hexagonal phase of CdS but the characteristic peak of the cubic phase ($d = 2.91 \text{ \AA}$) is also observed. It has been reported in the literature that the decrease in the ionization of Cd and/or S ions favours formation of cubic structure [169]. The Literature also reports formation of cubic CdS from the aqueous solution which contained NH_4^+ ions. In the present study, the source of sulphur for synthesis of cat-3 was thiourea, which converts to ammonium thiocyanate above 403 K [170]. Therefore, in cat-3, CdS was formed from the aqueous solution which contained NH_4^+ ions. The presence of NH_4^+ ions had decreased the ionization of Cd ions and therefore cubic form of CdS is formed. However, peak of GO/rGO is not seen in cat-2 and 3 due low concentrations and more scan rate (Fig I.3.4 inset). It is might be possible that rGO peak superimpose with CdS peak in cat-3. Unit cell parameters 'a' and 'c' of the hexagonal phase CdS for all catalysts were calculated, and are presented in Table I.3.4. The standard are found to be

$a=4.14\text{\AA}$ and $c=6.715\text{\AA}$. Variations in the values of ‘a’ and ‘c’ from the standards have been observed in catalyst-1 and catalyst-2. However, since the peaks are broad and therefore peak positions might not be accurately determined, therefore, we consider these variations insignificant. Line broadening data were corrected for instrumental broadening and crystallite sizes of CdS in catalysts were calculated by the Scherrer equation. Sizes were estimated to be 5, 5 and 22 nm respectively. It should be mentioned that cat- 1 and 2 have crystallite of similar sizes.

Table- I.3.3.: XRD Results catalysts for CdS

Standard Values of d and miller indices				Experimental Values of d		
Hexagonal		Cubic		Catalyst-1	Catalyst-2	Catalyst-3
Miller Indices hkl	Hexagonal phase d($\text{\AA}$)	Miller Indices hkl	Cubic phase d($\text{\AA}$)	d($\text{\AA}$)	d($\text{\AA}$)	d($\text{\AA}$)
100	3.58	-	-	-	-	3.49
002	3.36	111	3.36	3.31	3.32	3.32
101	3.16	-	-	-	-	3.13
102	2.45	200	2.91	-	-	2.88
110	2.06	220	2.06	2.06	2.05	2.048
112	1.76	311	1.75	1.75	1.75	1.75
004	1.67	-	-	-	-	1.67
202	1.58	222	1.68	-	-	-
203	1.39	331	1.33	-	-	1.33

Table- I.3.4: c/a ratios and crystallize size of CdS in different catalyst.

S.No	Catalyst	c (Å)	a (Å)	c/a	crystallize Size (nm)
1	Cat-1	6.62	4.14	1.60	5
2	Cat-2	6.64	4.11	1.62	5
3	Cat-3	6.64	4.11	1.61	22
4	Standard	6.715	4.14	1.62	--

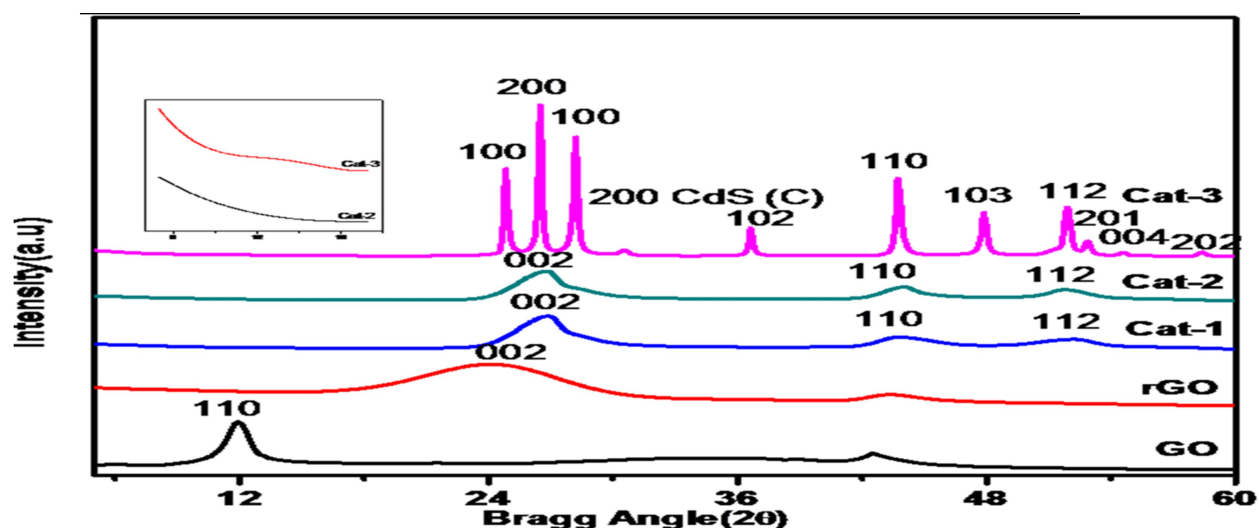


Fig I.3.4: XRD patterns of catalysts CdS, (c): Cubic phase of CdS

In contrast cat -3 has a much bigger crystalline size of CdS. Electrodes prepared from cat-2 and 3 exhibited superior activities as compared to electrode prepared using cat-1. It should be mentioned that catalyst-1 was bare CdS whereas catalyst-2 and 3 were CdS supported on rGO prepared by different techniques. It clearly shows the effect of rGO in the catalysts.

I.3.6.3 Diffuse Reflectance Spectroscopy

Optical absorption studies using diffused reflectance spectroscopy (DRS) were carried out for all catalysts and are presented in Fig.I.3.5. Steep changes in the absorbance are seen at ~ 625 , ~ 560 and ~ 580 nm for cat-1, 2 and 3 respectively, which gradually flat out below 500 nm. The steep changes in the absorbance curves clearly indicate band gap excitation. Further, in cases of rGO supported catalysts, enhanced and rather continuous absorption in visible light spectrum is evident. This effect is more pronounced in catalyst-2. Akbarzadeh et al [171] ascribed the enhanced visible light response due to increment of surface electronic charge on CdS due to presence of GO/rGO. The direct band gap for catalysts were obtained by plotting value of $(\alpha h\nu)^2$ vs $h\nu$ (Fig I.3.5) and the intercept of the straight line on x-axis was taken as band gap (Table I.3.5). It is observed that GO incorporation has resulted into widening of the band gap of CdS as compared to bare CdS (cat-1). Similar increase in the band gap has been reported by earlier workers[167] due to quantum confinement of CdS nano particle. Blue shifting in absorbance of CdS supported on GO was happen when π to π^* transition occurred in C=C bond of GO. This increase in band gap is also ascribed to interfacial interaction between CdS and GO/rGO[172]. Thus, the results of DRS confirm that interfacial interaction between CdS and GO/rGO was present in cat-2 and 3 and more so in cat-2.

Table I.3.5: Band Gap of various catalysts

Catalyst	Band gap (eV)
Cat-1	2.06
Cat-2	2.24
Cat-3	2.13

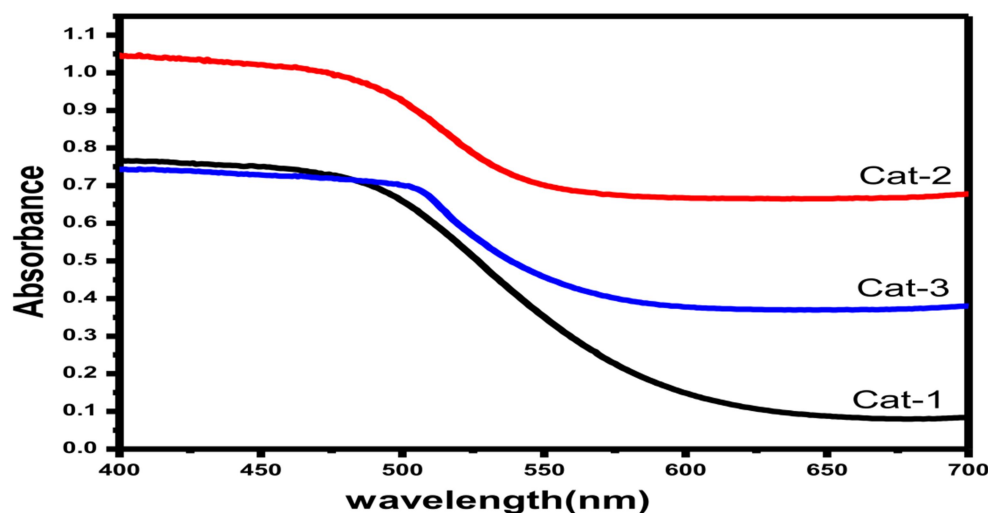


Fig I.3.5 DRS results of catalysts

I.3.6.4 X-Ray Photoelectron Spectroscopy (XPS) studies

The X-ray photoelectron spectroscopy (XPS) studies were conducted to ascertain the oxidation states of the chemical species present on the surface of the samples and their interaction. Catalysts as well as electrodes after insitu reduction were analyzed. Peaks were deconvoluted using Lorentzian- Gaussian method [173]. Results are shown in Fig I.3.6-I.3.8 and corresponding peak positions are given in Table I.3.6. It is observed from the spectra of catalysts that for Cd 3d orbital peaks are centered at 412.1 and 405.2 eV and are very close to reported values of Cd^{2+} 3d at 412.2 and 405.2 eV for 3d_{3/2} and 3d_{5/2} respectively[174, 175]. This indicates +2 oxidation states for Cd in the prepared catalyst. Further, it is also observed that in cat-2 and 3, peaks are shifted towards higher binding energies in comparison to unsupported CdS (cat-1). These catalysts were CdS supported on rGO. A Shift to higher binding energies is possible owing to the fact that GO/rGO has many strong electronegative species present on its surface which will necessarily affect the electron density of Cd^{2+} . In other words, a shift in peak position confirms a chemical interaction between CdS and support GO/rGO. The same was

observed by FTIR analysis. Further the shifts were observed to be more in cat-2. The XPS spectra of sulphur are also presented in Fig I.3.7 and peak positions for S-2p are tabulated in Table I.3.6. The doublet observed at 162.1 and 160.0 eV match with the standard value of $S2p_{1/2}$ and $S2p_{3/2}$ of CdS. S_{2p} peaks present in catalysts, follow similar pattern as was observed for Cd^{2+} , the S-2p peaks for cat-2 and cat-3 displayed shifts towards higher binding energies. Similarly, shift in S_{2p} peaks has been attributed to interaction between CdS and GO/rGO leading to redistribution of charge densities on Cd and S ions [176, 177]. As stated earlier, with the presence of highly electronegative groups on the surface of GO/rGO such interaction is possible causing positive shifts of binding energies for both Cd^{2+} and S^{2-} . It is in order to mention that Singh and Sinha [151] have reported shift in peak position of S^{2-} , when rGO was incorporated on with CdS. They have attributed the shift to a chemical interaction between CdS and rGO. In our study it is observed that this phenomenon is prominent in cat-2. Literature reports that an intimate contact between CdS and GO/rGO leading to a chemical interaction at the interface, promotes a better charge separation and improved water splitting activity [193].

Fig I.3.7 and Fig I.3.8 represents the XPS of electrodes E_2 and E_3 after electrochemical reduction. Depth profiling by Argon ion bombardment over the surface for 60s was also carried out for detailed investigation of the interactions of chemical species on the surface of these two electrodes. These results are presented in Fig I.4.7 & I.4.8. Peak values are listed in Table I.3.7. In general it is observed that the peaks corresponding to Cd^{2+} have shifted to higher values. Remarkably, the surface has two distinct doublets of S^{2-} . One of the doublets for both E_2 and E_3 has BE $S2p_{1/2}$ and $S2p_{3/2}$ close to those of cat-2 and cat-3, respectively. However, an additional doublet of $S2p_{1/2}$ and $S2p_{3/2}$ is observed in both the electrodes at higher binding energies. This clearly confirms

strengthening of interaction between CdS and rGO due to electrochemical reduction of GO to rGO. The ratios of $2p_{3/2}$ peaks of the two doublets were calculated and are shown in the table. A higher value of the ratio means a greater fraction of S^{2-} were at higher BE due to chemical interaction as mentioned above. It is seen from the table that this value is 2.71 for electrode E_2 in comparison of 0.32 for electrode E_3 . Fig I.3.7 and I.3.8. also provide XPS after etching for 60s. It is observed that typically all binding energies shift towards lower energy after 60s argon ion bombardment. The ratios of the peaks have also diminished from 2.71 to 0.98 for E_2 . This indicates that interactions between GO and CdS are mostly at the interface and decreases with the depth. It is also conclude that these interactions were more in electrode E_2 . It is order to mention that E_2 was prepared by precipitation technique and GO was reduced insitu during photoelectrochemical process, whereas E_3 was prepared by hydrothermal process and GO was reduced mostly during synthesis of catalyst. It is reported in the literature [195, 196] that BE of 163.8 eV is due to for C-S and C-S-C type species. Accordingly, on the basis of this discussion, the doublet of S^{2-} observed in E_2 and E_3 at higher BE been ascribed to presence of C-S type interaction. It is in order to mention that FTIR studies had also indicated presence C-S bond in these electrode (E_2 and E_3). The literature reports the possibilities of interaction between CdS and rGO through π^* orbital of carbon and n orbital of sulphur of CdS. Peng et al [178] reported the possible interactions between photocatalyst and carbon materials such as $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ between the n orbital of the CdS species and rGO. They had synthesized catalyst by precipitation method. Liu et al. [179] have also reported that the electronic transition of $\pi \rightarrow \pi^*$ of MWCNT and $n \rightarrow \pi^*$ between the n- orbital of the sulphur species of catalyst. We also propose such interactions in electrode E_2 and E_3 . However the extent of this

interaction was more in electrode E₂ where electrochemical reduction of GO to rGO was carried out and this electrode also showed a higher activity.

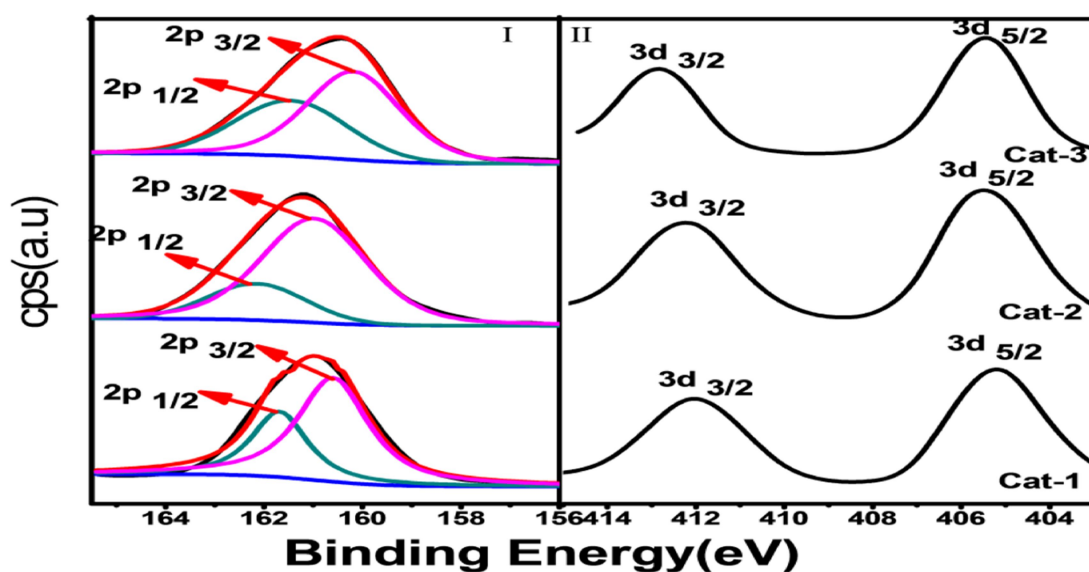


Fig I.3.6: XPS spectra of S-2p (I) and Cd-3d (II) in catalyst powder

I.3.6.5 Electrochemical Impedance spectroscopy (EIS) studies

EIS measurement was carried out to further investigate interactions and charge transfer between CdS and GO.

Table I.3.6: Peak position of Cd-3d and S-2p in catalysts

Catalyst	Peaks positions of catalyst			
	Cd 3d _{3/2} (eV)	Cd 3d _{5/2} (eV)	S2p _{1/2} (eV)	S2p _{3/2} (eV)
Cat-1	412.1	405.2	162.1	161.0
Cat-2	412.3	405.5	162.5	161.5
Cat-3	412.2	405.3	162.3	161.3

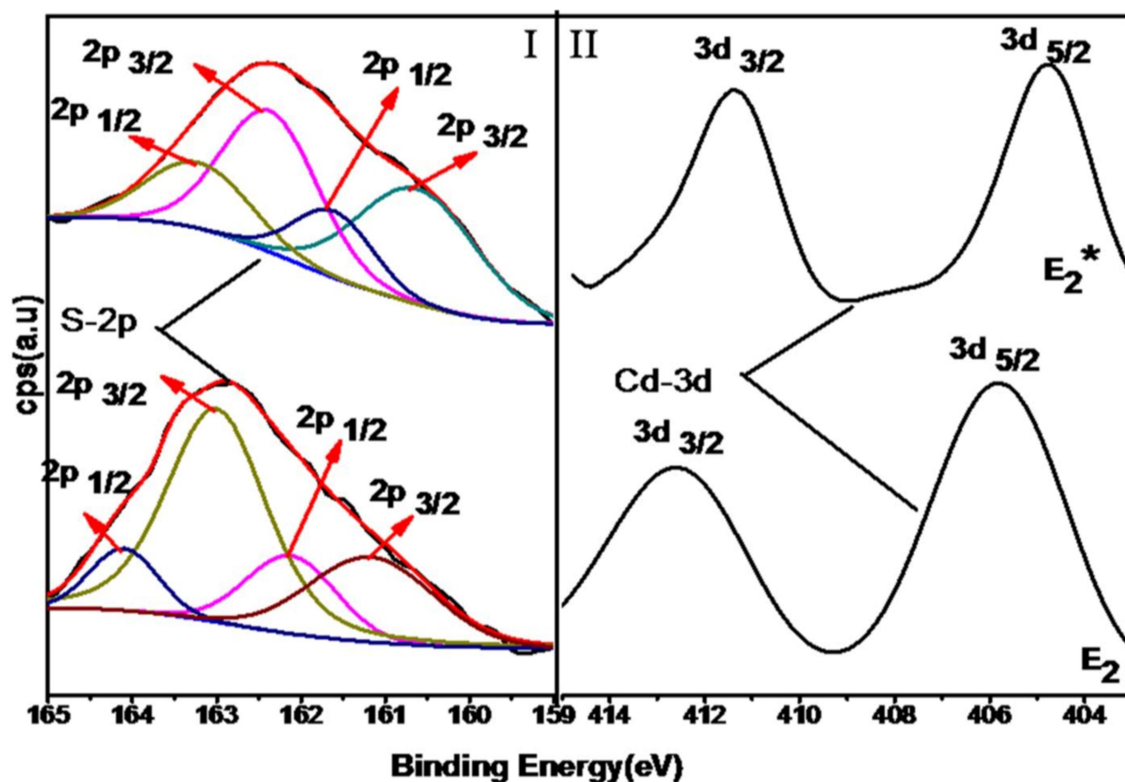


Fig I.3.7: XPS spectra of S-2p (I) and Cd-3d (II) for electrode E₂. (* surface etched for 60s)

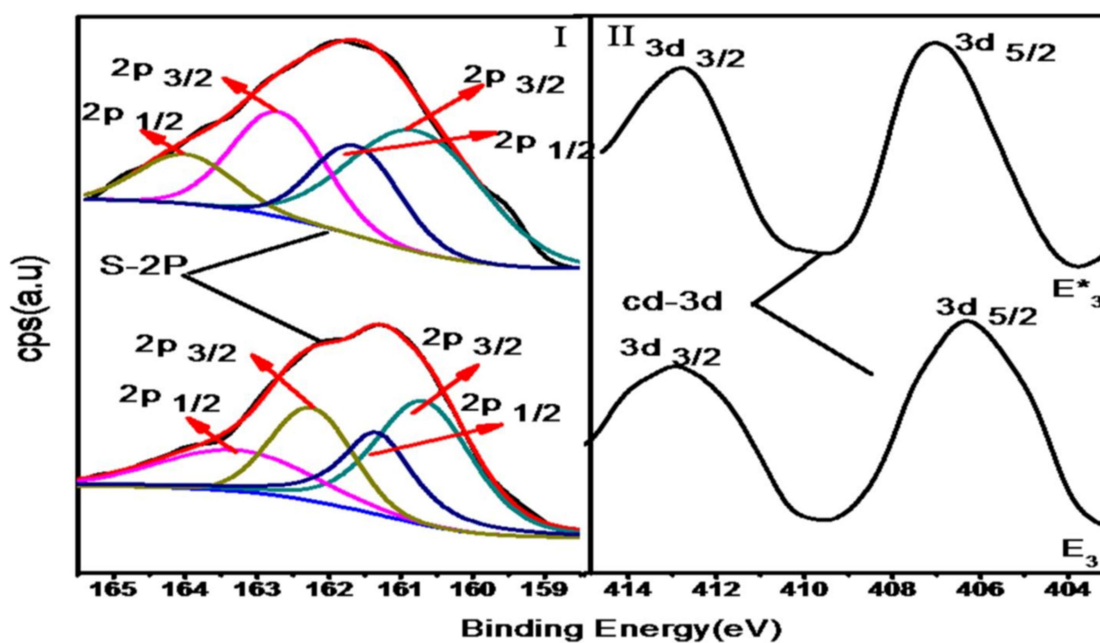


Fig I.3.8: XPS spectra of S-2p (I) and Cd-3d (II) for electrode E₃. (* surface etched for 60s)

Table I.3.7: Peak position of Cd-3d and S-2p in electrode

Electrode	Peak position of Cd ²⁺		Peak position of S ²⁻				Ratio
	3d _{3/2}	3d _{5/2}	Doublet (I)		Doublet (II)		
			2p _{1/2}	2p _{3/2}	2p _{1/2}	2p _{3/2}	$\frac{2p_{3/2}(I)}{2p_{3/2}(II)}$
E ₂	412.9	406.6	164.1	163.1	162.1	161.2	2.71
E ₂ *	412.8	406.3	163.6	162.7	162.0	161.0	0.98
E ₃	412.6	405.9	163.9	162.6	161.8	161.0	0.88
E ₃ *	411.5	404.9	163.5	162.2	161.4	160.7	0.58

Results of each electrode as Nyquist plots are shown in Fig I.3.9. In all the Nyquist plots, there are two regions, first a high frequency and second a low frequency region. In the higher frequency region, there is a semicircle arc and in lower frequency region typically a straight- line appears which correspond to mass transfer resistance [180]. A smaller radius of arc confirms lower interface resistance for charge transfer. It is observed that, with the introduction of GO/rGO in electrode E₂ and E₃, Nyquist plots shows smaller semicircles i.e, lower interface resistance for the electrode and subsequently faster charge transfer across the solid-solid interface. It is also observed that for cat-2 had the least resistance as compared to other catalysts. An equivalent circuit as shown in Fig I.3.10 was fitted. Values of R_s (solution resistance), R_i (interface resistance), C_i (interface capacitance) and Z (diffusion resistance) were calculated and are given in Table I.3.8. It is observed from the table that the solution resistances for three electrodes remain the same. However, a significant decrease in the interface resistance is observed. It was 2261 Ω for electrode E₁ and has gone down to 352 Ω for catalyst E₂. It is interesting to note that E₂ employed only insitu reduction of GO to rGO further improved the rGO-CdS interaction.

Table I.3.8: List of circuit parameters

Electrode	R_S (Ohm)	R_I (Ohm)	C_I (Farad)	Z (Ohm)
E_1	290	2261	4.126×10^{-4}	8.38×10^{-6}
E_2	295	352.3	6.9×10^{-4}	5.1×10^{-4}
E_3	295	715.6	7.5×10^{-4}	2.7×10^{-4}

I.3.6.6 Mott-Schottky Analysis

The Mott-Schottky plots of electrodes (E_1 , E_2 and E_3) are presented in Fig I.3.11. Space charge capacitances were measured by varying the potential between -0.3 and 0.7 V versus SHE. The frequency was kept constant at 1 kHz. M-S curves ($1/c^2$ vs V) were plotted to establish the type of semi conductivity, charge carrier density and the flat band potential by using equation 1 [181].

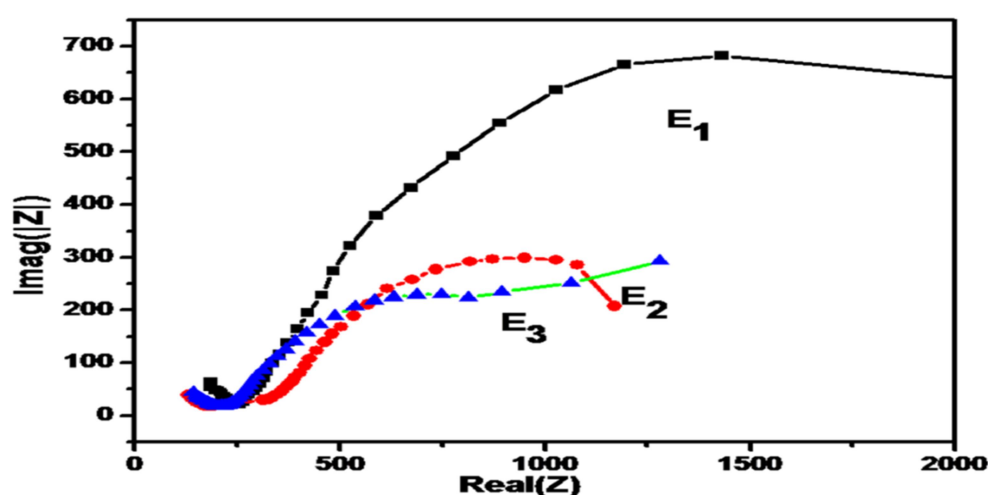
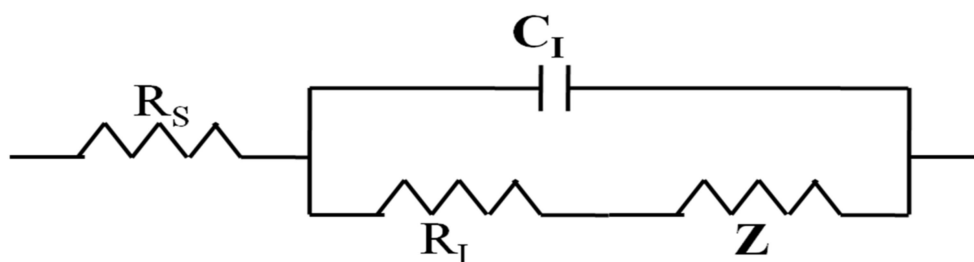
Fig I.3.9: EIS of various electrodes at 0.2 V vs SHE

Fig I.3.10: Equivalent circuit diagram of various electrodes

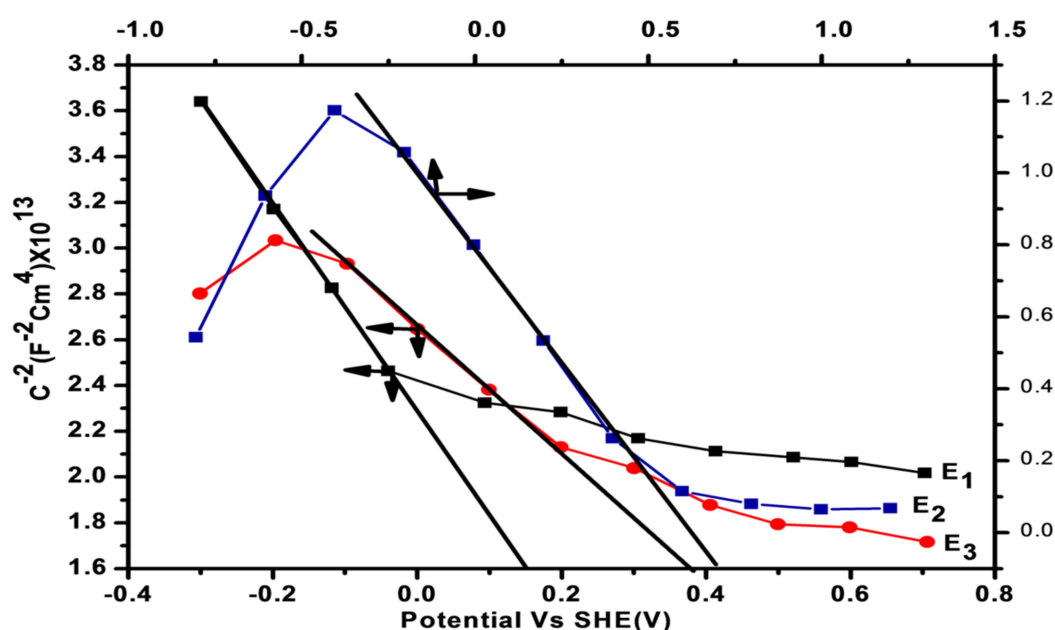
$$\frac{1}{C^2} = \frac{2}{\epsilon_0 \epsilon_r e N_A A^2} (V - V_{fb} - KT/q) \quad (1)$$

Where, C is the capacitance of space charge region, e is the electronic charge ($1.603 \times 10^{-19} \text{C}$), ϵ is the dielectric constant of CdS (9.0) [182], ϵ_0 is the permittivity of the vacuum ($8.854 \times 10^{-12} \text{ Fm}^{-1}$), N is the charge carrier density, A is the area of electrode ($25 \times 10^{-8} \text{ m}^2$), V is the applied potential, V_{fb} (V) is the flat band potential which can be obtained from the Mott- Schottky plot by measuring the intercept of straight line on x-axis, K is the Boltzmann's constant ($1.38 \times 10^{-23} \text{ J/K}$), T is the absolute temperature and KT/e is negligible at room temperature and 1 atmosphere pressure.

It is observed from the table I.3.9 that the flat band potential of catalyst-1 which was unsupported CdS is 0.1 V. Incorporation of CdS and rGO results into a greater flat band potential. It is observed to be the highest in E_2 (0.72V) which was in CdS supported on rGO and electrochemically reduced. It is known that a higher flat band potential ensures a greater band bending and efficient charge separation. Similarly it is also observed from the table that the highest charge density is associated with E_2 . This is order to mention that a higher charge density and an efficient charge separation due to a greater band bending shall result into a better photo activity of catalyst owing to a large number of photo generated electron – hole pairs being available for the reaction. It should be also mentioned that magnitude of the flat band potential as well as the charge carrier density and the activity follow the same trend viz, in descending order $E_2 > E_3 > E_1$. The same trend was followed by charge separation and charge transfer rate (cf EIS studies).

Table I.3.9: Flat band potential and carrier density of catalyst photocathode

Catalyst	$V_{fb}(V)$ vs SHE	Carrier Density(cm^{-3}) N_A
E_1	0.15	1.39×10^{18}
E_2	0.72	3.89×10^{19}
E_3	0.38	3.72×10^{19}

Fig I.3.11: Mott-Schottky plot of catalyst at 1 kHz in S^{2-} and SO_3^{2-} electrolyte

I.3.7 Mechanism

The hydrogen generation using photoelectrocatalytic systems relies on charge carrier generation and its migration route. The charge carrier migration routes depend on the conduction and valence band potentials of the semiconductor catalysts. A schematic diagram illustrating possible pathways of charge transfer in E_2 is shown in Fig I.3.12. Electron – hole pairs are created on the surface of CdS. The photo generated electrons migrate to the rGO from the conduction band of CdS and transported to the solid- liquid interface to carry out reduction reaction.

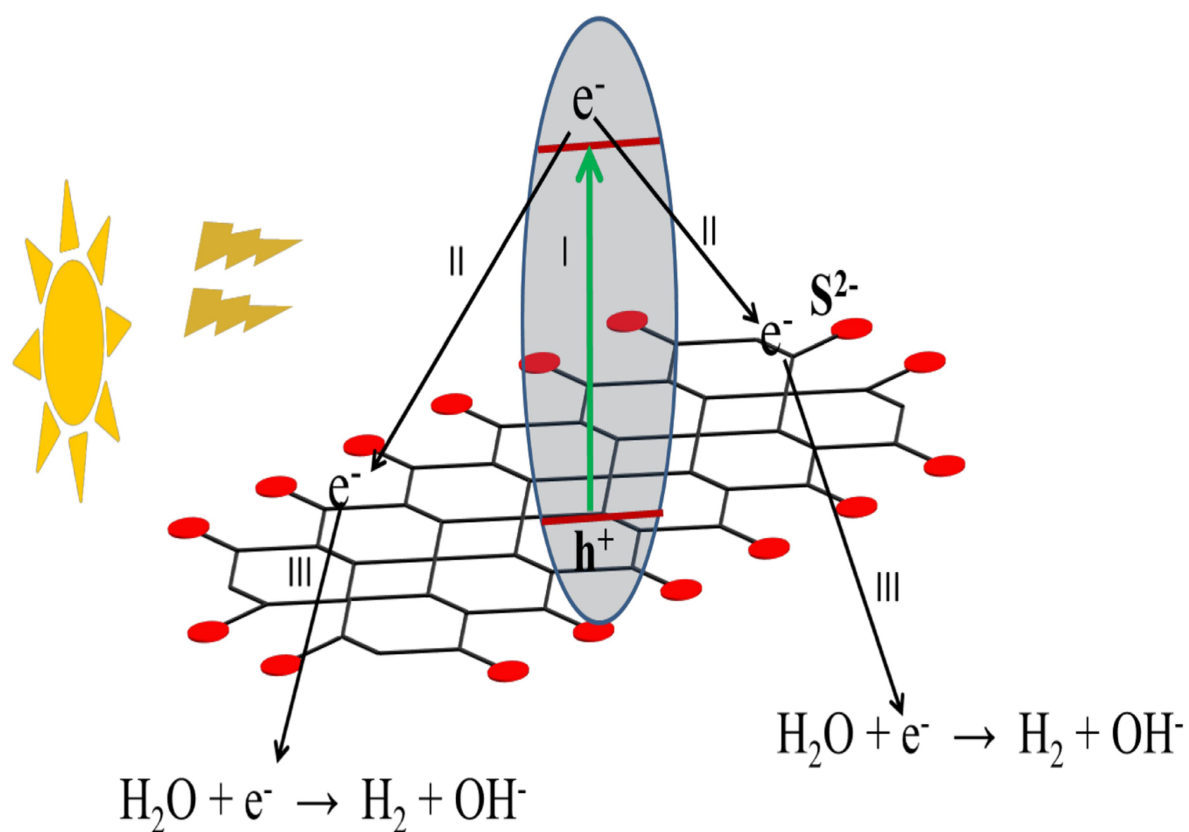


Fig I.3.12: Proposed mechanism of the system

Chapter - III

Section II: Optimization of rGO supported CdS **photoelectrocatalyst**

II. 3.1 General

The exploitation of solar radiation for the photo electrolysis of water to produce oxygen and hydrogen over photoelectrodes has presented a new possibility to generate renewable and green energy carrier [183]. However, it has presented a redoubtable challenge to the scientific community to design and develop new composite electrodes which allow efficient conversion of electrical energy into chemical energy. Direct band gap semiconductors are the major components of such composite systems. Suitable band edge positions of these materials and providing for restriction of photo generated electrons and holes to reduce recombination rates are the major challenges in their practical applications. These demand development of new materials with a wide photo response and reduced charge recombination rates [184, 185].

In particular, chalcogenides, especially CdS, have drawn much attention. CdS has a low band gap (~ 2.4 eV) and a proper band edge resulting in an enhanced photo electrochemical activity. Bare CdS suffers from high recombination rates of photo-generated electrons and holes and thus a low activity. The recombination can be reduced to some extent by synthesizing the catalysts in the form of different structures viz, nanoparticles, nanorods, heterojunctions etc [186-189]. Furthermore, incorporation of noble metals such as Pt, Au etc as co-catalyst is an effective way in restricting the charge recombination but the cost of these materials limits application of these materials [85]. Thus, much effort needs to be directed in designing inexpensive alternatives. Incorporation of carbonaceous material such as graphene oxide (GO)/reduced graphene oxide (rGO) is another effective approach. GO with a well- defined structure may serve as are excellent carbon hosts to modify structural stability, improve electronic conductivity, reduce charge recombination rate and enhance reaction kinetics of CdS [190-192]. With the adoption of a suitable preparation protocol, an intimate contact

leading formation of chemical interaction may develop between the CdS and GO/ rGO. Such interaction results into transfer to electrons from the conduction band to the rGO and thus restricting the recombination rate. Therefore, preparation of the composite becomes important. A common method of electrode fabrication consists of synthesis of rGO and CdS separately. Subsequently, these are mixed and put on a conducting support. The drawback of this method is that the desired chemical interaction between constituent species is not formed. Commonly, rGO is produced by reduction of GO. It can be achieved by chemical[125, 193], thermal[194], photocatalytic[195] and electrochemical reduction methods [196-198]. However, these methods are time consuming and expensive. Further, in these methods, oxygen containing functional groups are not fully removed in a single step and more processing steps are required [199-201].

A hydrothermal method is subsequently used for the preparation of CdS – rGO composites as mentioned above by different researcher. However, a little attention has been paid to reduce the GO in such a way that, GO sheets while getting reduced interacted with CdS as well.

Therefore, in the present work we have fabricated electrodes with CdS and GO and carried out in situ electrochemical reduction of GO to r GO. The process is relatively simple, fast, and affordable and promotes chemical interaction for a better activity.

In addition, the fraction of GO/ rGO in a composite plays an important role. A high amount of GO/ rGO may act as a shield for absorbing visible light by CdS and reduce its activity [175]. Recently, Lin et al. [202] reported an ultrasonic approach for preparation of r GO supported CdS for different proportions of rGO by choosing ammonia as both the complexing agent of the Cd^{2+} ions and a reducing agent of GO. During the process, rGO reduced and the resulting catalysts exhibited strong

interactions between rGO and CdS which provided a uniform dispersity of CdS particles on the rGO sheets. They observed that a CdS – GO with 10 wt % GO showed a better visible light photo-activity. Liu et al [203] synthesized nitrogen doped GO (50%) with CdS by hydrothermal method. They observed its excellent activity towards oxygen evolution reaction than 20% Pt/C –CdS. Fu et al [204] synthesized 1.0, 2.3 and 10 wt % of GO with CdS by ultra - sonication followed by hydrothermal method and observed that 10 wt % GO - CdS showed a better visible light photo catalytic activity due π - π stacking interaction of GO with CdS.

Additionally, material loading, electronic mobility and electrode stability highly depend on substrate (support). In this regard, Indium tin oxide (ITO), fluorinated tin oxide (FTO), glassy carbon, and Toray carbon paper (TCP) have been widely used as substrate[162].

The current section will discuss fabrication of a series of electrodes loaded with GO - CdS catalysts on TCP where in situ reduction of GO was carried electrochemically. Detailed characterization studies conclusively showed that this preparation technique resulted into a chemical interaction leading to formation of a heterojunction at the solid – solid interface which was responsible for a better charge separation and transport of electrons to the solid liquid interface for a better activity towards reduction of water to hydrogen in presence of visible light.

The best photoelectrochemical performance with high current density was obtained by CdS - GO (10 wt %). A higher loading of GO is resulted into shielding of CdS from absorbing light.

II.3.2 Experimental

II.3.2.1 Preparation of Electrode

(a) Synthesis of graphene oxide

The modified Hummers method [163] was employed to prepare graphene oxide (GO). In brief, 2 g of graphite flakes were added to 46 mL of 98% H_2SO_4 with a constant stirring keeping temperature always below 283 K. Subsequently, 8 g of potassium permanganate powder was added to the reaction mixture and the stirring was continued for further 2h. The reaction mixture was then allowed to equilibrate to the room temperature with continuous stirring. Thereafter, the mixture was kept inside a water bath for 1h at 308 K and 100 mL of distilled water was added to the mixture. 20 mL of 30% H_2O_2 was also added to this reaction mixture to dissolve residual permanganate. Finally, colored suspension was filtered and washed with 1 M HCl and followed by distilled water for three times. The residue was dried in oven at 333 K for 3 days and used as and when required.

The following catalysts were prepared:

Catalyst 1

It was bare CdS prepared by precipitation method. Briefly, 0.003M aqueous solution of cadmium sulfate was prepared and taken in a 1,000 mL beaker and 0.013M aqueous solution of Na_2S was added very slowly through a burette with continuous stirring. The precipitate of CdS was filtered and washed by 200 mL of double distilled water to remove impurities from the mixture. Finally, the precipitate was dried in an oven at 343K for 3h.

Catalyst-2

Graphene-CdS Composites were synthesized in two steps. In the first step, a requisite amount of graphene oxide was suspended in double-distilled water and ultrasonicated

for 1h. Required amount of CdSO_4 was added to the suspension and dissolved. The amount was calculated so that the weight of GO was 5% in the final product. In the next step, Na_2S solution was added slowly to the suspension to precipitate CdS. Finally, the solid mass, which was a composite of CdS and GO, was washed by double distilled water for three times and dried in oven at 343K for 3h.

Catalyst-3 and 4

Graphene-CdS Composites was prepared by same procedure as catalyst 2, however, the amount of GO in the final catalyst was 10 and 20 %, respectively.

II.3.2.2 Photoelectrodes:

Electrodes were fabricated on 5×5 mm TCP paper. In a typical fabrication, 50.0 μL of nafion solution was mixed with 1.0 mL of N, N –dimethylformamide (DMF) and 2.0 mg of catalyst was subsequently added and the mixture was ultrasonicated for 30 min to obtain homogeneous suspension. 20.0 μL of this mixture was drop casted on the TCP paper. During the fabrication, catalyst loading was kept at 0.15 mg/cm^2 . For an ohmic contact, prior to electrode fabrication a copper wire was pasted by silver glue on the back portion of the TCP. Epoxy resin was coated on the back surface and also on all the edges of the electrode. It ensured that electrochemical reactions took place only from the surface containing catalyst. The table below summarizes the catalysts and electrodes prepared and studied in the present work.

II.3.3 Activity of Photoelectrodes

Photoelectroactivity of photoelectrodes also studied in same experimental set – up as mention in section I.3.3

Table II.3.1: Summary of Catalysts/electrodes prepared in present study

Catalysts/Electrodes	Remarks
Cat-1	Unsupported CdS
Cat-2	5% GO was supported on CdS
Cat-3	10% GO was supported on CdS
Cat-4	20% GO was supported on CdS
E ₁	Electrode prepared from Cat-1
E ₂	Electrode prepared from Cat-2
E ₃	Electrode prepared from Cat-3
E ₄	Electrode prepared from Cat-4

II.3.4 Characterization Techniques

Catalyst and electrodes were characterized by FTIR, XRD, HRSEM, HRTEM, DRS PL, XPS, EIS and Mott – Schottky analysis. Detail of these characterization tools, which is used in this section, also described in section I.3.4

II.3.5 Results and discussion

II.3.5.1 Photo-electrochemical activity

At the beginning of each experiment, GO in the photo electrode was reduced electrochemically (in absence of light). Ambrosi et al [164] have reported the electrochemical reduction method of GO to rGO. Application of negative potential can eliminate most of the reducible oxygen functionalities. A cyclic voltammetry was carried out and a reduction peak at -1.2 V (SHE) was observed which was taken as reductive peak of GO to rGO. Electrodes were kept at -1.4 V for sufficient long time till the current density become negligible. Subsequent to the reduction of GO to rGO,

linear step voltammetry was carried out for the potential range of -0.6 to 0.6 V with respect to RHE. The results are shown in Fig II.3.1. Experiments were carried out in dark as well as in the light. Blank experiments with electrode not containing any photo catalyst (Electrode E) were also carried out. It is seen from the figure that the dark currents (in absence of light) were negligible for all electrodes in the complete range of voltage. However, when diffuse light of LED was applied on the photo electrodes, currents were observed with negative biasing whereas negligible effect of light was observed in positive biasing. No current was observed when the same experiment was carried out with electrode where no catalyst was deposited (Electrode E). It confirms the current was due to photoelectrochemical activity. Photocurrent density of 160.9 , 83.4 , 43.6 and $18.4 \text{ mA cm}^{-2} \text{ mg}^{-1}$ of CdS was obtained for E_3 , E_4 , E_2 and E_1 respectively at -0.6 V (RHE) . The low activity of E_1 may be understood as it was bare CdS; therefore, the charge recombination rate might be high. On the other hand E_2 , E_3 and E_4 were CdS supported on GO with GO/ rGO being 5, 10 and 20 wt %, respectively. It is further observed that E_3 had a better activity compare to E_2 and E_4 . The result shows that 10% loading of GO/ rGO in the CdS-GO/ rGO composite was optimum. It is also seen that photo currents are produced with negative biasing. It hints of p-type semi conductivity of the photo electrodes meaning there by that electrodes were photo cathode with positive holes (h^+) as majority charge carriers. Further, using electrode E_3 , and voltage at -1.0 V , and a run was continued for 3h and gases at the two electrodes were measured. Volume of gas evolved at the photocathode was 4.3 mL and its analysis by gas chromatography confirmed that it was pure hydrogen, whereas, only 0.3 mL of gas was produced at the counter electrode. The gas was analyzed to be oxygen; however its production was significantly less than stoichiometry. The decreased oxygen output at

anode is expected due to completing reaction of oxidation of S^{2-} and SO_3^{2-} at anode.

Reaction mechanism is same as written in Section I.

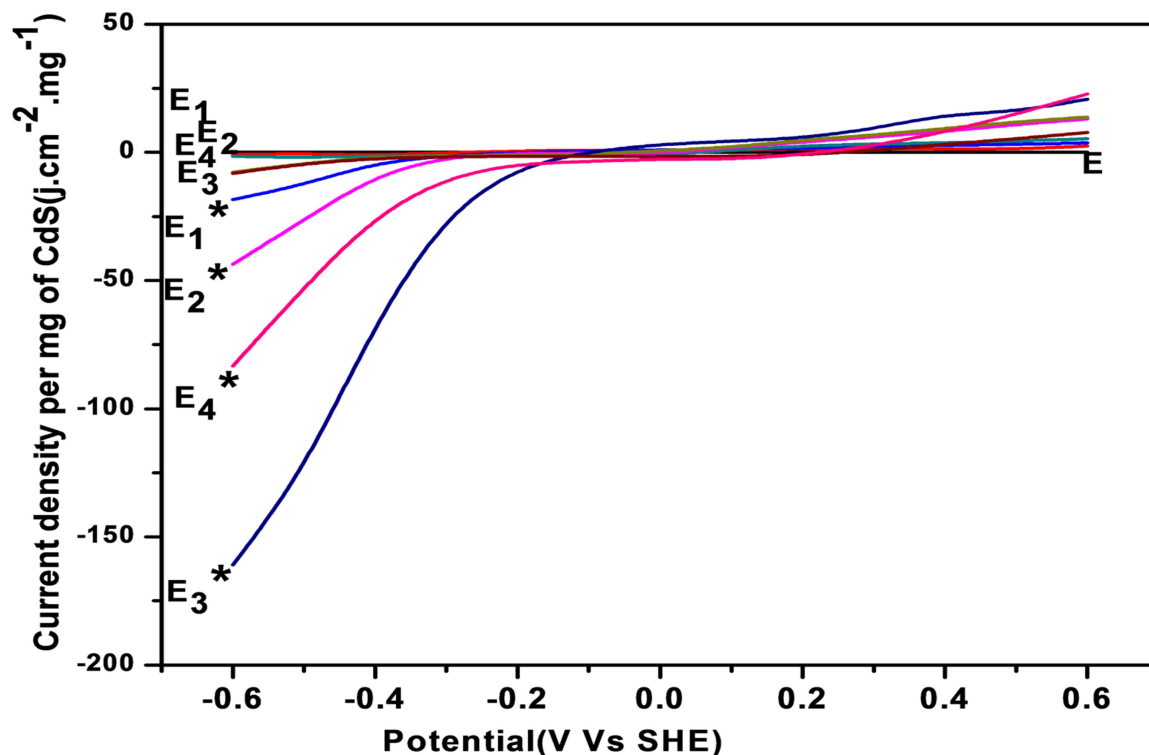


Fig II.3.1: LSV test of catalysts in S^{2-} and $S_2O_3^{2-}$ electrolyte: E_x & E_x^* are without and with light

II.3.5.2 Characterization studies

II.3.5.2.1 FTIR studies

Functional groups and bonds formed during catalyst synthesis were investigated using infra-red spectroscopy. FTIR was carried out for catalysts (Fig –II.3.2) and also for electrodes E_2 , E_3 and E_4 (Fig II.3.3) in the range of $500-900\text{ cm}^{-1}$. Analyses of these electrodes were carried out after electrochemical reduction of GO to rGO as discussed earlier. In all samples of catalyst and electrodes the characteristics peak of Cd-S stretching vibration in the range of $578-640\text{ cm}^{-1}$ is observed [165, 166]. One additional peak $\sim 700\text{ cm}^{-1}$ is also observed in CdS when catalyst was supported with GO. The

peak is also assigned to Cd-S stretching vibration. The observed shift is attributed to coupling of vibrations. Coupling of vibrations is a common phenomenon which causes shift in peak positions. We attribute the shift to the coupling of Cd-S and C-S vibration. Such a coupling indicates interaction between CdS and rGO. The same has been reported in the literature [151, 167]. The FTIR spectra of electrode (Fig II.3.3) additional peaks were at ~ 870 , and 980 cm^{-1} in cat-3. These peaks are attributed to C-S, C=S, stretching. Literature suggests C-S or C=S stretching vibration in these ranges[167].

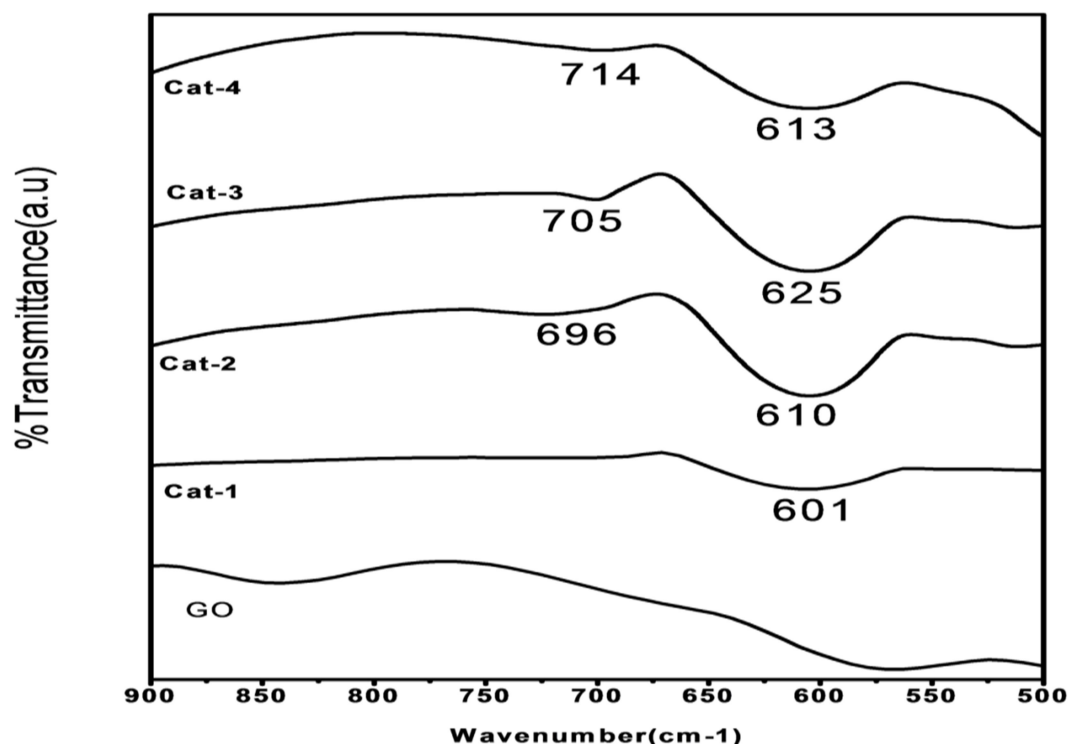


Fig II.3.2: FTIR spectra of Catalysts

However, these ranges are quite wide therefore, it is difficult to unequivocally assign above observed peaks to C-S or C=S stretching. Nevertheless, it is likely that in situ reduction, GO to rGO has resulted in an interaction between CdS and rGO through C-S or C=S bonds. Such peaks are prominent in the electrode E₃ (10% GO/ rGO) in comparison to electrode E₂ and E₄. Therefore, it is conclusively observed that

electrochemical reduction of GO to rGO has resulted into a chemical interaction between CdS and rGO and more over the interaction is seen to be more in cat-3 which had 10 wt % of GO/rGO.

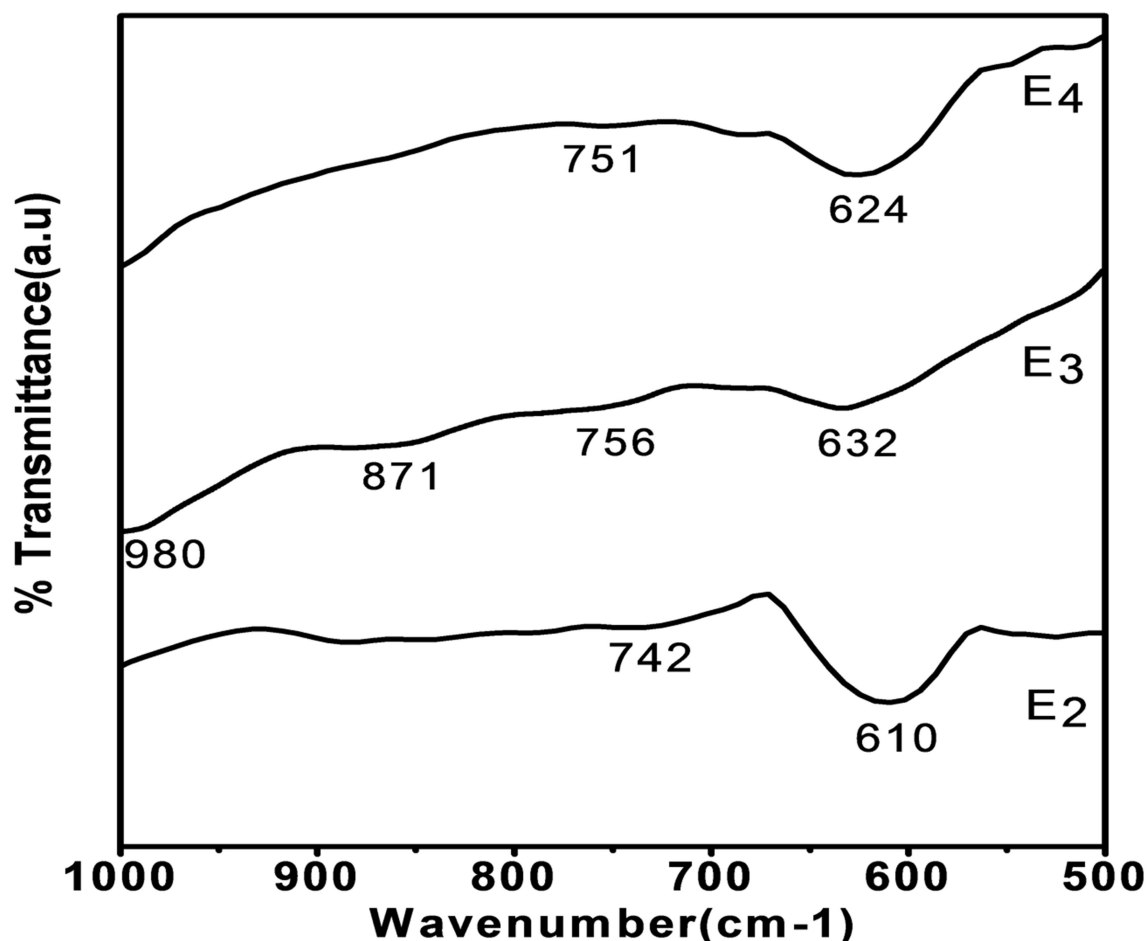


Fig II.3.3 FTIR spectra of electrodes

II.3.5.2.2 X-Ray Diffraction (XRD)

Crystallinity and phases of the prepared catalysts were identified using X-Ray Diffraction (XRD) pattern. Results are shown in Fig II.3.4. The observed and standard values of d (inter planner spacing) and corresponding planes (hkl) are given in Table-II.3.2. The broad peaks of CdS indicate its very small crystallites size in cat-1 and 2. It is also observed that there is no characteristic peak ($d= 2.91\text{\AA}$) of cubic phase in these

catalysts. Peaks appeared at $2\theta = 26.33, 43.59$ and 51.92° corresponding to (002), (110) and (112) planes of the hexagonal phase of CdS.

Unit cell parameters 'a' and 'c' of the hexagonal phase CdS for all catalysts were calculated, and are presented in Table II.3.3. The standard are found to be $a=4.14\text{\AA}$ and $c=6.715\text{\AA}$. Variations in the values of 'a' and 'c', from the standards have been observed in catalyst-1 and catalyst-2.

Table II.3.2 Results of XRD analysis of CdS in catalysts

d standard and miller indices				d experimental			
Hexagonal		Cubic		Cat-1	Cat-2	Cat-3	Cat-4
Miller Indices hkl	Hexagonal phase d($\text{\AA}$)	Miller Indices hkl	Cubic phase d($\text{\AA}$)	d($\text{\AA}$)	d($\text{\AA}$)	d($\text{\AA}$)	d($\text{\AA}$)
002	3.36	111	3.36	3.31	3.38	3.32	3.32
102	2.45	200	2.91	-	-	-	-
110	2.06	220	2.06	2.06	2.08	2.05	2.06
112	1.76	311	1.75	1.75	1.76	1.75	1.76

Table II.3.3: Unit cell parameters and crystallize size of CdS in catalysts.

S.No	Catalyst	c	a	c/a	Crystallize Size (nm)
1	Cat-1	6.62	4.14	1.60	5
2	Cat-2	6.78	4.17	1.63	3
3	Cat-3	6.64	4.11	1.62	5
4	Cat-4	6.64	4.11	1.61	5

However, since the peaks are broad and peak positions may not have been accurately determined, therefore, we consider these variations insignificant. Line broadening data were corrected for instrumental broadening and crystallize sizes of CdS in catalysts

were calculated by the Scherrer equation. Sizes were estimated to be 5, 3.5 and 5 nm respectively (Table II.3.3).

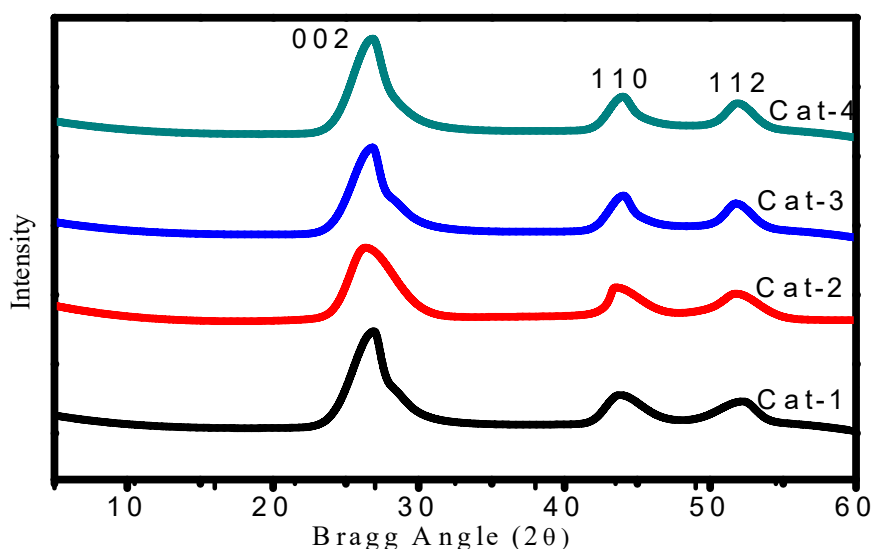


Fig II.3.4: XRD pattern of catalysts

II.3.5.2.3 High Resolution Scanning Electron Microscopy (HRSEM)

Morphology of catalysts was analysed using HRSEM. The results are shown in Fig II.3.5. The micrographs show spherical shaped CdS nano particles with particles sizes varying between 5 and 16 nm with some agglomeration.

In order to investigate the sulfur, oxygen, Carbon and cadmium elemental distribution, HRSEM and its corresponding colour mapping were carried out, as illustrated in Fig. II.3.6. It is clearly seen from the fig, the CdS and GO are uniformly distributed in catalyst 3 and 4 in intimate contact which would promote a chemical interaction between the two after in situ electrochemical reductions of GO to rGO. Surprisingly such uniform distribution is not observed in catalyst 2 which had only 5 wt% GO. The CdS and GO are seen to be rather segregated. Another observation is that carbon % is 5 times high in catalyst 4 as compared to catalyst 3.

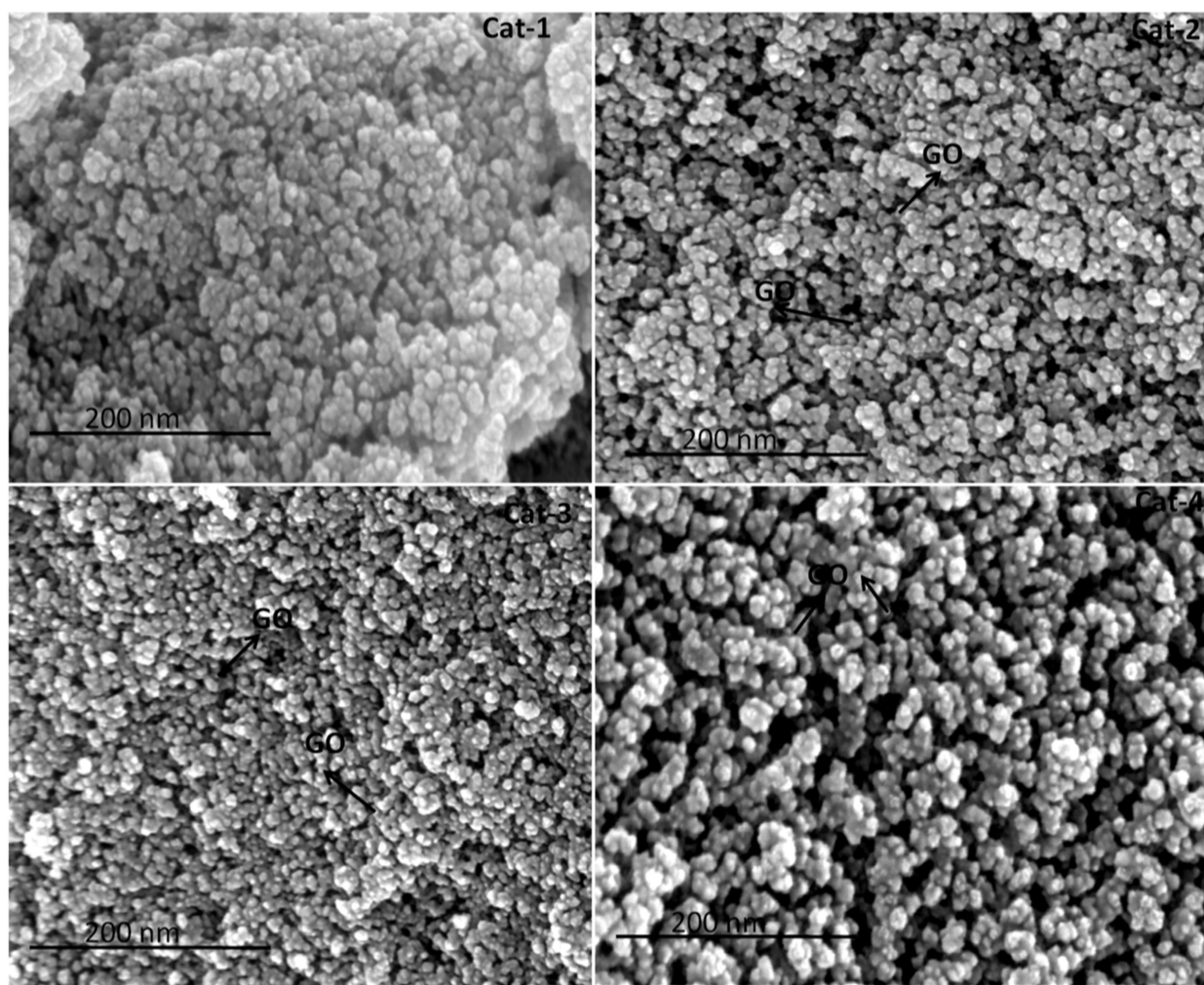


Fig II.3.5: HRSEM images of catalysts

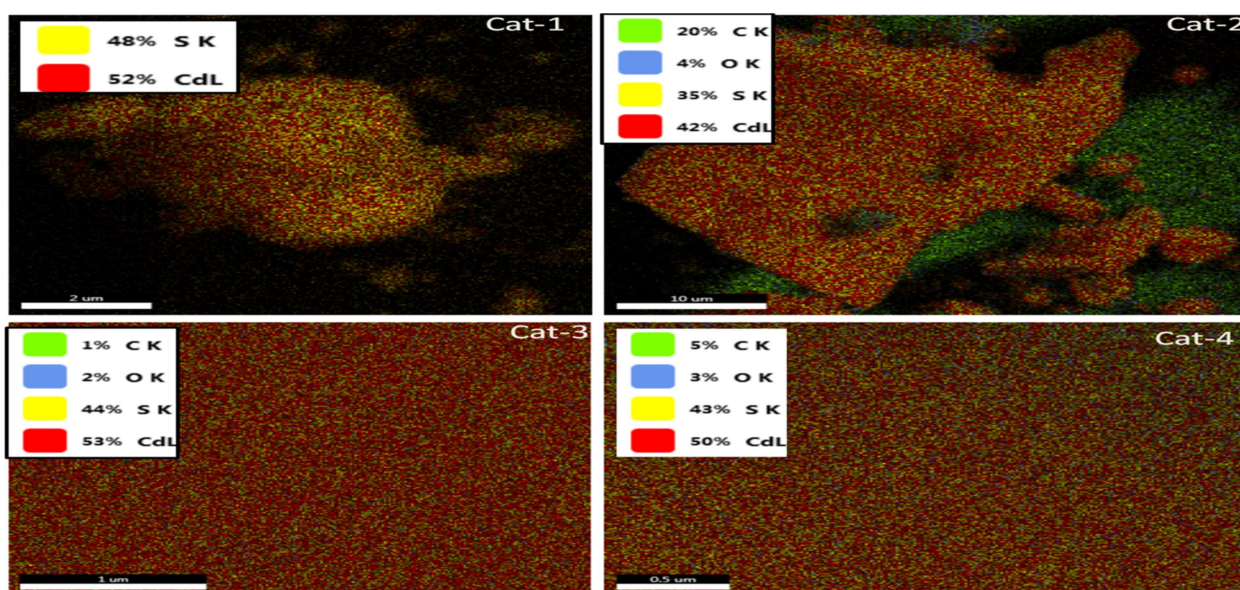


Fig II.3.6: Colour map of different catalysts using HRSEM

The wt % of GO in catalyst 3 and catalyst 4 were 10 and 20, respectively. This result confirms that as compared to catalyst 3, CdS in the catalyst 4 is shielded by carbon resulting into reduction in the absorption of light and consequently activity.

II.3.5.2.4 TEM and HRTEM analyses

TEM images of catalysts are shown in Fig II.3.7. Similar to the results of HRSEM, it is observed that more uniform distribution of CdS exists in catalyst 3 and 4 compared to catalyst 2 which was 5 wt % GO. Average particle sizes were measured by image j software and these varied between 3 and 15 nm as shown in histograms in Fig II.3.8. The average particle size of CdS in catalysts 4 is seen to be as high as 9 nm. On comparison of particles sizes with the crystallite sizes obtained by the XRD analysis, it is seen that agglomeration of CdS particles has taken place to some extent in catalyst 4 which had also the highest wt % of GO. The influence of GO on shape and morphology of the nano-systems has been reported in the literature [205].

Results of the selected area electron diffraction (SAED) of CdS are shown in Fig II.3.9. SAED clearly indicates polycrystalline nature of CdS [235]. The d values were calculated with help of image j software and hkl planes were assigned (Fig II.3.9). All the d values matched with the hexagonal phase of CdS in conformity with the results of XRD.

HRTEM images are shown in Fig II.3.10. The results are seen to be in conformity with those of HRSEM. The inter-planer spacing of ~ 0.33 nm are seen in all catalysts which correspond to the hexagonal phase of CdS. Uniform distributions of CdS and GO is seen in catalysts 3 and 4. Similarly as observed in HRSEM, the distribution is not seen to be as uniform in catalyst 2 which was a 5 wt% GO. The fringes of GO ($d \sim 0.84$ nm) are seen in catalysts 2 and 4. This is due to segregation of CdS and GO in catalyst 2.

Whereas, it confirms that GO has occluded CdS in catalyst 4. It is in order to mention that similar results were obtained by the analysis of catalysts by HRSEM.

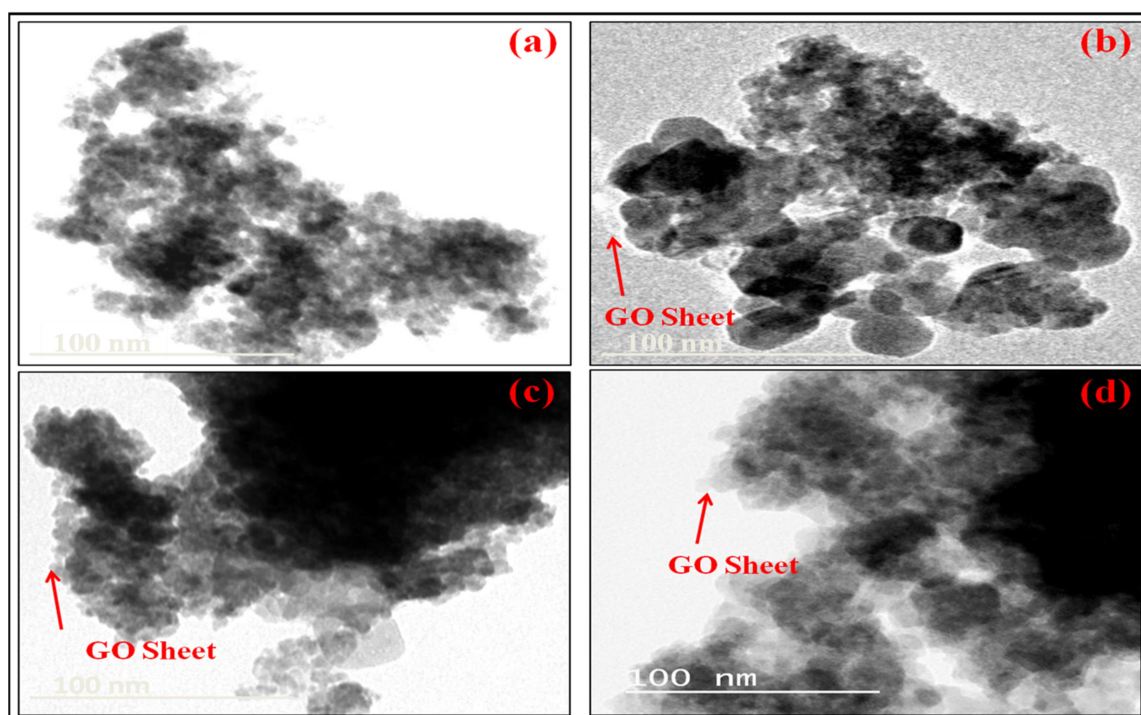


Fig II.3.7: TEM image of a: Cat-1, b: Cat-2, c: cat-3 and d: Cat-4

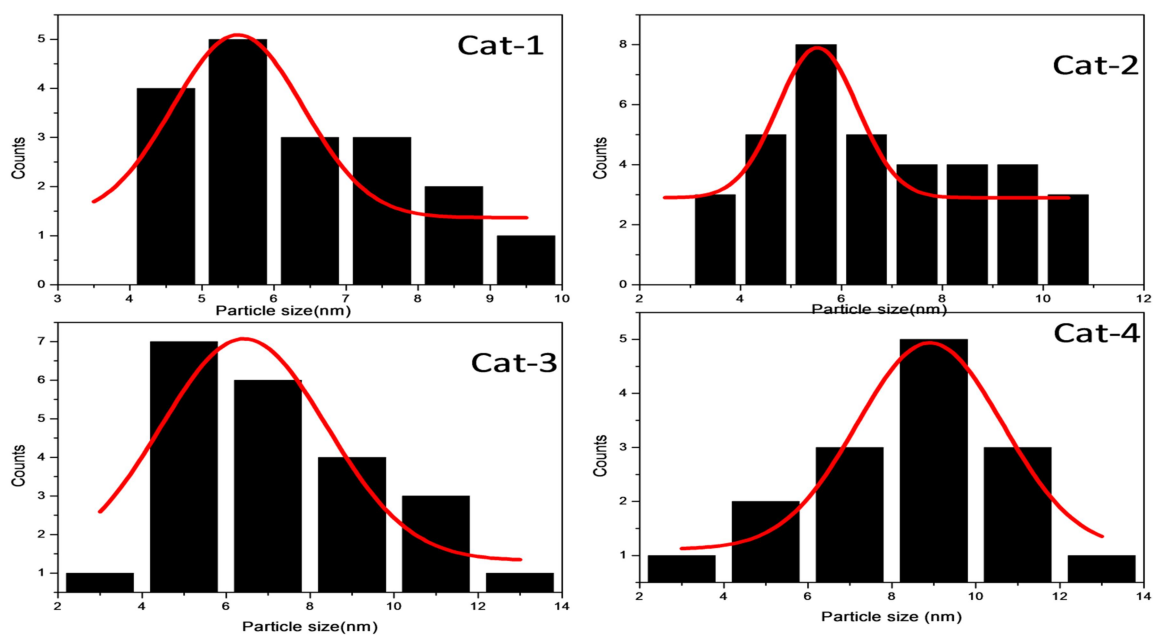


Fig II.3.8: Histogram of particle size of catalyst

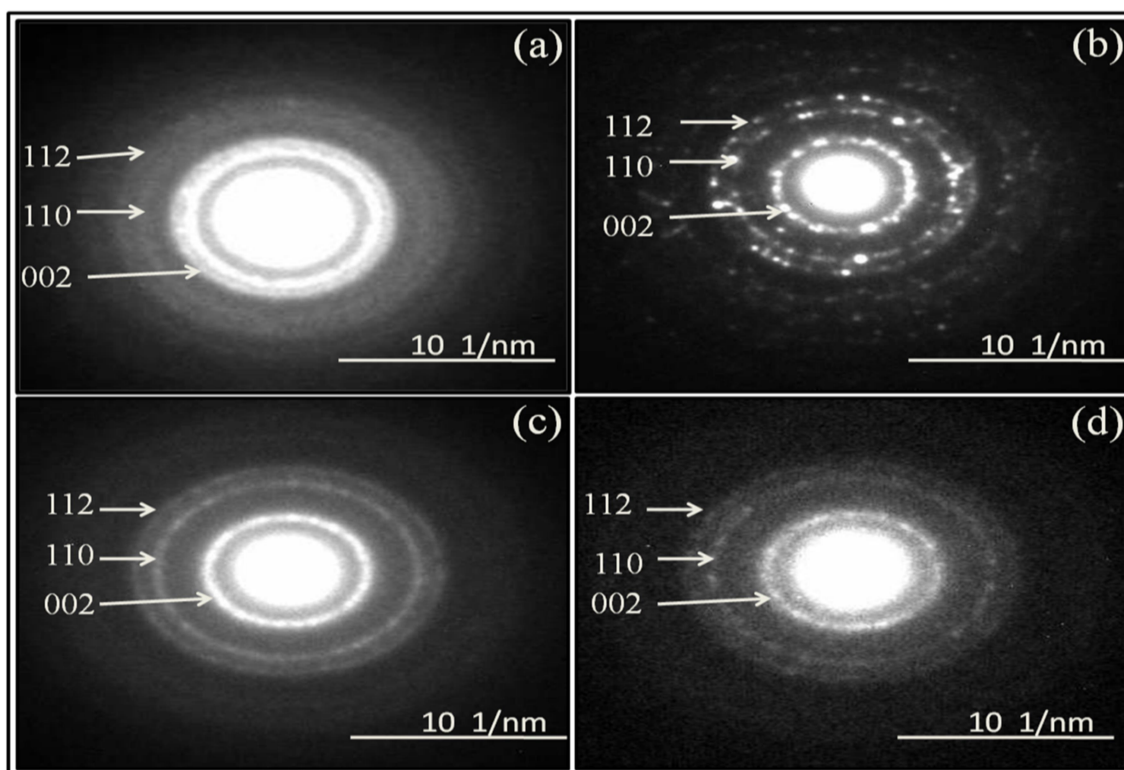


Fig II.3.9. SAED of a: Cat-1, b: Cat-2, c: cat-3 and d: Cat-4

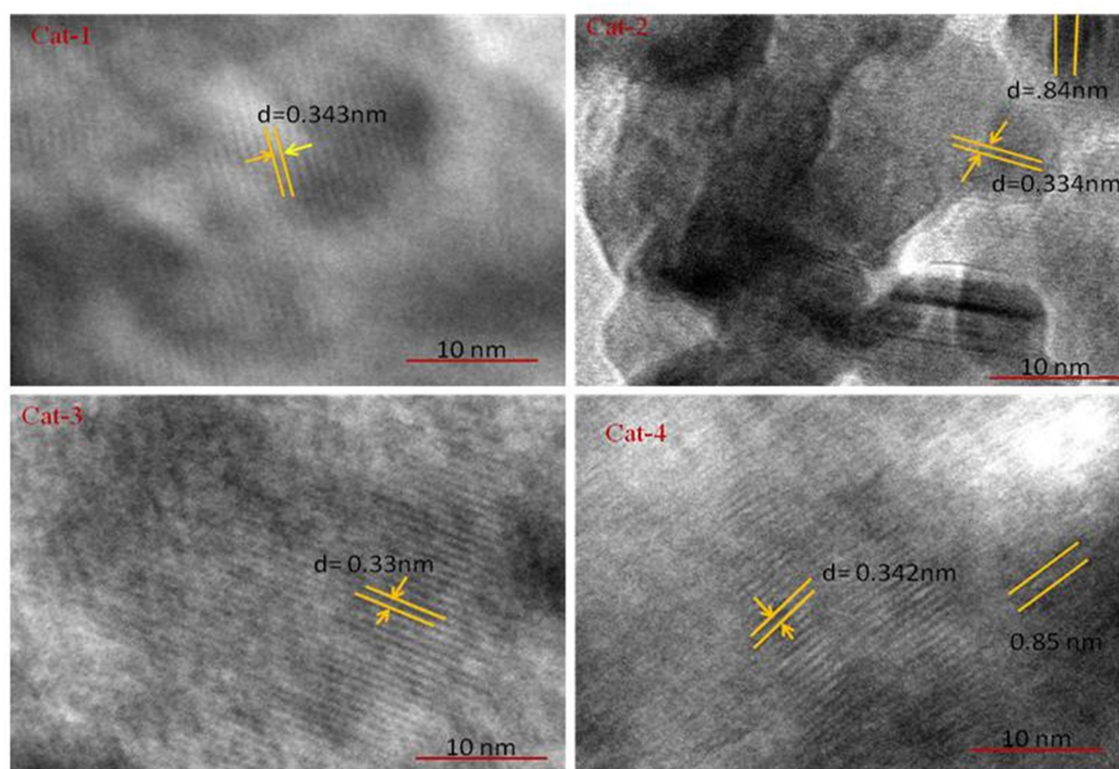


Fig II.3.10 HRTEM images of Cat-1(A), Cat-2(B), cat-3(C) and Cat-4(D)

II.3.5.2.5 Diffuse Reflectance Studies

Optical absorption studies using diffused reflectance spectroscopy (DRS) were carried out for CdS in catalyst synthesized shown in Fig. II.3.11. It was found that CdS in catalyst absorbed the incident radiations in between 400 and 700 nm. The absorbance spectra for all CdS in catalyst display steep change in absorbance slope at ~ 550 nm which gradually flattening out after 500 nm. Such steep change indicates onset of band gap excitation. It is also seen from the fig that absorption was significantly high for GO/rGO supported catalysts. Literature reports that greater charge carrier density may be a reason for enhanced absorption. We have also observed, as given in the Mott-Schottky analysis later, that there exist higher charge carrier densities in GO/rGO supported catalyst compare to bare CdS. .

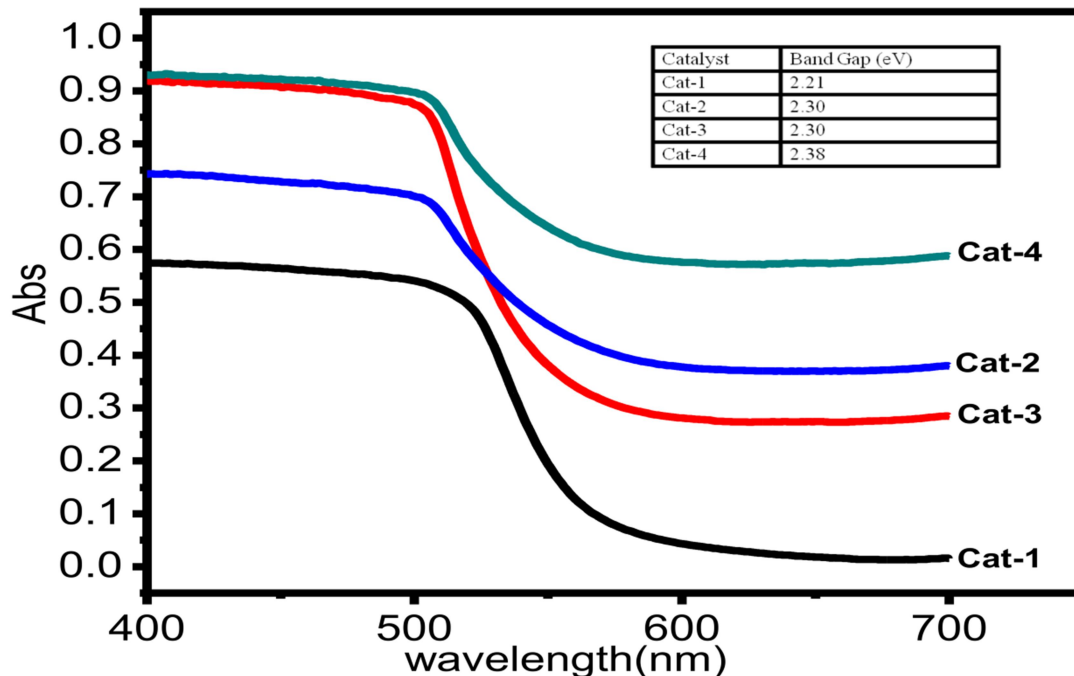


Fig II.3.11: Absorbance spectra and Band gap (inset) of CdS in different catalyst

The direct band gap for CdS in catalysts were obtained by plotting value of $(\alpha h\nu)^2$ against $h\nu$ and the values are shown in the inset. It is seen that incorporation GO has resulted into increase in the band gap of CdS. Similar increase in the band gap has been reported by earlier workers [167] due to quantum confinement of CdS nano particle. Blue shift in absorbance of CdS supported on GO have also been ascribed to π to π^* transitions occurring in C=C bond of GO. This increase in band gap is also attributed to the interfacial interaction between CdS and GO/rGO[172]

II.3.5.2.6 Photoluminescence studies

PL spectra of catalysts and electrodes, with the excitation wavelength 200 nm, are shown in Fig II.3.12 and II.3.13 respectively. Strong emission peaks appeared at ~ 530 nm. A higher charge recombination rate results into an enhanced PL intensity. If photo generated electrons are transferred from the conduction band of CdS to rGO, the recombination rate will be reduced and so will be the PL intensity. It is seen that catalysts 2, 3 and 4, which were GO supported had lesser PL intensity compared to the bare CdS (Catalyst-1)

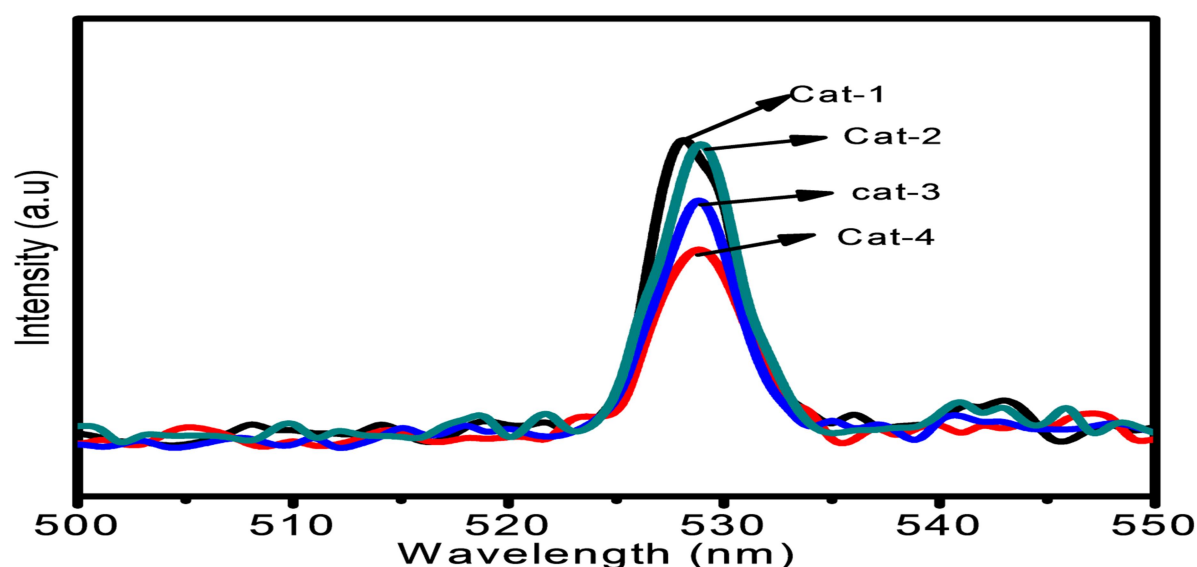


Fig II.3.12: Photoluminescence spectra of catalysts

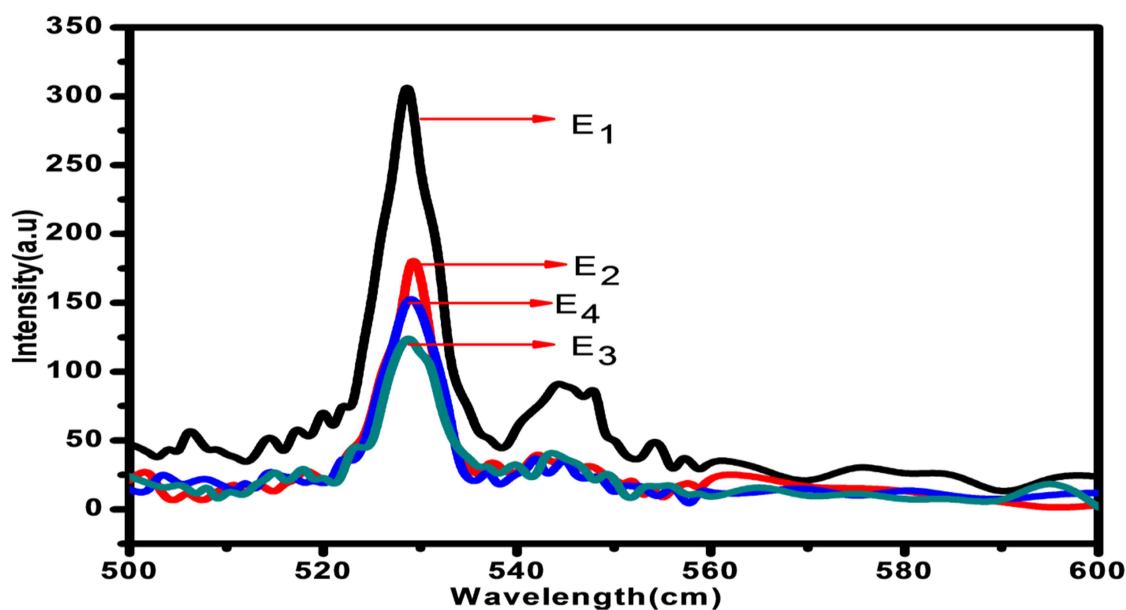


Fig II.3.13: Photoluminescence spectroscopy of electrodes

A remarkable observation is that when electrodes were made using these catalyst and GO was electrochemically reduced; the order of PL intensity had changed. The electrode prepared by cat 3 had least PL intensity. The electron transfer may only take place if an intimate contact leading a chemical interaction exists between rGO and CdS. Literature reports such an interaction through π^* orbital of C of r GO and n orbital of S of CdS [206]. We have also observed interaction of CdS and rGO by FTIR analysis.

The result shows that such synergistic effect has taken place to greater extent in electrode prepared by cat-3 which had 10 wt% GO. It is order to mention that this electrode showed highest activity also.

II.3.5.2.7 X-Ray Photoelectron Spectroscopy (XPS)

The X- ray photoelectron spectroscopy (XPS) studies were conducted to ascertain the oxidation states of the chemical species present on the surface of the samples and their interaction. Catalysts as well as electrodes after insitu reduction were analyzed. Peaks were deconvoluted using Lorentzian - Gaussian method [173]. Results for catalysts are

shown in Fig II.3.14 and corresponding peak positions are given in Table II.3.4. It is observed from the spectra of catalysts that for Cd 3d peaks are centred at 412.1 and 405.2 eV and are very close to reported values of Cd²⁺ 3d at 412.2 and 405.2 eV for 3d_{3/2} and 3d_{5/2} respectively [174, 175]. This indicates 2+ oxidation states for Cd in the catalysts. Further, it is also observed that in cat-2, 3 and 4, Cd peaks are shifted towards higher binding energies in comparison to unsupported CdS (cat-1). These catalysts were CdS supported on GO. A Shift to higher binding energies is possible owing to the fact that GO/rGO has many strong electronegative species present on its surface which will necessarily affect the electron density of Cd²⁺. In other words, a shift in peak position confirms chemical interaction between CdS and support GO. The same was observed by FTIR analysis. Further the shifts were observed to be more in cat-3. The XPS spectra of sulphur are also presented in Fig II.3.14 and peak positions for S-2p are tabulated in Table II.3.4 The doublet observed at 162.1 and 160.0 eV match with the standard value of S2p_{1/2} and S2p_{3/2} of CdS. S_{2p} peaks present in catalysts, follow similar pattern as was observed for Cd²⁺, the S 2p peaks for cat-3 and cat-4 displayed shifts towards higher binding energies. Similarly, the shift in S2p peaks has been attributed to interaction between CdS and GO, leading to redistribution of charge densities on Cd and S ions [176, 177]. As stated earlier, with the presence of highly electronegative groups on the surface of GO/rGO such interaction is possible causing positive shifts of binding energies for both Cd²⁺ and S²⁻. It is in order to mention that Singh and Sinha [151] have reported shift in peak position of S²⁻, when rGO was incorporated on with CdS. They have attributed the shift to a chemical interaction between CdS and rGO. In our study it is observed that this phenomenon is prominent in cat-3. Literature reports that an intimate contact between CdS and GO/rGO leading to a chemical interaction at the

interface, promotes a better charge separation and improved water splitting activity[207].

Fig II.3.15(a, b, c) represent the XPS of electrodes E₂, E₃ and E₄ after electrochemical reduction. Depth profiling by Argon ion bombardment over the surface for 60s was also carried out for detailed investigation of the interactions of chemical species on the surface of these three electrodes. These results are presented in figure. Peak values are listed in Table II.3.5. In general it is observed that the peaks corresponding to Cd²⁺ have shifted to higher values. Remarkably, electrode E₃ and E₄ showed two distinct doublet of S. These electrodes had 10 and 20 wt% rGO respectively. It is in order to mention that HRSEM and HRTEM results had shown that the CdS and rGO were uniformly distributed in these two catalysts. Two doublets were not observed in electrode E₂ which had only 5 wt % of rGO. The HRSEM and HRTEM had shown segregation of CdS and Go in this catalyst. The doublet (I) for E₂, E₃ and E₄ has BE S2p_{1/2} and S2p_{3/2} close to those of cat 2, cat-3 and cat-4, respectively. However, an additional doublet (II) of S2p_{1/2} and S2p_{3/2} is observed in both the electrodes (E₃ and E₄) at higher binding energies. This clearly confirms strengthening of interaction between CdS and rGO due to electrochemical reduction of GO to rGO. Such an interaction had taken place due to in situ reduction of GO to rGO and because of the uniform distribution of CdS and GO in these two catalysts leading to chemical interaction. The ratios of 2p_{3/2} peaks of the two doublets were calculated and are shown in the table II 3.5. A higher value of the ratio means a greater fraction of S²⁻ were at higher BE due to chemical interaction as mentioned above. It is seen from the table that this value is 2.71 for electrode E₃ in comparison of 1.4 for electrode E₄. Fig II.3.15(a,b &c) also provide XPS after etching for 60s. It is observed that typically all binding energies shift towards lower energy after 60s argon ion bombardment. The ratios of the peaks have also diminished

from 2.71 to 0.98 for E_3 . This indicates that interactions between GO and CdS are mostly at the interface and decreases with the depth. It is also conclude that these interactions were more in electrode E_3 . It is order to all electrodes were prepared by precipitation technique and GO was reduced in-situ during photoelectrochemical process. Accordingly, on the basis of this discussion, the doublet of S^{2-} observed in E_2 and E_3 at higher BE been ascribed to presence of C-S type interaction. It is in order to mention that FTIR studies had also indicated presence C-S bond in these electrode (E_2 , E_3 & E_4). The literature reports the possibilities of interaction between CdS and rGO through π^* orbital of carbon and n orbital of sulphur of CdS. Peng et al [178] reported the possible interactions between photocatalyst and carbon materials such as $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ between the n orbital of the CdS species and rGO. They had synthesized catalyst by precipitation method. Liu et al.[179] have also reported that the electronic transition of $\pi \rightarrow \pi^*$ of MWCNT and $n \rightarrow \pi^*$ between the n- orbital of the sulphur species of catalyst. We also propose such interactions in electrode E_2 , E_3 and E_4 . However the extent of this interaction was more in electrode E_3 which was 10 wt % rGO. A 10 wt % loading of GO/ rGO is seen to be optimum.

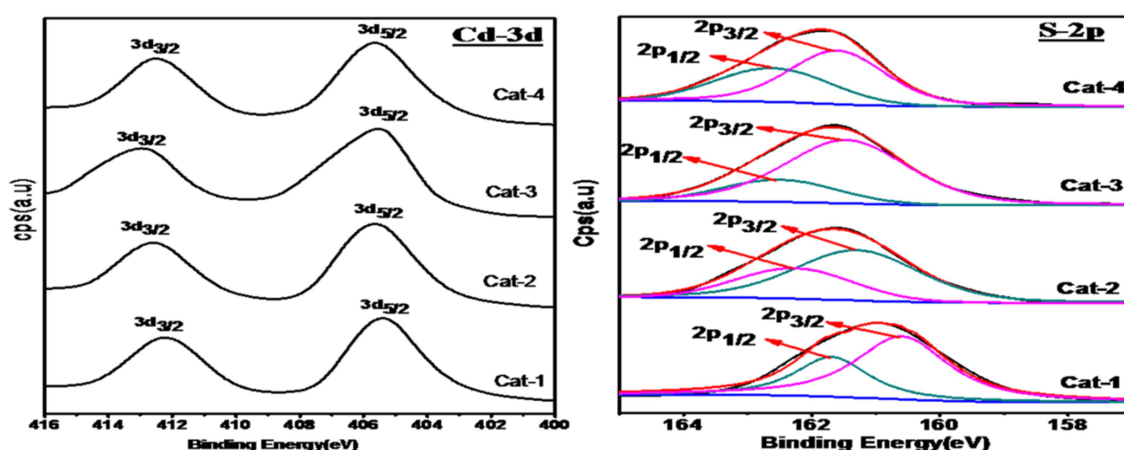


Fig II.3.14: XPS spectra of Cd-3d and S-2pin catalysts

Table II.3.4: Peak positions of Cd 3d and S-2p in catalyst

Catalyst	Peaks positions in catalysts			
	Cd 3d _{3/2} (eV)	Cd 3d _{5/2} (eV)	S2p _{1/2} (eV)	S2p _{3/2} (eV)
Cat-1	412.2	405.2	162.1	161.0
Cat-2	412.6	405.5	162.3	161.2
Cat-3	412.7	405.8	162.2	161.2
Cat-3	412.7	405.7	162.7	161.6

A lower wt % (catalyst 2) leads to insignificant interaction between CdS and rGO. It is in order to mention that this catalyst might also have two doublets of S but the intensity of the second doublet (II) was insignificant therefore it was not becoming possible to deconvolute precisely. Similarly, a higher wt % results into chemical interaction but it also lead to shielding of CdS by rGO as seen by HRSEM and HRTEM results and consequently lower activity.

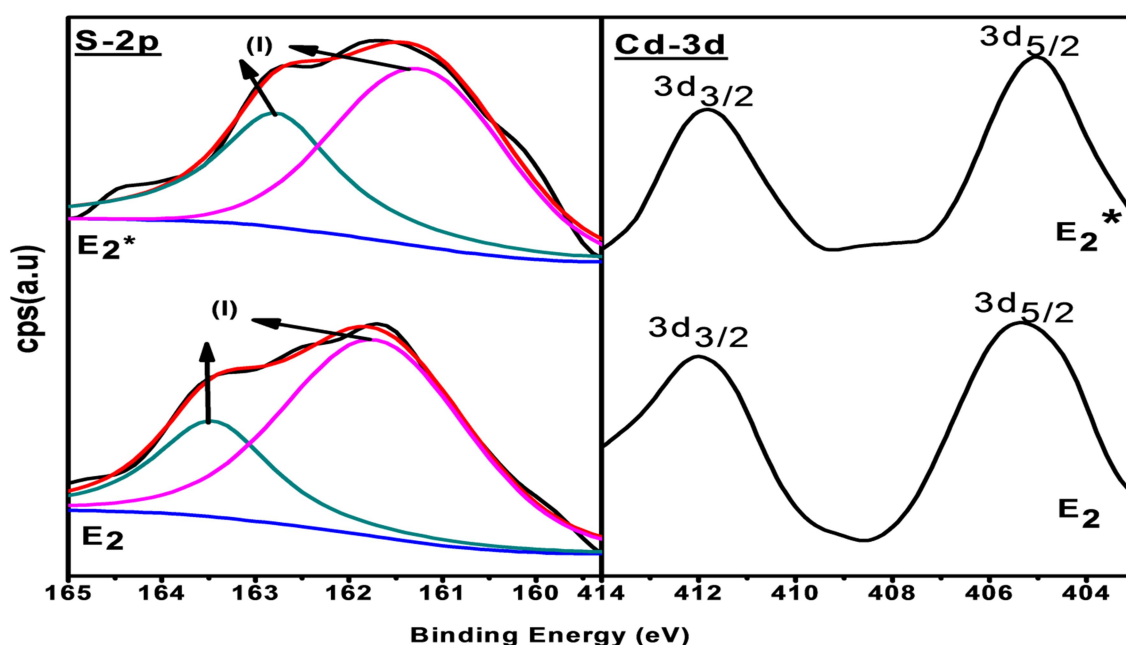
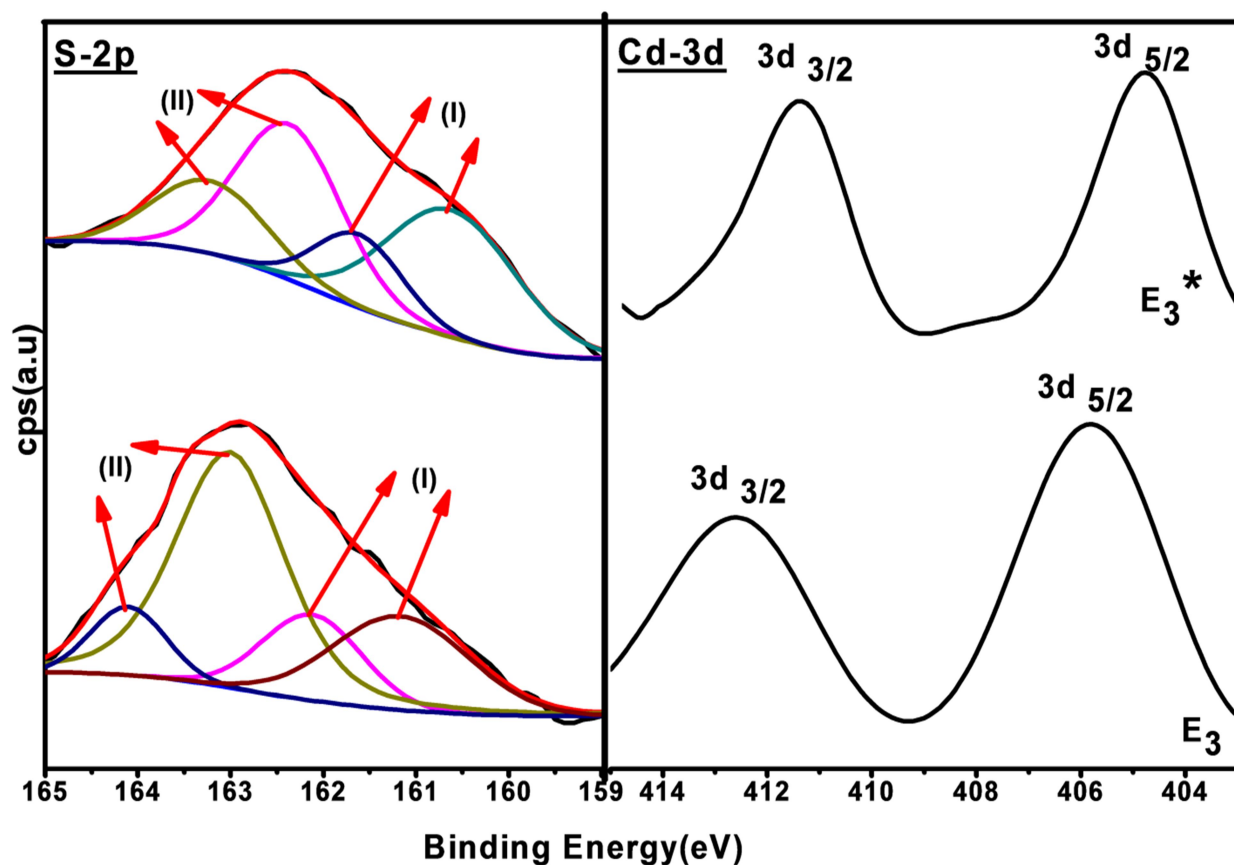


Fig II.3.15(a): XPS spectra of S-2p and Cd-3d for electrode E₂. (* surface etched for 60s)

Table II.3.5: Peak positions of Cd 3d and S-2p in electrodes

Electrode	Peak position of Cd ²⁺		Peak position of S ²⁻				Ratio $\frac{2p_{3/2}(II)}{2p_{3/2}(I)}$
	3d _{3/2}	3d _{5/2}	Doublet (II)		Doublet (I)		
			2p _{1/2}	2p _{3/2}	2p _{1/2}	2p _{3/2}	
E ₂	412.2	405.2	---	---	163.4	161.7	--
E ₂ *	412	405	---	---	162.8	161.4	--
E ₃	412.9	406.6	164.1	163.1	162.1	161.2	2.71
E ₃ *	412.8	406.3	163.6	162.7	162.0	161.0	0.98
E ₄	412.6	405.9	163.9	162.6	161.8	161.0	1.4
E ₄ *	411.5	404.9	163.5	162.2	161.4	160.7	1.14

Fig II.3.15(b): XPS spectra of S-2p and Cd-3d for electrode E₃. (* surface etched for 60s)

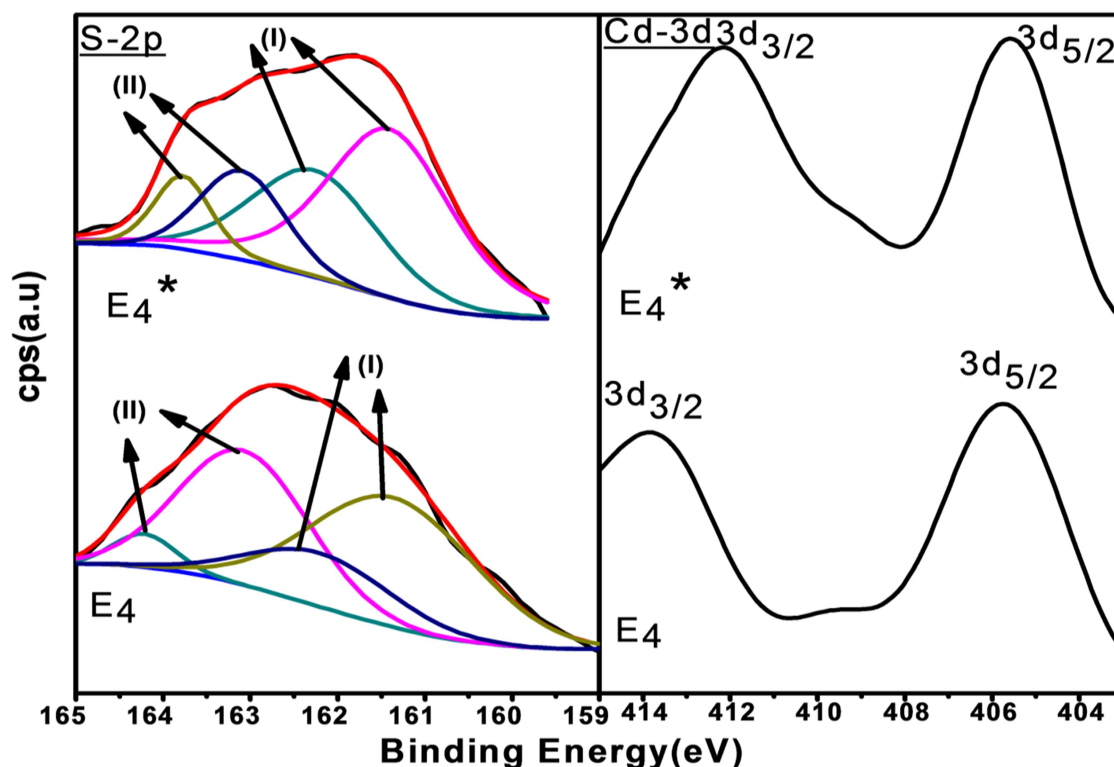


Fig II.3.15(c): XPS spectra of S-2p and Cd-3d for electrode E₄. (* surface etched for 60s)

II.3.5.2.8 Electrochemical Impedance spectroscopy (EIS) studies

EIS measurement was carried out to further investigate interactions and charge transfer between CdS and GO. Results of each electrode as Nyquist plots are shown in Fig II.3.16. In all the Nyquist plots, there are two regions, first a high frequency and second a low frequency region. In the higher frequency region, a semicircle arc and in lower frequency region typically a straight- line appear which correspond to mass transfer resistance [180]. A smaller radius of arc confirms lower interface resistance for charge transfer. It is observed that, with the introduction of GO/rGO in electrodes E₂, E₃ and E₄, Nyquist plots show smaller semicircles i.e, lower interface resistance for the electrodes and subsequently faster charge transfer to the solid-liquid interface for the reaction. It is also observed that E₃ had the least resistance as compared to other catalysts.

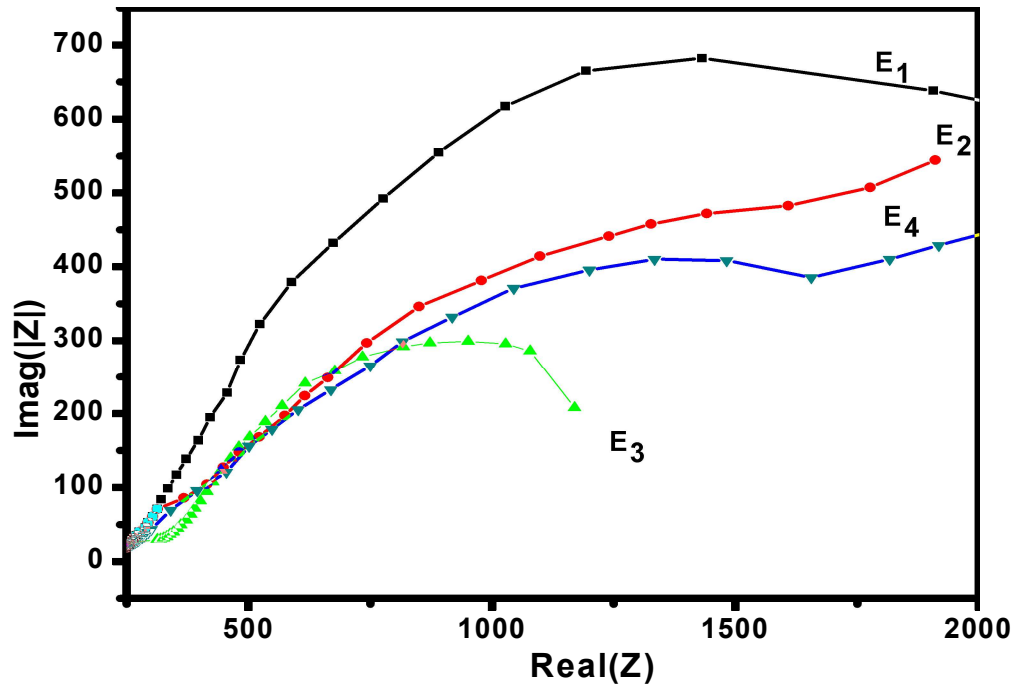


Fig II.3.16: EIS of various electrodes at 0.2 V vs SHE

II.3.5.2.8 Mott-Schottky Analysis

The Mott-Schottky plots of electrodes (E_1 , E_2 and E_3) are presented in Fig II.3.17. Space charge capacitances were measured by varying the potential between -0.3 and 0.7 V versus SHE for electrodes E_1 & E_2 and -0.8 to 0.5 V for electrodes E_3 and E_4 . The frequency was kept constant at 1 kHz. M-S curves ($1/C^2$ vs V) were plotted to establish the type of semi conductivity, charge carrier density and the flat band potential by using equation 1 [181].

$$\frac{1}{C^2} = \frac{2}{\epsilon_0 \epsilon_r e N_A A^2} (V - V_{fb} - KT/q) \quad (1)$$

Where, C is the capacitance of space charge region, e is the electronic charge (1.603×10^{-19} C), ϵ is the dielectric constant of CdS (9.0 Fm^{-1}) [182], ϵ_0 is the permittivity of the vacuum ($8.854 \times 10^{-12} \text{ Fm}^{-1}$), N is the charge carrier density, A is the area of electrode ($25 \times 10^{-8} \text{ m}^2$), V is the applied potential, V_{fb} (V) is the flat band potential

which can be obtained from the Mott- Schottky plot by measuring the intercept of straight line on x-axis, K is the Boltzmann's constant (1.38×10^{-23} J/K), T is the absolute temperature and KT/e is negligible at room temperature and one atmosphere pressure. All the M-S plots had a linear portion and the nature of slopes confirms that these catalysts had p-type semiconductivity. This was also concluded earlier because photo responses on these catalysts were observed with negative biasing.

Flat band potentials and charge carrier densities are given in table II.3.6. It is observed from the table that the flat band potential of E_1 which was unsupported CdS is 0.1. Incorporation of r GO in CdS results into greater flat band potentials. It is observed to be the highest in E_3 (0.42V) which was CdS supported on rGO (10 wt %) and electrochemically reduced in situ. It is known that a higher flat band potential ensures a greater band bending and efficient charge separation. Similarly, it is also observed from the table that the highest charge density is associated with E_3 . This is order to mention that a higher charge density and an efficient charge separation due to a greater band bending shall result into a better photo activity of catalyst owing to a large number of photo generated electron – hole pairs being available for the reaction.

Table II.3.6: Flat band potential and carrier density of catalyst photocathode

Catalyst	$V_{fb}(V)$ vs SHE	Carrier Density(cm^{-3}) N_A
E_1	0.15	1.39×10^{18}
E_2	0.31	1.05×10^{19}
E_3	0.42	3.89×10^{19}
E_4	0.38	3.56×10^{19}

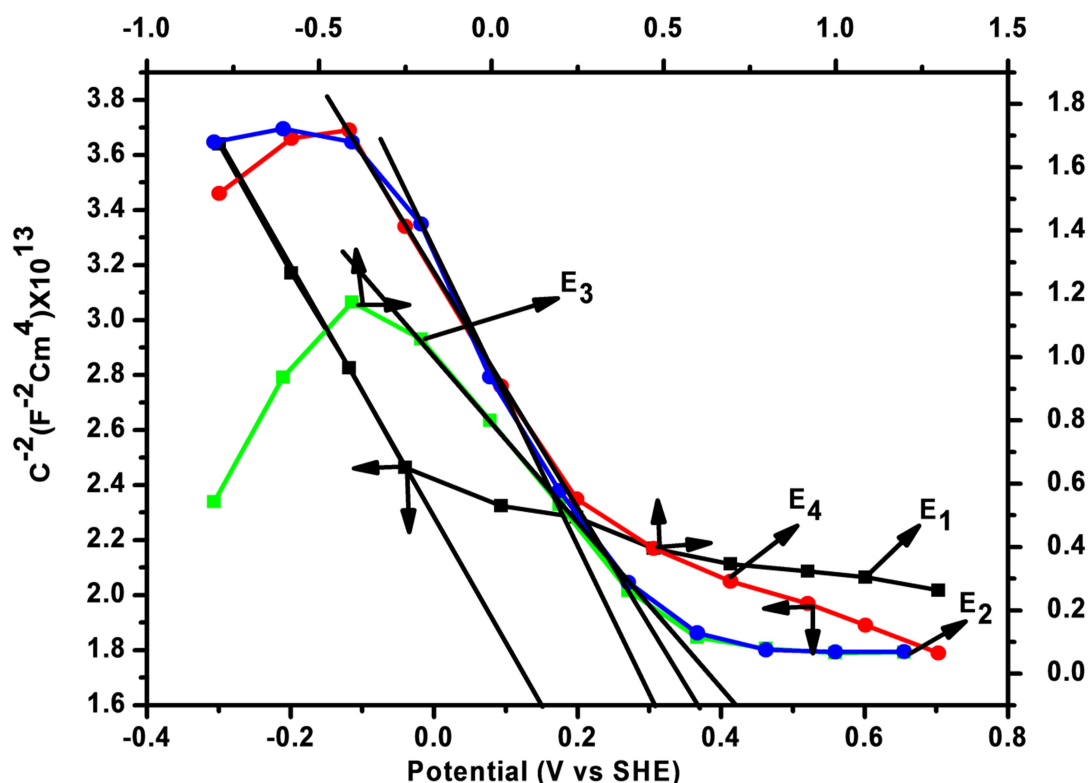


Fig II.3.17: Mott-Schottky plot of catalyst at 1 kHz in S^{2-} and SO_3^{2-} electrolyte

. It should be also mentioned that magnitude of the flat band potential as well as the charge carrier density and the activity follow the same trend, viz, in descending order $E_3 > E_4 > E_2 > E_1$. The same trend was followed by charge separation and charge transfer rate (EIS and PL studies as reported above). It should also be mentioned that there is not much difference in charge carrier densities and the flat band potentials for electrode E_3 and E_4 . In split of that electrode E_3 had much superior activity compared to electrode E_4 . The electrode E_4 had 20 wt% rGO in comparison to 10 wt% rGO in electrode E_3 . It is therefore concluded, that 10 wt% rGO was an optimum loading. An excess rGO had resulted into shielding of CdS which prevented light radiation to interact with CdS causing a decrease in the electron – hole pairs generation rate. On the other hand, a lower weight fraction of GO (less than 10 wt %) results into insignificant chemical

interaction between CdS and rGO which could not effectively prevent charge recombination.

II.3.7 Mechanism

The hydrogen generation using photoelectrocatalytic systems relies on charge carrier generation and its migration route. The charge carrier migration routes depend on the conduction and valence band potentials of the semiconductor catalysts. A schematic diagram illustrating possible pathway of charge transfer in E₃ is shown in Fig II.3.18. Electron – hole pairs are created on the surface of CdS when irradiated. The photo generated electrons migrate to the rGO from the conduction band of CdS and transported to the solid- liquid interface to carry out reduction reaction. It is obvious that a higher rate of generation of electron hole pairs, a lower recombination rate and a faster transfer of electron to the solid-liquid interface shall provide a better activity.

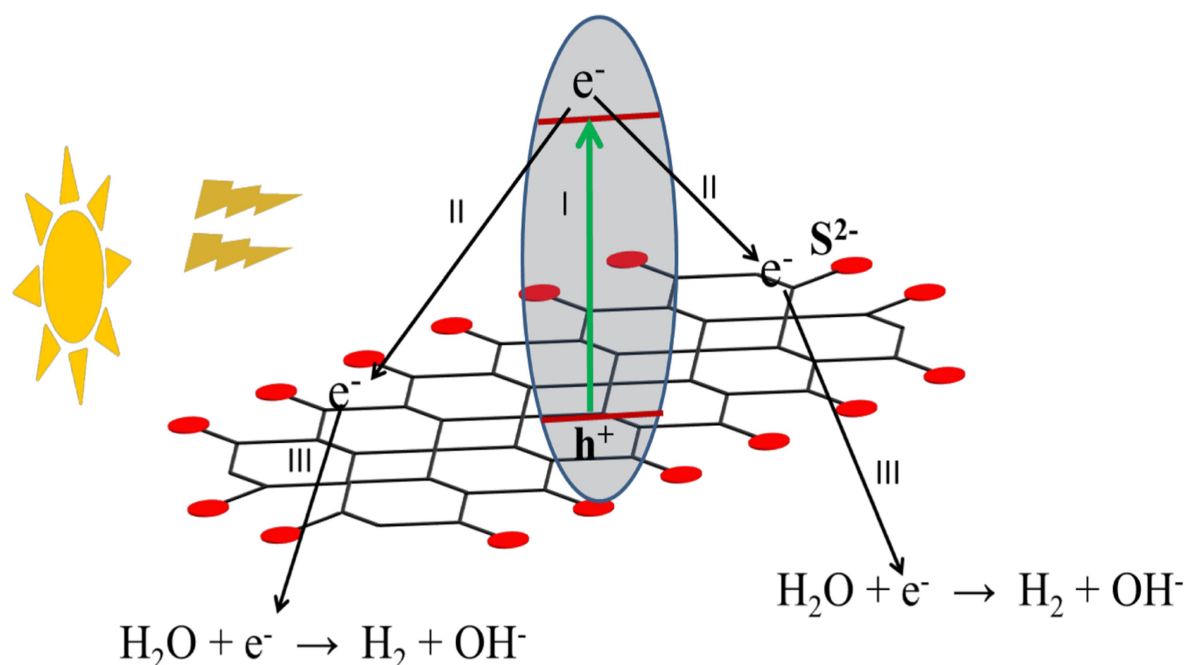


Fig II.3.18: Proposed mechanism of the system

Chapter- III

Section III: Development of rGO supported CdS-MoS₂ photoelectrocatalyst

III.3.1 General

Solar radiation assisted hydrogen generation through water splitting over photocatalytic electrodes has a great potential to become source of sustainable and clean energy. This has motivated intensive research in the area of photo electrochemical electrode development for efficient water splitting [208]. In this direction, initially, titanium dioxide (TiO_2) was reported as photoactive catalysts for water splitting. But its wide band gap seriously undermined the photocatalytic activity in the visible band of light [209]. In particular, chalcogenides are obvious choice due to lower band gap and position of their band edges are suitable for water splitting [141].

Exfoliated molybdenum disulfide (MoS_2) with lower band gap (1.62 eV) and with a proper band edge position is one such material that can produce hydrogen efficiently [210]. Further, layered MoS_2 structure allows better stacking through S layers sandwiched between two Mo layers, held together by a weak van der Waals interaction [211]. This layered structure would facilitate better solar light absorption, enabling higher water splitting activity [212]. Many researchers have worked on MoS_2 as a single semiconductor for water splitting. H. Tributsch [213] was first to synthesize p-type MoS_2 semiconductor and used it as an electrode for photoelectrochemical reaction. Chen et al [214] fabricated unsupported MoS_2 and compared with WS_2 . They observed that MoS_2 was more active catalyst at lower temperatures. Recently, Wu et al [215] observed formation of hydroxyl radical by splitting of water from nanoflower MoS_2 . MoS_2 mainly exists in two different phase, i.e., 1T- MoS_2 and 2H- MoS_2 . 1T phase of MoS_2 shows better activity towards water splitting as compare to 2H phase of MoS_2 . The Mo atoms in 2H- MoS_2 arranged in trigonal prismatic, which show insulating properties [216]. In contrast, in the case of 1T- MoS_2 one S atom is translated with respect to Mo layer, and form octahedral structure around Mo atoms. This translated S

atom provides active site for the chemical reaction [217]. If both of these phases combine together, both electrical conductivity as well as stability are improved synchronously [218]. Recently, liu et al. [219] synthesized mixed phase of MoS₂, and incorporated with TiO₂. They observed that activity towards hydrogen evolution increased two times as compared to TiO₂@Pt. Raghu et al.[220] also reported mixed phase of MoS₂ which was further mixed with a few layers of rGO for potential use as super capacitor. MoS₂ semiconductors when excited by solar light, generated electron-hole pairs. With bare MoS₂ there is a greater possibility of recombination of these charges which results into a lower efficiency [221]. If MoS₂ is combined with graphene oxide (GO) or reduced graphene oxide (rGO) or other semiconductors photo-generated electrons may be transferred from the conduction band of one semiconductor to that of another and possibilities of recombination gets reduced. GO/rGO is the obvious choice due to well – defined lamellar structure similarly to MoS₂ and also may serve as an excellent carbon host to modify structural stability, improve the electronic conductivity and trigger enhanced reaction kinetics of MoS₂. Recently, Yu et al.[222] synthesized rGO supported MoS₂ and reported efficient hydrogen production by photocatalytic process due to synergetic effect of rGO and MoS₂. You et al. [223] also prepared three dimensional MoS₂/rGO foam based sulfur cathode with improved electrochemical performance for lithium sulfur batteries. They attributed this to the electron transfer from 2H MoS₂ to 1T MoS₂ in the MoS₂/rGO composite during cell charge/ discharge process. Zhang et al. [224] also synthesized MoS₂ supported on rGO nanoflakes and reported enhanced electrochemical performances due to synergetic effect of rGO with MoS₂.

It has been reported that optical properties of MoS₂ changes when it is combined with other semiconductor. Researchers have incorporated many co-catalyst with MoS₂ such

as WS₂ [225], Ag nanoparticle [226], Ni-Co [227, 228] etc which resulted into enhanced efficiencies towards water splitting. Researcher have also reported incorporation of CdS with MoS₂ and they have observed that heterojunction formed between these two catalysts, improved activity towards hydrogen evolution [229]. Han et al [230], have also reported formation of core shell nanowire formed between CdS and MoS₂ and for improved hydrogen evolution under visible light.

The literature reports intensive work on pristine MoS₂ and binary system of semiconductor, which was able to enhance activity towards water splitting. However there are few works on ternary system of semiconductors consisting of MoS₂. Zhang et al [231], synthesized MoS₂ with Fe₂O₃ and CdS by hydrothermal process and they reported high efficiency towards water splitting due to proper charge transfer in ternary system. It has been reported that ternary system of mixed phase of MoS₂ with Pt and TiO₂ improved the efficiency towards hydrogen evolution due to exposed active edge sites of MoS₂ sheets [232]. However, still more attempt are needed to develop an efficient ternary system, so that charge recombination reduces and produces hydrogen efficiently. Ternary system of MoS₂ with rGO-CdS was reported with a high efficiency towards water splitting by photocatalytic process due to formation eutectic cluster which facilitated separation of photo generated charge. [233]. It has been reported that under visible light, CdS-MoS₂-rGO reduces 4-nitrophenol with high efficiency than bare CdS due to greater charge transfer by semiconductor [234]. Li et al. have reported synthesis of MoS₂-CdS-rGO composite by photo deposition techniques [235]. It involved multiple reactions in contrast to the commonly reported hydrothermal technique.

Table III.3.1: Performances of catalysts reported are summarized in below:

Material	Substrate Used	Light Source	Electrolyte	Result (mA/cm ²)	References
CdS/1T-MoS ₂ /GO	ITO	300 W Xe	0.1M Na ₂ SO ₄	57	Zhao et al (2020)
CdS/MoS ₂ /GO	NA	NA	0.5M H ₂ SO ₄	10	Cheng et al (2020)
CdS/MoS ₂	ITO	300 W Xe	0.1M Na ₂ SO ₄	2.2	Xu et al (2019)
CdS/1-TMoS ₂	ITO	100 W Incandescent Lamp	0.5M Na ₂ SO ₄	227	Lian et (2019)
CdS/1-TMoS ₂	ITO	100 W Incandescent Lamp	0.5M Na ₂ SO ₄	165	Lian et (2019)
CdS/MoS ₂	FTO	300 W Xe	Na ₂ S (0.25 M) and Na ₂ SO ₃ (0.35 M)	15.2	Zheng et al (2019)
CdS/MoS ₂	ITO	Without Light	0.5M Na ₂ SO ₄	25	Liu et al (2019)
GR/CdS/MoS ₂	FTO	300 W Xe	0.2M Na ₂ SO ₄	24	Yang et al (2015)
GR/CdS/MoS₂	Carbon Paper	10W LED	Na₂S (0.25 M) and Na₂SO₃ (0.35 M)	24	Present work

Herein we report hydrothermal synthesis of MoS₂, rGO-MoS₂, CdS-MoS₂ and CdS-MoS₂ supported on rGO catalysts. Electrodes prepared by using rGO-CdS-MoS₂ catalyst demonstrated superior water splitting efficiency. Catalysts were characterized by FTIR, XRD, HRSEM, HRTEM DRS, XPS and EIS etc. The micro structure, as determined by characterization techniques, has been correlated with the preparation

variables and the photo activity. Formation of heterojunction and the mixed phase of MoS_2 have been attributed to the superior activity.

III.3.2. Experimental

III.3.2.1 Preparation of Electrode

(a) Graphene Oxide (GO)

The modified Hummers method[236] was employed to prepare graphene oxide (GO). In a typical reaction, 2 g of graphite flakes were added slowly to 46 mL of 98% H_2SO_4 with a constant stirring. The addition rate was maintained such that the temperature always remained below 283 K. Subsequently, 8 g of potassium permanganate powder was added to the reaction mixture with stirring. The reaction mixture was then allowed to equilibrate to the room temperature with continuous stirring. Thereafter, the resulting mass was kept inside a water bath for 1h at 308 K and 100 mL of distilled water was added thereafter. Subsequently, 20 mL of H_2O_2 (30%) was added to dissolved residual permanganate was dissolved. Finally, coloured suspension was filtered and washed with 1 M HCl and subsequently with distilled water. The residue was dried in oven at 333 K for 3 days and used as and when required.

The graphene was used as precursor to support MoS_2 and CdS. Since, catalyst were prepared by hydrothermal technique, we anticipated that during the hydrothermal process GO would be reduced to rGO. The characterization results reported below confirms our assumption.

(a) Catalyst 1

In a typical catalyst synthesis, 3.2 g of ammonium heptamolybdate was dissolved in 40 mL of double distilled water. Thiourea (6.85g) was subsequently added to the solution and stirred for 1 h to get a clear solution. The solution was transferred into a 50 mL

Teflon lined stainless steel autoclave and kept at a temperature of 473K for 24h. It was then allowed to cool down naturally to room temperature. The obtained product was then washed with 200 mL double distilled water and subsequently with 50 mL ethanol and dried at 343K in vacuum oven for 6h.

(c) Catalyst 2

For the preparation of catalyst 2, the required amount of graphene oxide (GO) was mixed in 40 mL of double distilled water and sonicated to 30 min. After sonication, prerequisite amount of ammonium heptamolybdate and thiourea were mixed with the suspension of GO and placed in autoclave. Rest of the process was same as for catalyst 1. The final composition was rGO: MoS₂ in the weight ratio of 1:9

(d) Catalyst 3

The catalyst 3 was synthesized by dissolving prerequisite amount of CdSO₄ and 3.2 g of ammonium heptamolybdate in double-distilled water to obtain CdS-MoS₂ in weight ratio of 1:1 in the catalyst. After that, 9 gm of thiourea was added in that mixture was stirred and again stirred for 1h. The solution was then transferred into 50 mL Teflon lined stainless steel autoclave and rest of the process was same as for catalyst 2.

(e) Catalyst 4

Catalyst 4 was synthesized by suspending 0.5g of GO in 40 mL of double distilled water and sonicating it to 30 min. Rest of the synthetic processes were identical to the synthesis of catalyst 3. The final composition of the catalyst (rGO : CdS : MoS₂) 0.1:1:1 by weight.

(f) Photocathode Fabrication:

Photoelectrodes (PC) were fabricated on Toray carbon paper (TCP) of 0.5 cm × 0.5 cm dimension as mention earlier section I and II. In a typical fabrication, 50 μ L of nafion

solution was mixed with 1 mL of N, N –dimethylformamide (DMF). 2.00 mg of catalyst was added to this solution under constant sonication for 30 min to obtain homogenous mixture. 20 μ L of this mixture was drop casted on the TCP and kept in ambient atmosphere for some time for the evaporation of the solvent. During the fabrication the catalyst loading was kept at 0.15 mg/cm². For the ohmic contact, prior to electrode fabrication a copper wire was pasted by silver glue on the back portion of the TCP. An epoxy resin was coated on the back surface and also all the edges of the electrode, so that electrochemical reaction could take place only from the surface containing catalyst.

A total of 4 electrodes are prepared by using respective catalyst. A summary of catalyst and electrodes studied in the present work is given in Table III.3.1

Table III.3.2: Summary of Catalysts/electrodes prepared in present study

Catalysts/Electrodes	Remarks
Cat-1	Unsupported MoS ₂
Cat-2	rGO supported on MoS ₂
Cat-3	Unsupported CdS- MoS ₂ composite
Cat-4	rGO supported CdS- MoS ₂ composite
E ₁	Electrode prepared from Cat-1
E ₂	Electrode prepared from Cat-2
E ₃	Electrode prepared from Cat-3
E ₄	Electrode prepared from Cat-4

III.3.3 Activity of Photoelectrodes

Photoelectroactivity of photoelectrodes also studied in same experimental set – up as mention in section I.3.3

II.3.4 Characterization Techniques

Catalyst and electrodes were characterized by FTIR, XRD, HRSEM, HRTEM, DRS, XPS, EIS and Mott – Schottky analysis. Detail of these characterization tools, which is used in this section, also described in section I.3.4

III.3.5 Results and Discussion

III.3.5.1 Photo-electrochemical activity

The water splitting performance was ascertained by carrying out experiment under dark and light conditions and recording the current density (J) with respect to applied potential (V) for each photoelectrode. The potential range of -0.6 to 0.6 V with respect to normal hydrogen electrode (NHE) was applied. The results are shown in Fig III.3.1. It is observed from the figure that the dark current (in absence of light) was negligible for all catalyst in the complete range of voltage, studied. Small currents may be due to presence of surface states in the semiconductor photocatalysts. It is observed that in presence of light the current density increased with negative biasing. Effect of light was not observed with positive biasing (up to 0.6 V vs SHE). It means depletion layer is formed in the photoelectrode near interface with negative biasing. Whereas, with positive biasing, accumulation layer forms and hence, no effect of light is observed. Such characteristics confirm that all the photoelectrode were having p-type semiconductivity with positive holes being majority charge carriers. With the p-type behaviour, the photoelectrodes behaves like cathode whereas the Pt counter electrode work as anode. 5.8 mL and 0.6 mL of gases evolved at cathode and anode respectively during 3h of experiment. The analysis of gases by gas chromatography confirmed that the gas evolved at cathode was hydrogen and that of anode was oxygen. It is further observed that corresponding to the volume of hydrogen evolved, the oxygen should

have been 2.9 mL. However, the volume of oxygen gas evolved was very negligible and non-stoichiometric. Since other ions S^{2-} and SO_3^{2-} were present in the electrolyte, we conclude that the principle anode reaction was



and the cathodic reaction (in alkaline medium)



Whenever visible light was applied on the semiconductor, electron-hole pairs get generated. The electrons reduces the water molecule under negative biasing and produces hydrogen and hole generated was consumed by hole scavenger (S^{2-} & SO_3^{2-}).

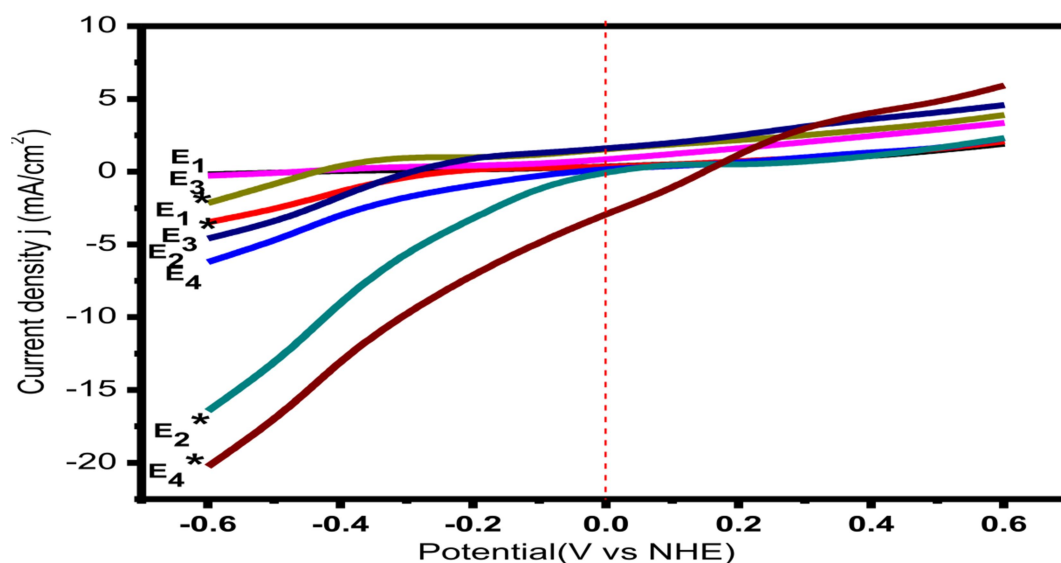


Fig III.3.1: Result of Linear Sweep Voltammetry in Dark and light (marked as *) in S^{2-} and SO_3^{2-} electrolyte

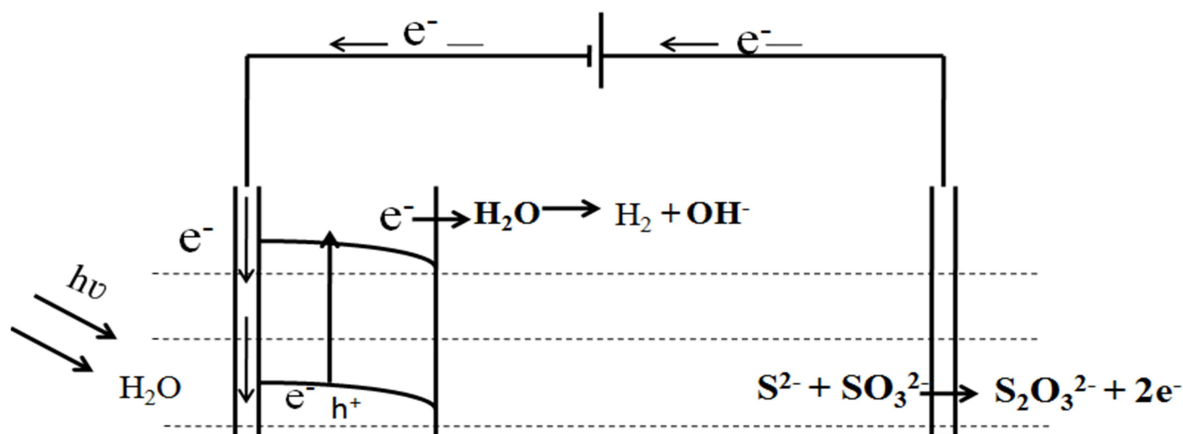


Fig III.3.2: Schematic diagram of the electrochemical process

A schematic diagram of the electrochemical process taking place inside the cell is shown in Fig III.3.2. Further, photocurrent densities of 20.2, 16.4, 3.4 and 2.1 mA cm⁻² were obtained for Cat-4, Cat-2, Cat-3 and Cat-1 respectively at -0.6V (w.r.t SHE). Current densities can't be compared from the reported values in the literature because each investigation has used a light source of different intensity and wave length. In the present study a diffuse light of low wattage was used.

III.3.5.2 Characterization studies

III.3.5.2.1 FTIR studies

The functional groups present in the catalysts were confirmed with the Fourier transform infrared spectroscopy (FTIR). Results are shown in Fig III.3.3. The Cat-1 (unsupported MoS₂) revealed major absorption peak at ~ 431 cm⁻¹ which has been assigned to Mo-S bond stretching [237]. The Mo-S peak was present in all catalyst, however it has shifted with respect to unsupported MoS₂ (431 cm⁻¹). This peak appears at 401, 409 and 425 cm⁻¹ for cat-4, cat-2 and cat-3 respectively. Coupling of vibration is a common phenomenon which cause shift in peak positions. Further the shift is almost negligible in cat-3 which was a composite of CdS and MoS₂. On the other hand, the

shifts are $\sim 30 \text{ cm}^{-1}$ in catalyst-2 and 4. Therefore, we attribute the observed shifts primarily to the coupling of Mo-S and C-S vibrations. It is order to mention that electrodes prepared by cat-2 and cat-4 showed excellent activities. Earlier works reported electronic interactions between C and S through π^* orbital of GO/rGO and n orbital of S of CdS [151, 238]. We expect similar interaction between MoS_2 and GO/rGO electrodes prepared by cat-2 and cat-4. Further, the FTIR peaks corresponding to $\sim 526, 524, 531$ and 530 cm^{-1} may be attributed to the $(\text{S-S})^{2-}$ bond [239]. Peak $\sim 620 \text{ cm}^{-1}$ corresponds to the Mo-S bond [240]. Literature also reports $\sim 630 \text{ cm}^{-1}$ peak corresponds to Cd-S bond [241].

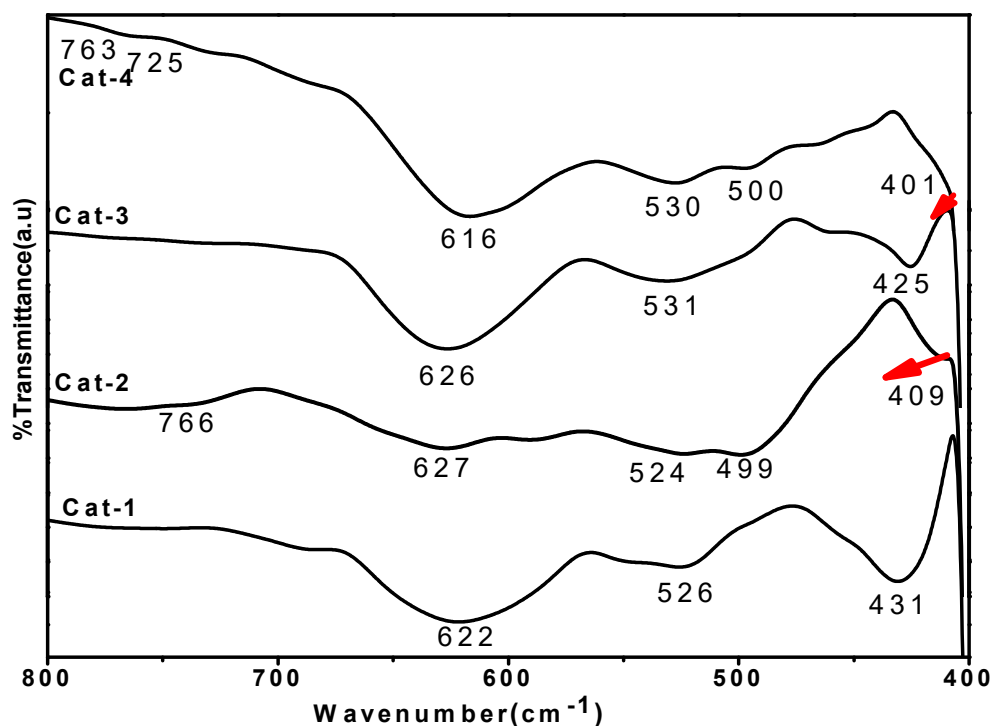


Fig III.3.3: FTIR spectra of catalysts

Therefore, increase in the peak intensity of MoS_2 at 620 cm^{-1} , when CdS was incorporated, may be due to superimposition of peaks at $\sim 600 \text{ cm}^{-1}$. Weak peaks are

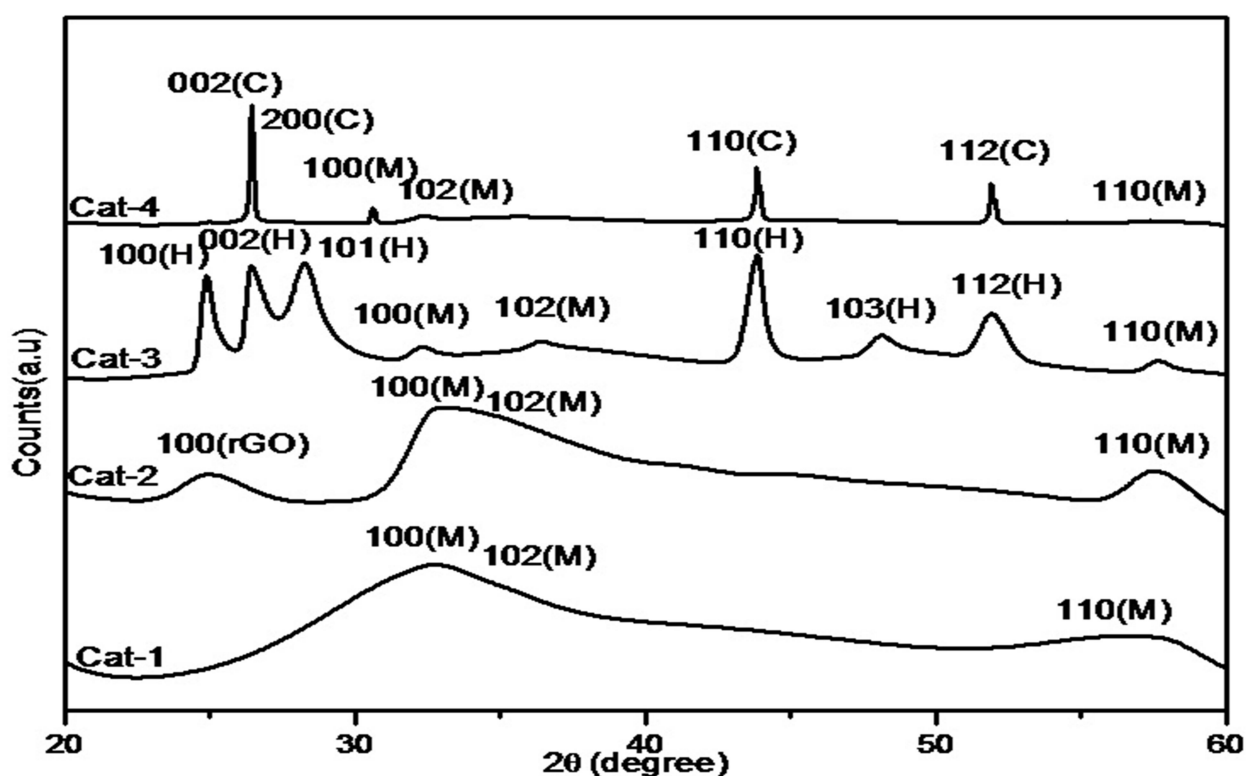
observed at 763 cm^{-1} , in cat -2 and 725 and 763 cm^{-1} in cat-4 which may be attributed to C-S bond. C-S stretching is confirmed by presences of peaks in the range of $570\text{-}720\text{ cm}^{-1}$ [242-244]. The possibilities of C-S bond formation between C of GO/rGO and S of MoS_2/CdS has been described above.

III.3.5.2.2 X-Ray Diffraction (XRD) studies

Various phases and crystallinity of the catalysts were determined by x-ray diffraction spectra (Fig III.3.4). The XRD patterns of all the catalyst revealed diffused peaks of MoS_2 at $2\theta = 32.8, 35.08$ and 57.66° . The d values are $2.72, 2.56$ and $1.59\text{\AA}$ corresponding to (100), (102) and (110) planes respectively, of hexagonal phase of MoS_2 (JCPDS PDF no. 65-1951). MoS_2 is reported to have a layered structure [245-247]. Therefore, broadness of XRD peaks indicates formation of thin sheets of MoS_2 . The characteristic peak of rGO at $2\theta = 24.8^\circ$ corresponding to (002) plane [248] is also observed in cat-2 and 4. It confirms that GO was reduced to rGO by the hydrothermal process during the catalyst preparation as mentioned earlier in section: III.4.2.2 catalyst preparation Cat-3 and cat-4 exhibit intense peaks of CdS. Both the catalysts contain MoS_2 and CdS. In addition cat-4 also contains rGO. The intense CdS peaks indicate that CdS was high crystalline. Further, analysis of cat-3 revealed presence of (002), (110) and (112) plane, of CdS corresponding to the hexagonal phase of CdS [249]. On the other hand cat-4 comprising of $\text{MoS}_2\text{-CdS}$ supported on rGO, CdS was present in the cubic phase as well as the hexagonal phase.

It is order to mention that both cat-3 and cat-4 were prepared by same method and contained CdS and MoS_2 except that cat-4 also contained rGO. The above results show that, when MoS_2 ads CdS are synthesized together with CdS in presence of rGO (cat-4), CdS was largely in cubic phase. It has been reported earlier that lowering of ionization

of Cd and S atoms results in formation of cubic phase [169]. Therefore, we visualized that an electronic interaction between species may have resulted in lower ionization of Cd and/or S causing the formation of CdS in cat-4. It has been also reported [250] that, owing to greater internal electric field and lower effective mass the hexagonal phase of CdS is more active photocatalyst. However, we have reported that cat-4 (containing largely cubic CdS) is more active compared to cat-3 (containing hexagonal CdS). It is therefore, concluded that presence of rGO in cat-4 has resulted into a higher activity offsetting the loss due to presence of less active cubic phase of CdS.



FigIII.3.4: XRD spectra of catalysts C: Cubic phase CdS H: Hexagonal phase CdS M: hexagonal MoS₂

The d values of (102) peaks of MoS₂ were calculated and were found to be at 2.56, 2.7, 2.57 and 2.63 Å for cat-1 to 4 respectively. It is observed that as compared to cat-1 the d values were higher for other catalysts which contained CdS and/or rGO. It means the

incorporation of CdS and rGO has resulted into exfoliation to S-Mo-S layers by intercalation of rGO/CdS between the layered structures of MoS₂. Such an exfoliation has also been reported by Khawnla et al. in syntheses of MoS₂ modified carbon nanosphere [240, 251].

III.3.5.2.3 Morphology studies

HRSEM

Morphological variations in catalysts were analyzed by the high resolution scanning electron microscopy (HRSEM) and the results are presented in Fig.III.3.5. It is seen that all the catalyst exhibit nanoflake type morphology forming many nano petals with crumples and ripples. The lateral sizes of flake vary between 16 and 25 nm. In comparison to cat - 1 and 3 & cat - 2 and 4, this contained rGO in addition to MoS₂ have slightly different morphologies.

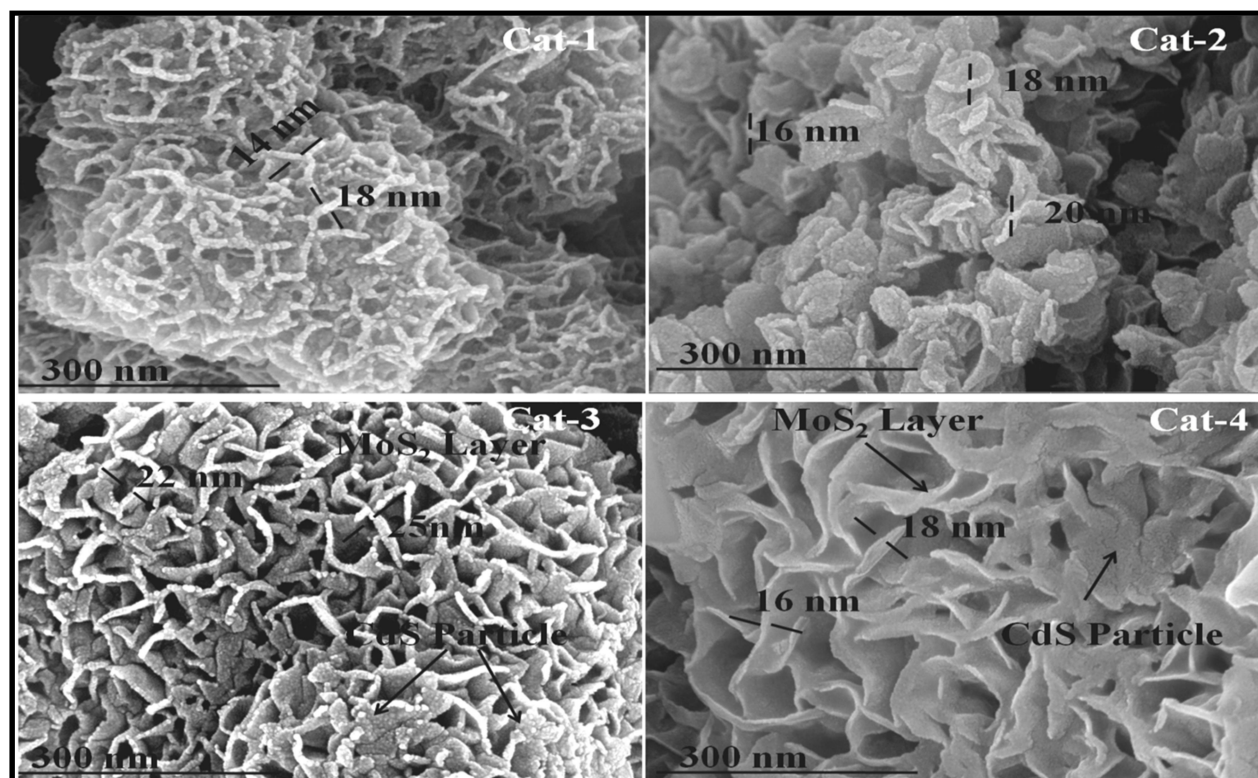
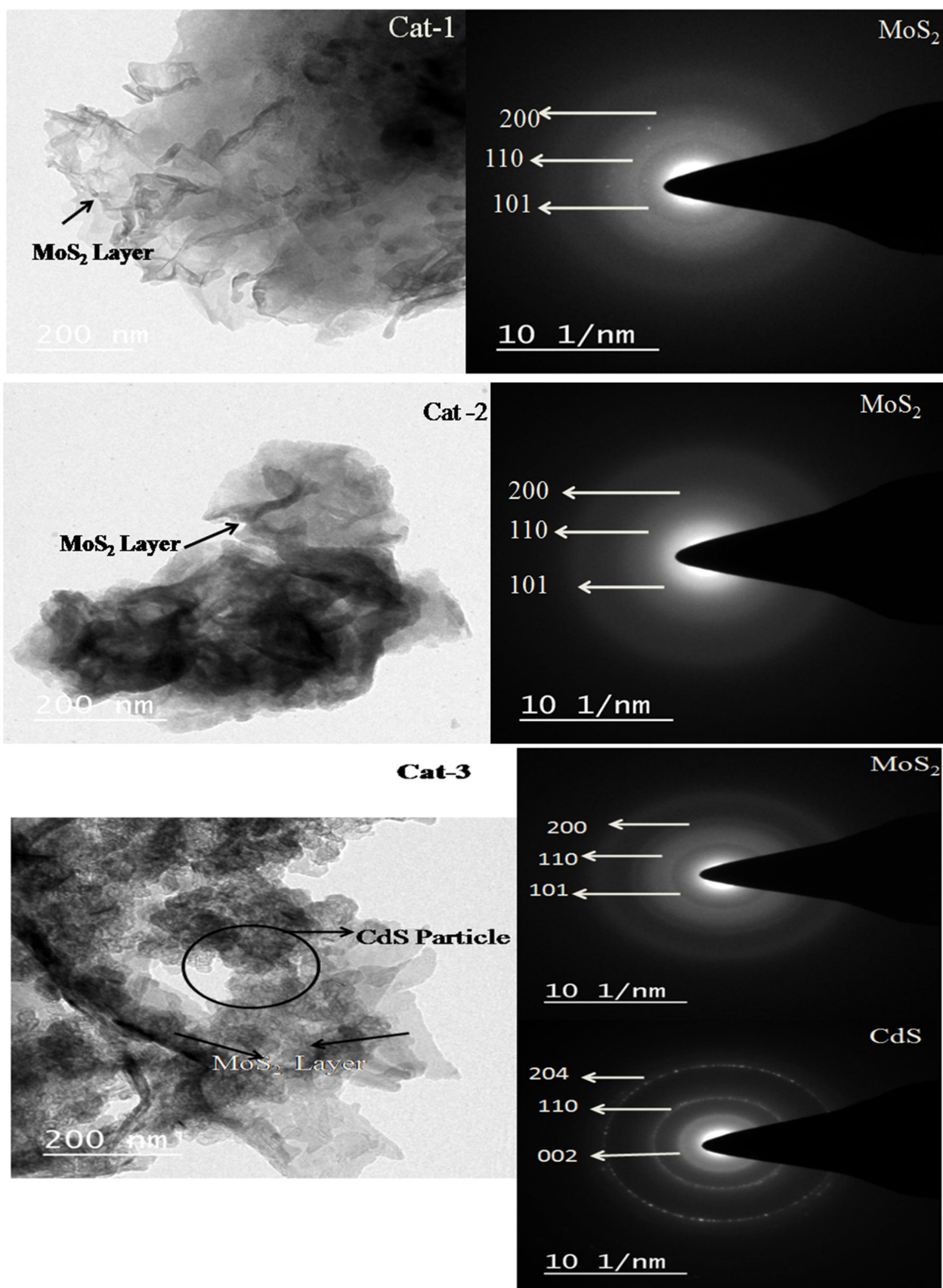


Fig III.3.5: HRSEM images of catalysts

The orientations of layers are random. Since, both MoS₂ and rGO have layered structures, and they have made flakes. It is anticipated that the uniform dispersion with random orientation of rGO in MoS₂ has resulted into an intimate contact between the two leading to chemical interaction and improved photoactivity. Formation of an intimate contact between rGO & MoS₂ leading to a chemical interaction has been reported in the literature [252-254]. Further, Cat- 2 and 4 contains CdS also, CdS particles are seen on the surface of flakes. The XRD data as discussed above indicated exfoliation of layers of MoS₂, therefore, CdS particles may also have been intercalated between the layers of MoS₂.

Transmission Electron Microscopy (TEM)

TEM images and SAED pattern of the catalysts are shown in Fig III.3.6. Similar to HRSEM results, layers of MoS₂ are present in all catalysts. In addition, in catalyst 2 and 4 (which contain rGO also), rGO is also present as layers. The layers of rGO & MoS₂ are rather indistinguishable. The CdS are also seen in catalyst 2 and 4. The Particles are largely spherical and embedded in MoS₂ layers. The XRD data, HRSEM and TEM analyses confirm that layers of MoS₂ and rGO (in cat-2 and 4) form nanopetal like structure in which CdS nanoparticles are embedded in between the nanopetals. The SAED patterns obtained for MoS₂ were found to be rather diffused. Crystal planes were identified which correspond to the hexagonal phase of MoS₂ confirming the result of the XRD analysis. The SAED of CdS in catalyst-2 gave d-spacing 1.24, 2.06 and 1.77Å which correspond to (212), (110) and (200) planes of the hexagonal phase. In contrast, the SAED of cat-4 d-values of 2.06, 2.95 and 3.25Å were obtained which correspond to the cubic phase of CdS and matches to results of XRD analysis.



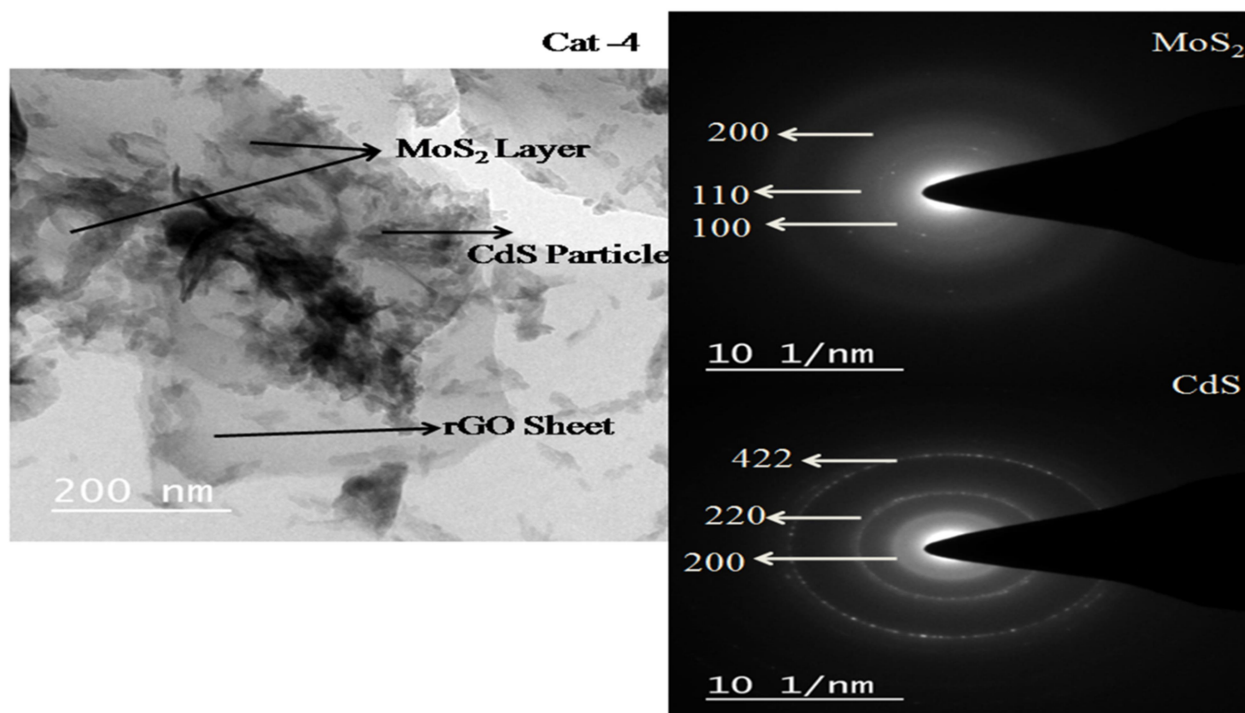


Fig III.3.6: TEM and corresponding SAED of catalysts.

On the basis of HRSEM, TEM and XRD analyses schematic diagram of catalyst preparation is shown in the Fig III.3.7. It is in order to mention that chemical interaction of sulphur atom may be interacted with Mo sheets, Cd atoms and rGO sheets as seen in figure. Cd atoms intercalated in between the layers of Mo and on the surface of rGO sheets.

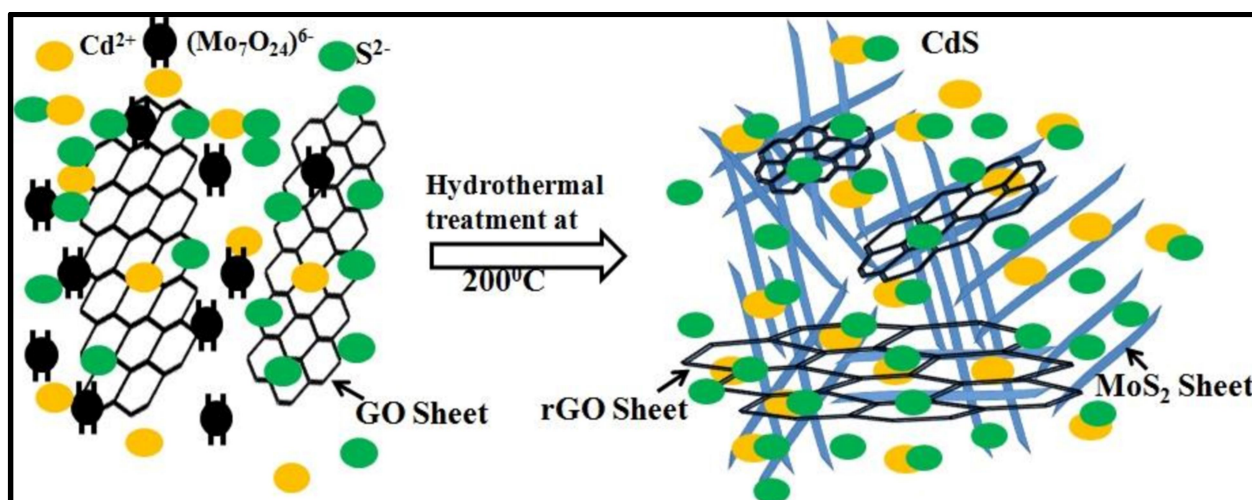


Fig III.3.7: Schematic diagram of catalysts preparation

III.3.5.2.4 Diffuse Reflectance Spectroscopy (DRS) Studies

Light absorption characteristics of catalysts were studied by diffuse reflectance spectroscopy (DRS) in the wave length range between 400 and 700 nm. Results are presented in Fig III.3.8. It is observed that nature of absorption spectra remains invariant to catalyst investigated. All the catalysts absorb light in the visible region.

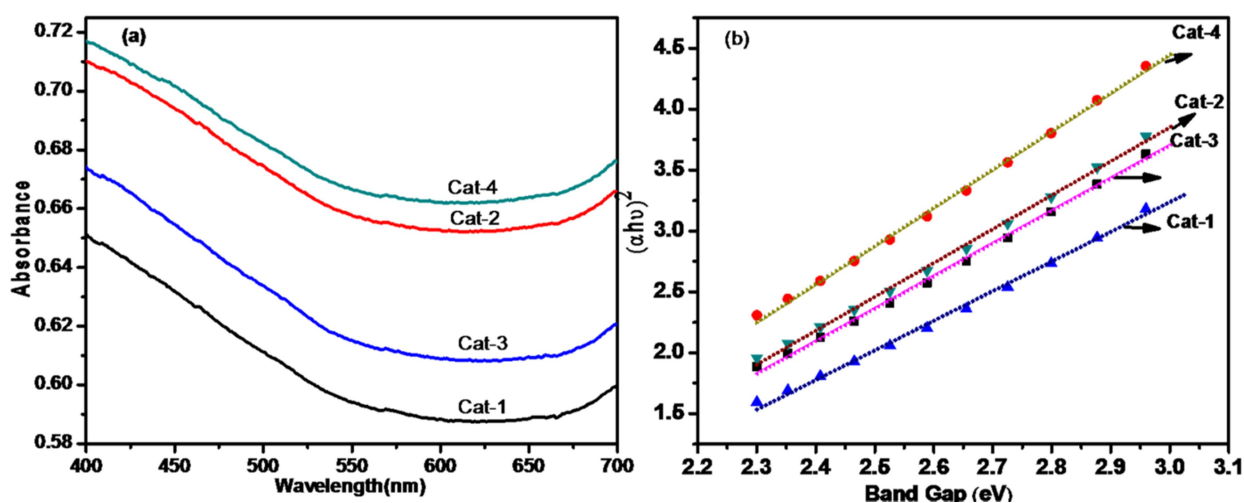


Fig III.3.8: DRS and Tauc plot of catalyst

Further, it is also observed that on incorporation of rGO in MoS₂ (Cat-2 and Cat-4), light absorption in visible region improves substantially. Similar observations have been also reported by other groups [255, 256].

It is clearly observed that though cat-3 and 4 contained CdS the absorption edge of CdS was not observed. The band gap for each catalyst was evaluated using Tauc plot. $((\alpha h\nu)^2 \text{ vs eV})$ as shown in Fig III.3.8 (b). The intercept at the x-axis provided the band gap as given in Table III.3.2. The results show that the band gap for cat-2 and cat-4 has decreased slightly. These two catalyst contained rGO. In a recent studies, enhanced absorption and narrowing of band gap of semiconductor have been reported, when these semiconductor form composite with rGO [234, 257, 258]. These studies have been

concluded that the higher absorption was due to increment in surface electric charge of semiconductor due to rGO and stronger coupling between rGO and semiconductor. Further, due to interfacial interaction between a semiconductor and rGO, facilitating absorption of light of longer wavelength localized states within the band gap.

Table III.3.3 Band gap of photocathodes

Serial No.	Catalyst	Band Gap (eV)
1	Catalyst 1	1.67
2	Catalyst 2	1.59
3	Catalyst 3	1.67
4	Catalyst 4	1.60

In view of the above reported works and the analyses of FTIR and XPS (discussed below) results, it is concluded that electronic interaction between rGO and MoS₂ exists in cat-2 and cat-4 which has resulted into a better photo response and narrowing of the band Gap. Both these effects should results into a better photo activity of catalysts which have been actually observed in the present study.

III.3.5.2.5 X-Ray Photoelectroscopy (XPS) studies

Results by X-Ray Photoelectroscopy (XPS) are presented in Fig III.3.9 ‘a’ and Fig III.3.9 ‘b’. XPS spectra were referenced against C 1s peak at 284.6 eV. These were deconvoluted using the Lorentzian- Gaussian method [173]. Deconvoluted peaks are also shown in the Fig III.3.9 (a, b). The peak positions are given in Table III.3.4a, III.3.4b & III.4.4c for Mo, S and Cd, respectively. The XPS reveals that the microstructures present on the surface of the catalyst are quite different from those of the bulk. The XRD results have shown that Mo was present in all catalyst as MoS₂ in hexagonal phase. On the contrary, XPS result shows that there are three distinct phases of Mo present on the surface, viz, Mo⁴⁺ (hexagonal phase, 2H), Mo⁶⁺ and Mo⁴⁺ (Trigonal phase, 1T). Earlier workers [259] have reported binding energies of 232.8 & 229.5 eV

for $3d_{3/2}$ & $3d_{5/2}$ for Mo^{4+} peaks of hexagonal phase. Similarly these two peaks are reported to appear at 232.2 & 228.9 eV for Mo^{4+} (Trigonal phase) [223] and 235.8 & 232.7 eV for Mo^{6+} [260]. On the comparison with the reported values, the first doublet (I) has been assigned to Mo^{4+} (1T). The second doublet (II) has been assigned to Mo^{4+} (2H) and the third doublet (III) has been assigned to Mo^{6+} . Ratios of peak intensities of $3d_{5/2}$ peaks of Mo^{4+} (1T) vs Mo^{4+} (2H) and Mo^{6+} vs Mo^{4+} (2H) are also given in Table 3a. It is observed that Mo^{4+} (1T) phase was not observed in Cat-1 (unsupported MoS_2). However, this phase is there on the surface of Cat-2 which was MoS_2 supported on rGO. It is further observed from the table Mo^{4+} (1T) phase becomes more prominent when CdS was also added to catalyst (cf Cat-3 & Cat-4). Similarly, the relative intensities of Mo^{6+} are seen to be higher when in catalyst contained rGO & CdS in comparison to unsupported MoS_2 . Mo^{6+} species may be due to partially oxidized MoS_2 complexes [261]. However, the intensity of Mo^{6+} is observed to be high when rGO was incorporated into MoS_2 (Cat-2 and Cat-4). This observation hints at interaction of MoS_2 with the oxygen atoms presents on rGO. It is in order to mention that the presence of mixed phase of Mo has also been reported in MoS_2 modified carbon nanosphere [262].

The spectra of Cd^{2+} and corresponding peak values are shown in Fig III.3.9b and Table III.3.4.c respectively. The literature reports the BE of Cd^{2+} in pure CdS at 405.3 ($3d_{5/2}$) and 412.0 ($3d_{3/2}$) eV [263]. A comparison shows that these values are slightly higher at 405.8 and 412.3 eV, respectively for Cat-2 which was MoS_2 -CdS. It means that the electronic density of Cd has decreased when in presence of Mo. Since Mo is more electronegative compared to Cd such a charge distribution may be feasible. Similar phenomena have been reported in the literature [151, 264]. In case of Cat-4 which also contained rGO the peaks of Cd^{2+} appears at 411.9 ($3d_{3/2}$) and 405.1 ($3d_{5/2}$), respectively.

Since, rGO contain many electronegative groups on the surface, therefore, redistribution of charge density on Cd^{2+} is feasible.

The XPS spectra of S 2p in cat-1 have only one doublet with $2p_{1/2}$ & $2p_{3/2}$ at 162.2 and 161.1 eV. The Literature reports [265] S^{2-} peaks at 162.6 & 161.4 eV for MoS_2 (2H) and 162.5 & 161.3 eV for CdS. The reported binding energy values of S^{2-} in cat-1, are matches with those of MoS_2 (2H). However, it is observed that for other catalysts a second doublet also appears at lower binding energies (cf Fig III.3.9a and Table III.3.4b). These catalysts had the trigonal phase of MoS_2 (1T) also. The corresponding S^{2-} peaks in MoS_2 (1T) are reported to appear at lower binding energies of 162.0 and 160.8 eV respectively. Therefore the doublet appeared at lower binding energies in Cat-2 Cat-3 and Cat-4 is assigned to S^{2-} of trigonal phase of MoS_2 .

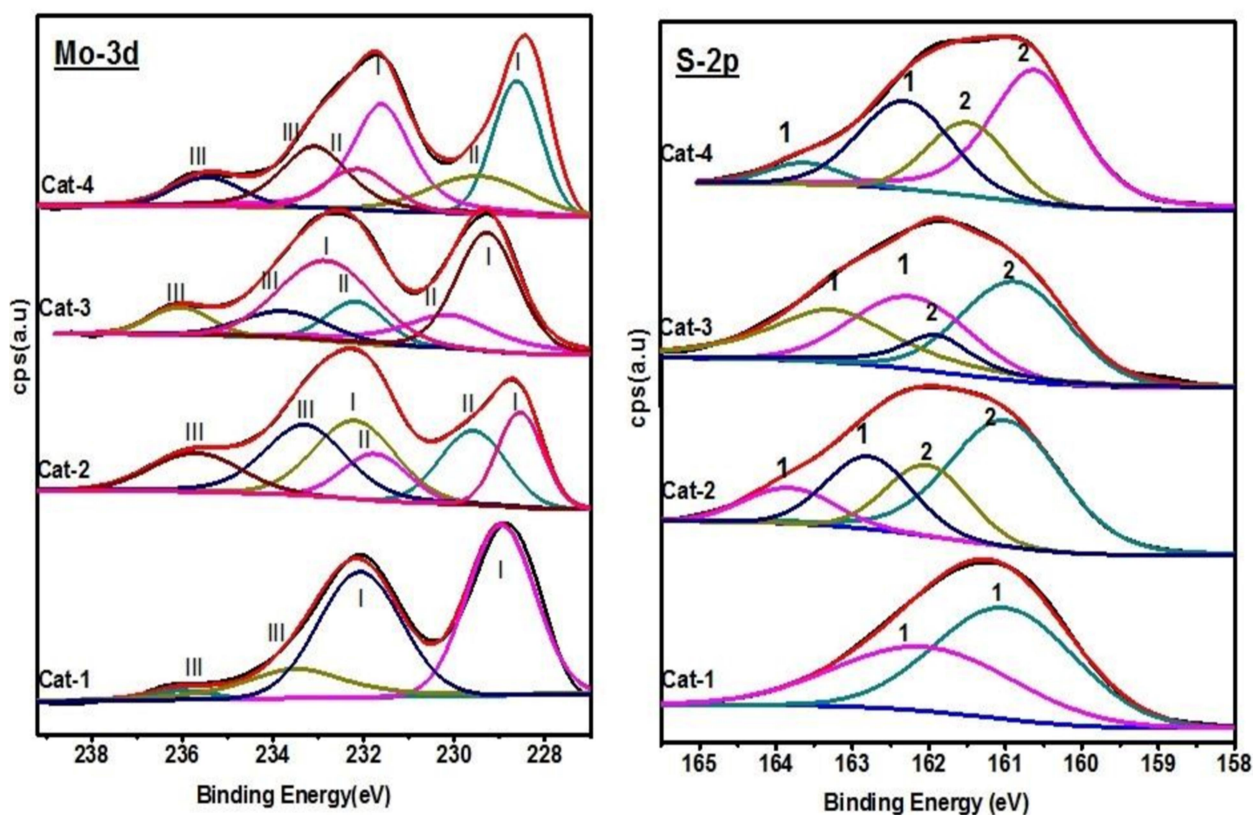


Fig III.3.9a: XPS spectra of Mo-3d and S-2p in different catalyst I: Mo^{4+} (1T), II: Mo^{4+} (2H), III, Mo^{6+} 1: For S^{2-} (for MoS_2 2H and CdS), 2: For S^{2-} (For MoS_2 1T)

An analysis of BE data reveals that the presence of one species affects the interaction between the other species. The chemical species present in catalysts have different electro-negativities, therefore with their chemical interaction the electronic densities are bound to alter leading to change in the binding energies. Such changes in BE are pronounced especially in cat-4. In other words, it may be stated that the species present in the catalyst, viz, CdS, MoS₂ and rGO have chemically interacted with each other to a greater extent in cat-4. It should be mentioned that Cat-4 showed the highest activity also.

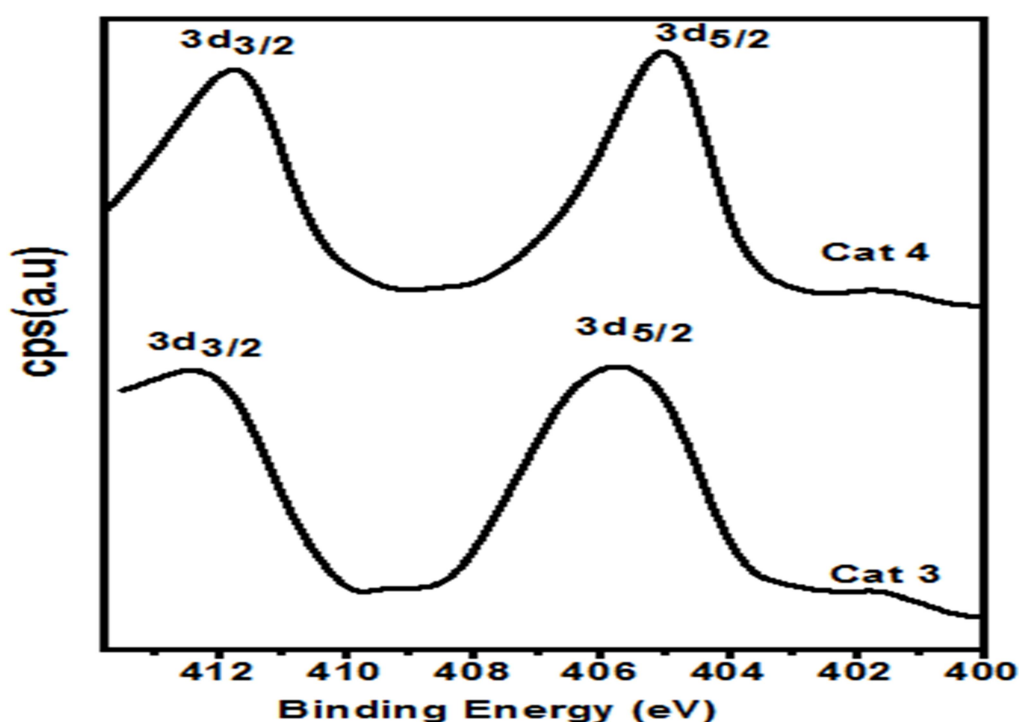


Fig III.3.9b: XPS spectra of Cd²⁺ in catalyst 3 and 4

These chemical interactions will lead to the formation of heterojunction at the interface facilitating charge separation and charge transfer to solid liquid interface and thus will enhance the activity of catalysts. Literature reports many works where formation of heterojunction resulted into a better photo response [266-268]. It is also observed that when CdS and rGO are incorporated with MoS₂, it has resulted into formation of mixed phase at the interface. Literature reports [269, 270] that the trigonal phase of MoS₂ has

metallic character and a high electronic conductivity which along with rGO can facilitate electron transfer for a better activity as discussed above.

Table III.3.4(a): Peak position of Mo 3d in different catalyst

Sample	Mo peak position (eV)						Ratio of intensities	
	1 st doublet I: Mo ⁴⁺ (1T)		2 nd doublet II: Mo ⁴⁺ (2H)		3 rd doublet III: Mo ⁶⁺		$\frac{3d_{5/2}Mo^{4+} (1T)}{3d_{5/2}Mo^{4+} (2H)}$	$\frac{3d_{5/2}Mo^{6+}}{3d_{5/2}Mo^{4+} (2H)}$
	3d _{3/2}	3d _{5/2}	3d _{3/2}	3d _{5/2}	3d _{3/2}	3d _{5/2}		
Cat- 1	--	--	232.1	229.0	236.0	233.5	----	0.15
Cat- 2	231.7	228.6	232.2	229.5	235.7	233.2	1.29	0.75
Cat- 3	231.6	228.5	231.6	229.4	235.6	233.1	3.51	0.22
Cat- 4	231.3	228.2	231.8	229.1	235.3	232.8	3.66	0.46

Table III.3.4 (b): Peak position of S 2p in different catalyst

Sample	S 2p peak position (eV)			
	1 st doublet MoS ₂ (2H) and CdS		2 nd doublet MoS ₂ (1T)	
	2p _{1/2}	2p _{3/2}	2p _{1/2}	2p _{3/2}
Cat- 1	162.2	161.0	-	-
Cat- 2	163.8	162.8	162.0	161.0
Cat- 3	163.2	162.2	161.9	161.0
Cat- 4	163.5	162.1	161.2	160.2

Table III.3.4(c): Peak position of Cd²⁺ in different catalyst

Sample	Cd ²⁺ peak position (eV)	
	3d _{3/2}	3d _{5/2}
Cat- 3	412.3	405.8
Cat- 4	411.9	405.1

Therefore, it is concluded that preparation of CdS-MoS₂-rGO in the present hydrothermal technique has resulted into formation of heterojunction at the interface between the species and appearance of trigonal phase of MoS₂. Both these effect have facilitated effective charge separation and charge transfer. Such an effect was more pronounced in catalyst-4 which has the highest activity.

III.3.5.2.6 Electrochemical Impedance Spectroscopy (EIS) studies

Results of Electrochemical impedance spectroscopy (EIS) are presented in Fig III.3.10. The Nyquist plot shows two frequency regions: (i) a semicircle in the high frequency region and (ii) an inclined straight line in the low frequency region. The semicircles in the high frequency region: (i) a semicircle in the high frequency region and (ii) an inclined straight line in the low frequency region. The semicircles in the high frequency region mainly associate with charge transfer resistance [271, 272]. While the inclined straight line in the low frequency region is associated with the mass transfer resistance. The electron transfer properties of the samples are represented by the radii of the semicircles. The smaller the radius, faster is the electron – hole ($e^- - h^+$) separation and electron transfer rates.

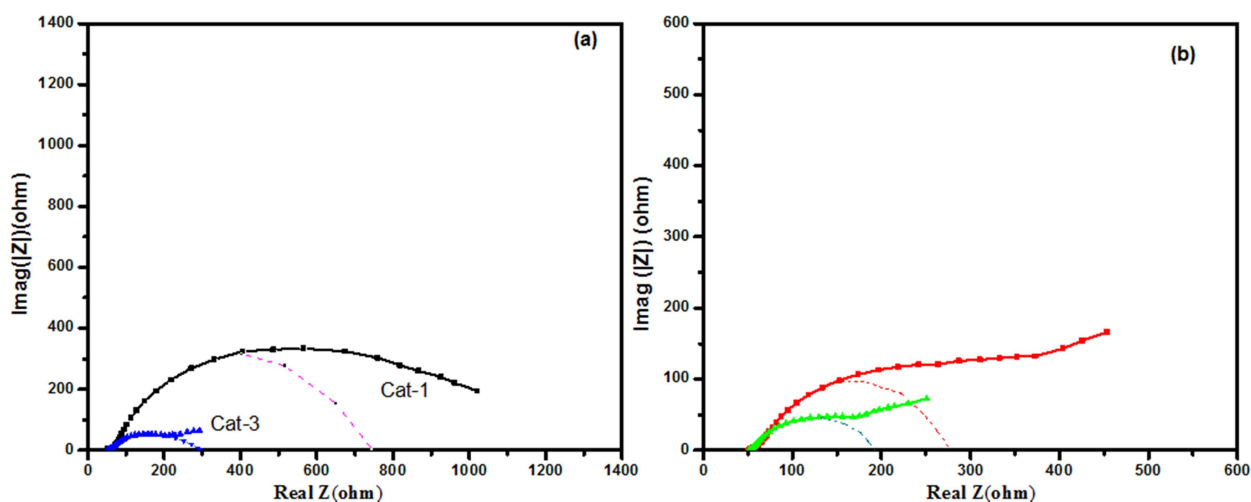


Fig III.3.10: EIS results of catalyst at $-0.2V$ vs SHE in S^{2-} and SO_3^{2-} electrolyte

In the present study, it is observed from the figure that Catalyst-1, (unsupported MoS₂) has highest resistance and catalyst-4 (MoS₂-CdS/rGO) has the least resistance. The resistances in the descending order are Cat-1 > Cat-3 > Cat-2 > Cat-4. Thus incorporation of CdS and /or rGO in MoS₂ has resulted in lowering of resistances and subsequently faster electron-hole separation and electron transfer rate. The effect is seen to be more

pronounced when rGO is incorporated into MoS₂ (Cat-2 and Cat-4) in comparison to Cat-3 where only CdS was incorporated. This is in order to mention that the activity in descending order were found to be Cat-4>Cat-2>Cat-3>Cat-1.

Thus, activities of catalysts correlate well with the rate of electron-hole separation and electron transfer rate. Therefore, it is concluded that formation of heterojunction between the species at the solid – solid interfaces, presence of mixed phase of MoS₂ and rGO has enhanced these rates in cat-2, 3 and 4. As discussed in the earlier section, such an interaction is more in Cat-4 where cdS and rGO both were incorporated to MoS₂. Consequently activity of Catalyst-4 is seen to be the highest.

III.3.5.2.7 Mott-Schottky Analysis

The electronic properties, viz, charge carrier type, charge carrier density, and flat band potentials of catalysts were investigated by the Mott–Schottky (M-S) analyses and results are presented in Fig III.3.11. The space charge capacitances (C) were measured by varying the potential (V) between –0.6 and 0.9 V verses SHE. The frequency was kept constant at 1.0 kHz. The analyses were carried out in dark condition using the same electrolyte which was there for activity measurements. M-S curves ($1/C^2$ vs V) were plotted to establish the type of semi conductivity , charge density and the flat band potential by using equation - 1 [273].

$$\frac{1}{C^2} = \frac{2}{\epsilon_0 \epsilon_r e N A^2} (V - V_{fb} - KT/q) \quad (1)$$

Where, C is the capacitance of space charge region, e –is the electronic charge (1.603×10^{-19} C), ϵ is the dielectric constant of MoS₂ (6.52 Fm^{-1}) [48], ϵ_0 is the permittivity of the vacuum ($8.854 \times 10^{-12} \text{ Fm}^{-1}$), N is the charge carrier density, A is the area of electrode ($25 \times 10^{-6} \text{ m}^2$), V is the applied potential, $V_{fb}(V)$ is the flat band

potential. V_{fb} can be obtained from the Mott-Schottky plot by measuring the intercept of straight line on x-axis, K is the Boltzmann's constant (1.38×10^{-23} J/K), T is the absolute temperature and KT/e is negligible at room temperature and 1 atmosphere pressure

.Table III.3.5: Flat band potential and carrier density of catalyst photocathode

Catalyst	V_{fb} (V) vs SHE	Carrier Density $N(\text{mL})^{-1}$
Catalyst 1	0.2	3.5×10^{14}
Catalyst 2	0.33	1.3×10^{15}
Catalyst 3	0.26	6.0×10^{14}
Catalyst 4	0.82	1.4×10^{15}

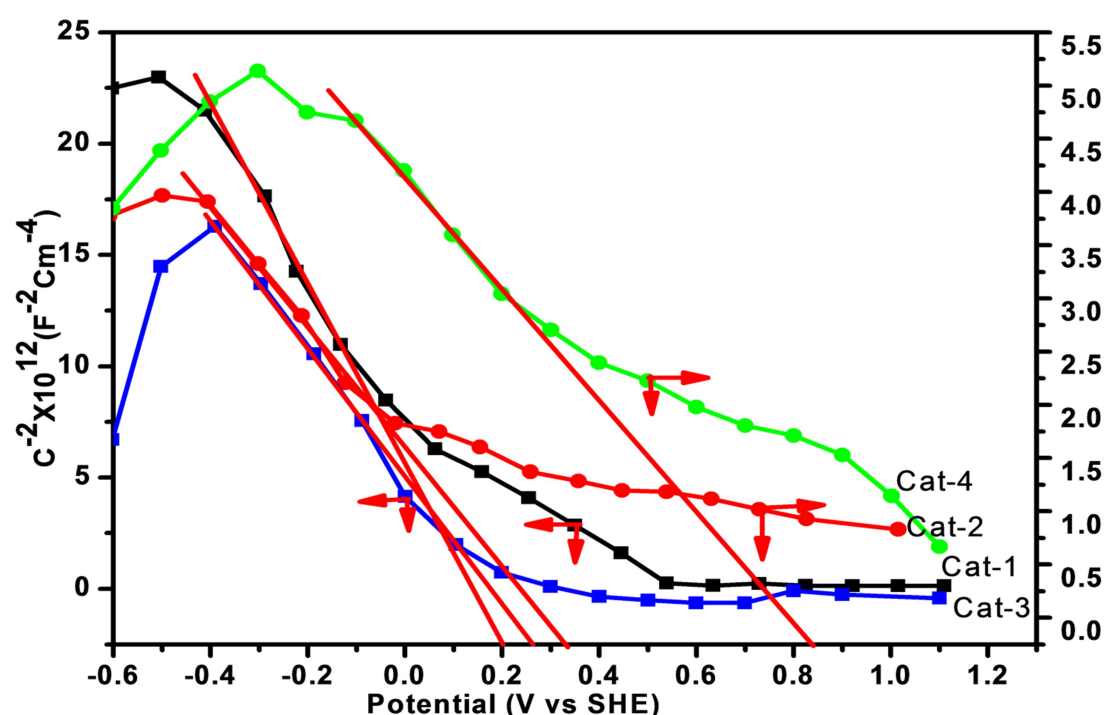


Fig III.3.11: Mott-Schottky plot of catalyst at 1.0 kHz in S^{2-} and SO_3^{2-} electrolyte

It is seen from the figure that all curve have linear regions. Negative slopes are observed for all the catalysts; establishing p-type semi conductivity [274]. The intercept on the x-

axis of the straight line yielded the flat band potentials. The values are given in Table III.3.5

. It is observed from the table that the flat band potential of catalyst-1 which is unsupported MoS₂ is 0.2. Incorporation of CdS and/or rGO results into a greater flat band potential. It is observed to be the highest in Cat-4 (0.82V) which was in MoS₂-CdS supported on rGO. It is order to mention that a greater flat band potential ensures a higher band bending and efficient charge separation. Similarly it is also observed from the table that highest charge density associated with Cat-4 which is MoS₂-CdS supported on rGO. A higher charge density and an efficient charge separation due to a greater band bending result into a better photo activity of catalyst owing to a large number of photo generated electron – hole pairs being available for the reaction. It should be also mentioned that magnitude of the flat band potentials as well as the charge carrier density and the activity follow the same trend, viz, in descending order Cat-4>Cat-2>Cat-3>Cat-1. The same trend was followed by charge separation and charge transfer rates (cf EIS studies).

III.3.3 Mechanism

The hydrogen generation using photoelectrocatalytic systems relies on charge carrier generation and its migration route. The charge carrier migration routes depend on the conduction and valence band potentials of the semiconductor catalysts. A schematic diagram illustrating possible pathways of charge transfer in catalyst -4 (MoS₂-CdS-rGO) is shown in Fig III.3.12. It has been assumed most of electron – hole pairs are created on the surface of MoS₂ (cf DRS results). The photo generated electrons migrate to the rGO from the conduction band of MoS₂ and are transported to the solid- solid interface to carry out reduction reaction (Path I). Electron – hole pairs are also generated

on the surface of CdS. These electrons can migrate to rGO (path II) or can jump to the conduction band of MoS₂ and subsequently to rGO (path III followed by path I).

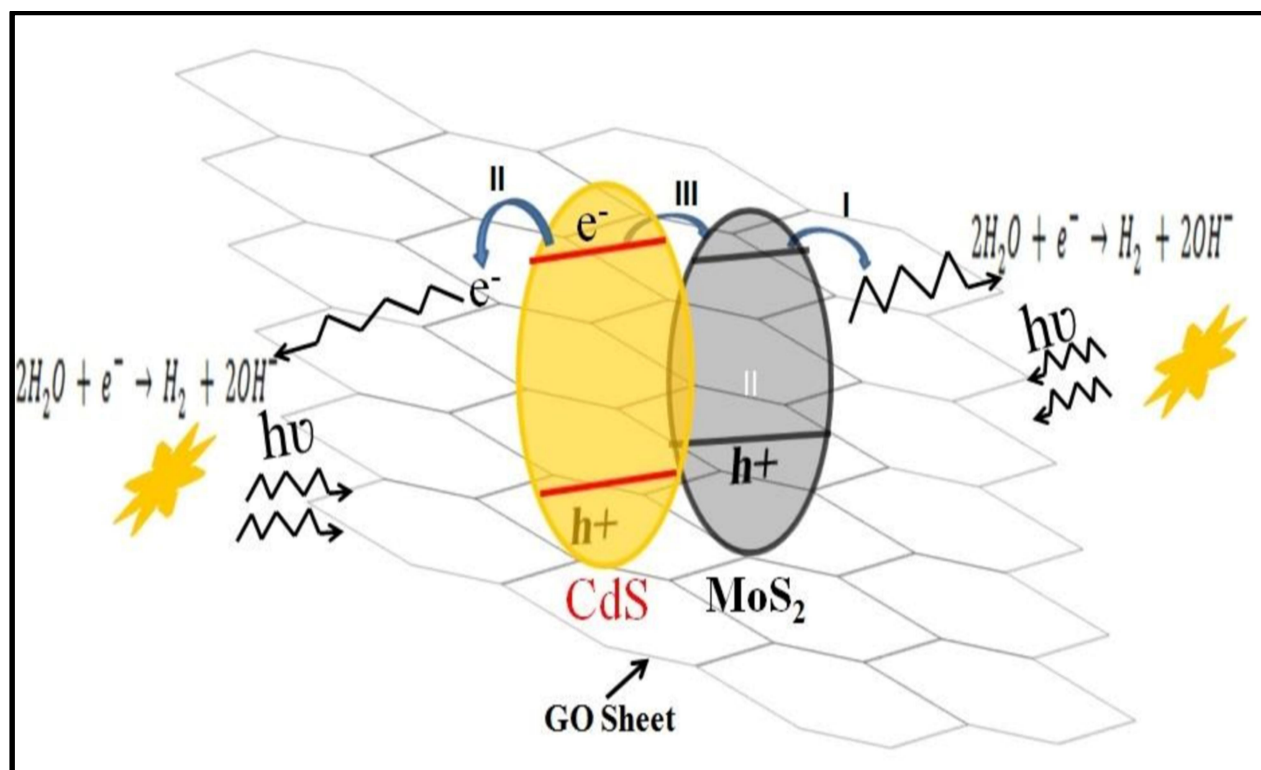


Fig III.3.12: Schematic diagram of charge transfer in cat-4

