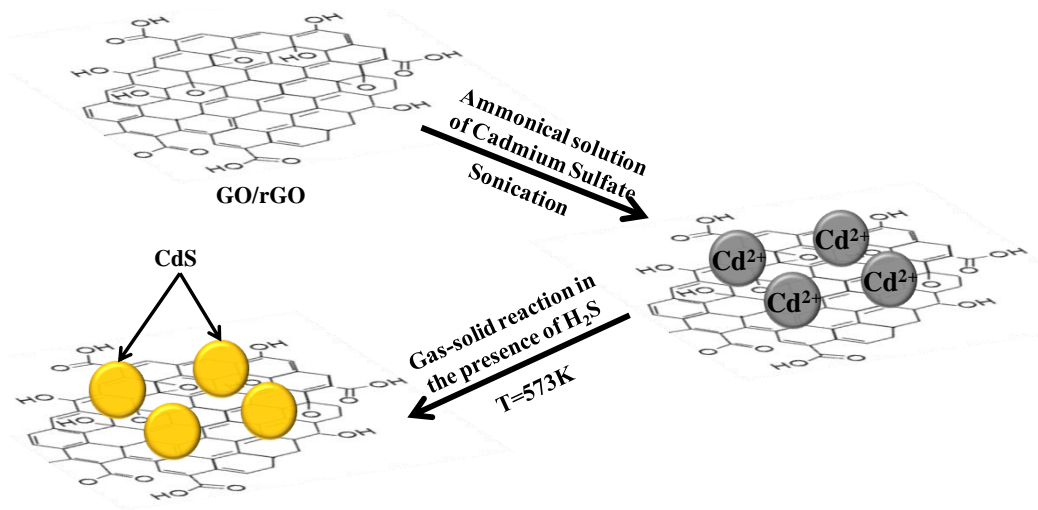


CHAPTER 3



Chapter

Experimental

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3.1 Preparation of photocatalysts

In an earlier work in our laboratory [167,168,280-282], CdS was found to be an effective photocatalyst for H₂ production by photocatalytic dissociation of water using visible light. The preparation technique of CdS had a critical influence on its structure and activity.

In the present work we have prepared GO/rGO based CdS catalyst by various different techniques and these have been studied.

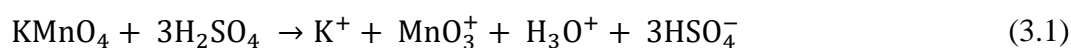
Earlier work carried out in our laboratory had demonstrated that CdS prepared by reacting solid cadmium sulphate with H₂S gas (solid-gas reaction) at 573 K resulted in formation of *n*-type CdS. It was concluded that the reaction carried out at an elevated temperature yielded the non-stoichiometric composition of CdS having a sulphur deficiency and hence showed *n*-type semiconductivity [281]. The *n*-type CdS was found to be efficient for dissociation of water. Therefore, in the present study, catalysts were prepared by impregnation method followed by solid-gas reaction at elevated temperature. Catalyst was also prepared by following most common technique as reported in the literature [201–209] i.e. hydrothermal technique for the comparison purpose.

It was reported in previous study in our laboratory [167,168,280,282,283] that use of ammoniacal solution of precursor resulted into a more active catalyst compared to when an aqueous solution was used. A higher concentration of active ingredients was observed near the external surface of the support when ammonia was used as an impregnating solution. Such a distribution is desirable for the photocatalytic reactions, since light cannot penetrate deep inside the

porous matrix of the support. When solid particles are impregnated with a solution which contains a volatile liquid such as ammonia, the gas evolved forces the liquid column in capillaries to the external surface. Therefore, drying takes place near the external surface. In contrast, in absence of a volatile gas in liquid, as the drying progresses, the liquid column will recede inside the interior of the capillary column. Therefore drying in presence of volatile gas in solution will result in a higher concentration of the active ingredient on the outer surface of catalyst [284]. Therefore, in the present work also ammoniacal solutions of cadmium sulphate were used.

- **Synthesis of Graphene oxide (GO)**

GO was synthesized by following a most widely adopted top down method i.e. modified Hummers' method as reported in the literature [285,286]. In this method, sulphuric acid and potassium permanganate are used as a strong oxidizing agent. Sodium nitrate is used a substitute of nitric acid.



In our preparation, graphite flakes (2 g) and sodium nitrates (2 g) were well mixed. Then 92 mL concentrated H₂SO₄ (98%) was carefully added drop wise into this mixture in a 500 mL volumetric flask kept an in ice bath under constant stirring (using magnetic stirrer). This suspension was constantly stirred for 1 h on ice bath. Further, KMnO₄ (12 g) was slowly added into the suspension under constant stirring. The greenish suspension was then put in a water bath for 1 day. The temperature of water bath was maintained at

308 K. This suspension was diluted by adding 75 mL H₂O with slow addition. During this step, the temperature of the suspension rapidly rose to nearly 353 K and the colour gradually became brown. Then, additional 180 mL H₂O was added. Finally this suspension was treated by adding 40 mL of 20 % H₂O₂, and stirred for 0.5 h. It resulted into reduction of residual permanganate and manganese dioxide into colourless soluble manganese sulphate and the appearance of suspension turned bright yellow from brown. The final product (GO) was collected by vacuum filtration subsequently washed repeatedly with 4% HCl solution followed by distilled water. After filtration, the oxidized graphene was dried under vacuum condition at 333 K for 4 days.

- **Reduction of Graphene oxide**

GO (600 mg) was dispersed into H₂O (300 mL) and put on a sonication bath for 0.5 h. The pH of this suspension was adjusted to 2.0 by addition of 37 % HCl solution. Then Zn powder (1,200 mg) was gradually added into the suspension and sonication was continued for 15 min. After the sonication, the top part of the brown suspension turned transparent. Black precipitates were allowed to settle down. Concentrated HCl (30 mL) was carefully added into this suspension to dissolve excessive Zn powder [287].

- **Catalyst preparation**

Following six catalysts were prepared where rGO/GO was used as support. In earlier work on our laboratory with CdS supported on alumina, best results were obtained for the Al₂O₃:CdS = 2:1(w/w). Therefore, in the present work also the same ratio, i.e., rGO:CdS = 2:1 was fixed. i.e., rGO:CdS = 2:1 was fixed.

Catalyst 1: It was unsupported CdS, prepared by gas-solid reaction. Requisite amount of cadmium sulphate (3CdSO₄.8H₂O) was placed into a fixed bed tubular reactor, where H₂S gas was passed at 573 K for 2 h to convert Cd-precursor to CdS.

Catalyst 2: This catalyst was GO supported CdS. For preparation of this catalyst, required amount of GO was added into calculated volume of dilute ammoniacal solution of cadmium sulphate (5 mmol) to have a weight ratio of 2:1 (2 part GO and one part CdS) in the final catalyst. The resulting mass was first dried on water bath at 358 K with stirring and subsequently in oven at 383 K for overnight. The dried granules were then put into fixed bed reactor and reacted with H₂S gas in similar manner as was done for catalyst-1.

Catalyst 3: This catalyst was rGO supported CdS. This was prepared in the same manner as catalyst-2 except that rGO was used as a support in place of GO for catalyst-3.

Catalyst 4: This catalyst was also rGO supported CdS. It was prepared by a hydrothermal method in which Cd-precursor (cadmium sulphate, 5 mmol) was dissolved into ammonia solution to make a dilute solution, in which the required amount of rGO was added. A dilute aqueous solution of Na₂S was then added slowly to this mixture till the precipitation was complete. The resulting mixture was put into Teflon-lined autoclave that was kept at oven for overnight at 453 K. The final product was washed several times and finally dried at 343 K.

Catalyst 5 and 6: Apart from these, two more catalysts were also prepared for sake of comparison of activity of catalysts by adopting the solid-gas method as discussed above. In which GO and CdS [catalyst-1] was well mixed physically in mortal & pestle and was denoted catalyst-5. The quantity of CdS and GO in catalyst-5 was in the same ratio as that in the catalysts-2 to 4. Catalyst-6 was a physical mixture of CdS (prepared as catalyst-1) and rGO. It had the same composition of CdS and rGO as catalysts-2 to 4. The mixture was prepared by

Table 3.1: Catalysts used in the present study

Sr.	Catalyst		Composition (in weight ratio CdS : GO/rGO)	Summary of preparation method
	Catalyst-1	CdS		
1.	Catalyst-1	CdS	Pure and unsupported	CdSO ₄ reacted with H ₂ S at 573 K
2.	Catalyst-2	GO:CdS	2:1	Impregnation of GO with ammoniacal solution of CdSO ₄ , dried, reacted with H ₂ S at 573 K
3.	Catalyst-3	rGO:CdS	2:1	Impregnation of rGO with ammoniacal solution of CdSO ₄ , dried, reacted with H ₂ S at 573 K
4.	Catalyst-4	rGO:CdS	2:1	Hydrothermal treatment at 453 K
5.	Catalyst-5	GO:CdS	2:1	Physically well mixed in mortal and pestle
6.	Catalyst-6	rGO:CdS	2:1	Physically well mixed in mortal and pestle

mixing and grounding the required amounts of CdS and rGO to a fine powder in a pastel and mortar. A summary of the catalysts prepared in the present study is given in Table 3.1.

3.2 Experimental set-up for photocatalytic reaction

A semi batch reactor was chosen for the present study. Fig 3.1 and Fig. 3.2 shows the details of the reactor. It consisted of a 250 mL four-necked flat-bottomed flask photoreactor made of Pyrex glass [Fig. 3.2 (a)], in which one side (vertical surface ~7 cm) was made flat through which emitted light entered in the reactor. Provisions were also made for sampling of the reaction mixture and for the measurement of temperature and pH. Standard cone and socket joints were used for connecting different parts of the reactor. There was a provision for

purging of gas in the reaction mixture. A 100 W Oriel Mercury-Xenon lamp was employed as the light source [Fig. 3.2 (d)].

Gas outlet of the reactor was connected to an inverted burette [Fig. 3.2 (e)]. The gas evolved from the reaction was collected into the inverted burette filled with water. One end of burette was connected with aspirator bottle. The volume of gas was determined by measuring the volume of water displaced by the gas. During the measurement, the level of water in the aspirator bottle and that in the burette was made equal. It ensured that the collection was at atmospheric pressure and temperature. As the variation in temperature of water over which gas collected, was within ± 5 K for average temperature of 303 K, no correction in the volume was carried out. It ensured that the pressure inside the reactor was near atmospheric pressure.

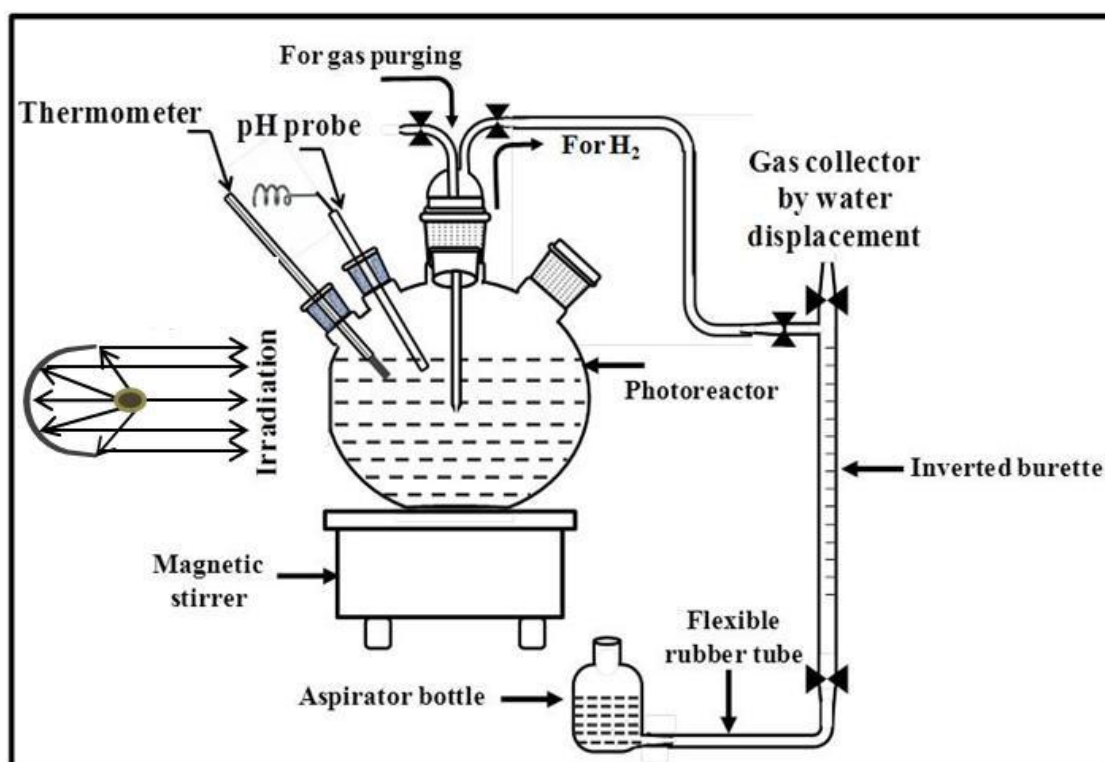


Figure 3.1: Schematic diagram of experimental set-up for photocatalytic reaction.

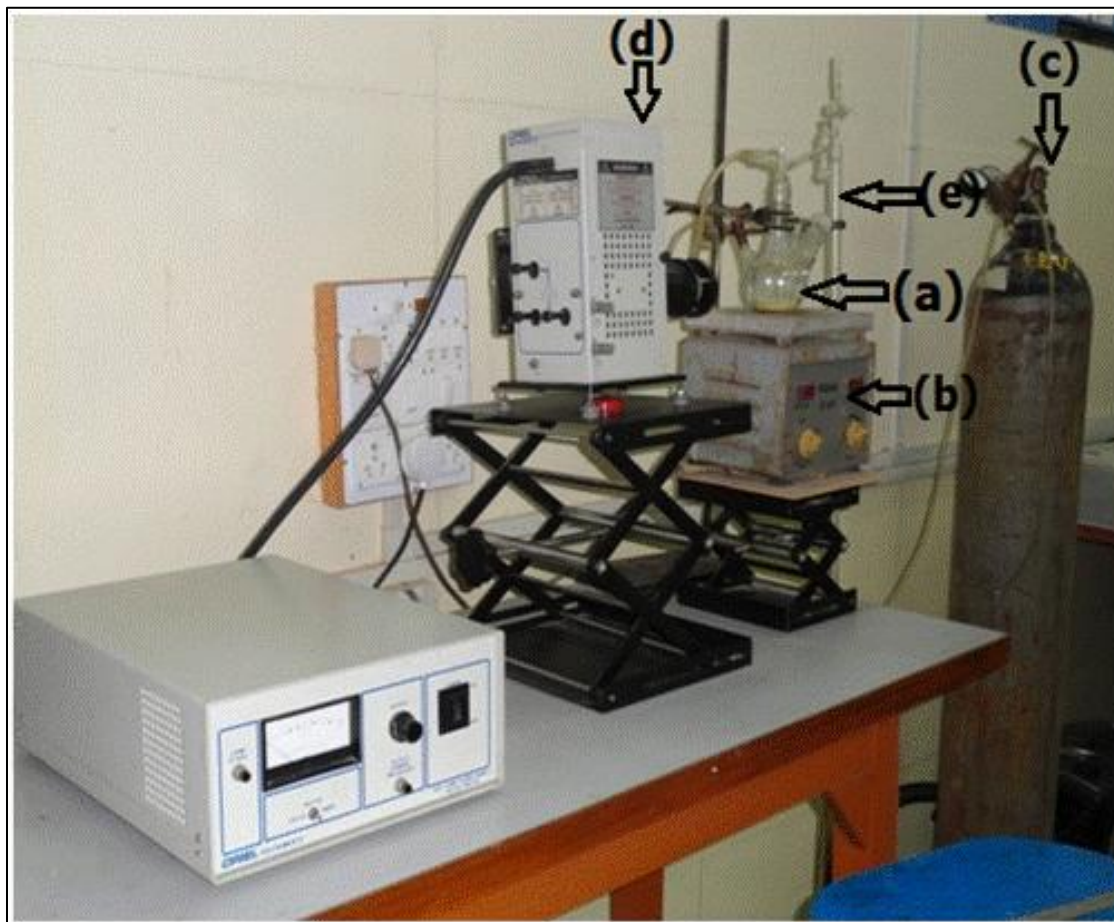


Figure 3.2: Experimental set-up (a) reactor, (b) magnetic stirrer, (c) N₂- gas cylinder, (d) light source, (e) gas collector.

One gram of photocatalyst (~200 mesh size) was suspended into 250 mL of aqueous solution of 0.01 M sulphite (Na₂S) and 0.004 M sulphide (Na₂SO₃) as a sacrificial agent. The pH was maintained at 8.6 during the experiment by adding requisite amount of 1 M NaOH and 1 M acetic acid solution. Before the light irradiation, nitrogen gas was purged for 1 h to remove dissolved O₂ from solution.

The collected gas was analysed by Nucon Gas Chromatograph model 5700, using a 5 Å molecular sieve column attached with thermal conductivity detector. The temperature of injector was maintained at 393 K. Temperatures of oven and TCD were

at 373 K and 423 K, respectively. Nitrogen (N₂) gas was used as the carrier gas. Flow rate of carrier gas was set at 40 mL.min⁻¹.

3.3 Characterization of catalysts

Structural information of catalysts is essential to understand and explore the relationship between their photocatalytic activities and microstructures as well as their preparation techniques. In present study, appropriate characterization techniques were applied as given in the Table 3.2.

Table 3.2: Characterization techniques used in present study

Sr. No.	Characterization technique	Characteristics 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)	Charges recombination study
5.	Transmission electron microscope (TEM)	Imaging and particle size
6.	Selected area diffraction pattern (SAED)	Crystal structure
7.	X-ray photoelectron spectroscopy (XPS)	Surface analysis, and depth profiling
8.	Temperature programmed oxidation (TPO)	Oxidation profile and study the interaction of CdS with support
9.	Electrochemical impedance spectroscopy (EIS)	Study of charge transfer rate and conductivity

3.3.1 Fourier-transform infra red spectroscopy (FTIR)

In the present study, a Nicolet 5700 (Thermo Electron) FTIR spectrophotometer was used to record FTIR spectra in mid IR range (4000–600 cm^{-1}). An average of 16 spectra in diffuse reflectance mode was recorded at room temperature at the resolution of 8 cm^{-1} . KBr was used as a reference material. About 1 mg of the sample and 100 mg of KBr were well ground with the help of pastel and mortar. Spectra were obtained for wave numbers between 500 and 3500 cm^{-1} .

3.3.2 X-Ray diffraction (XRD)

X-ray diffraction technique is used to study the structural information of materials. In this technique, the incident X-rays interacts with the specimen and diffracts. Finally diffracted patterns are collected by occurrence of constructive interference accordingly Bragg's Law:

$$n\lambda = 2d_{hkl}\sin\theta \quad (3.4)$$

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

λ = wavelength of the incident X-rays

d_{hkl} = the interplanar spacing, and

θ = at which the constructive reaches the maximum i.e. the diffraction angle

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

$$D = \frac{K\lambda}{FWHM\cos\theta} \quad (3.5)$$

Where, K = Scherrer constant,

$FWHM$ = full width at half maximum of the reflection peak that has the same maximum intensity in the diffraction pattern,

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

In present study, X-ray diffraction patterns of the prepared photocatalysts were obtained from a Rigaku Ultima IV diffractometer using Cu-K α irradiation. The calculated d-values were matched with standard data for identification of different phases present in various catalysts. The mean crystallite size of CdS in catalysts was calculated by the measuring the line broadening and using the using Scherrer formula (Eqⁿ. 3.2).

Actually, peak broadening arises from three sources:

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

The instrument contribution needs to be "subtracted" from β_{total} by following Eqⁿ. 3.6 to get actual broadening due to sample.

$$\beta_{\text{total}}^2 = \beta_{\text{instrument}}^2 + \beta_{\text{sample}}^2 \quad (3.6)$$

We neglected the broadening due to strain. The instrumental broadening is obtained from the diffraction pattern of a "standard sample" which consists of large crystallites. In our case standard sample was 'Si' and the value of broadening due to instrument was 0.79.

3.3.3 Diffuse reflectance spectroscopy (DRS)

It is an effective spectroscopic tool to estimate the band gap of semiconductor photocatalyst and the absorbance spectrum. When the powdered sample is radiated with light, a portion is regularly reflected at a powder surface and the remaining are either absorbed or transmitted through the powder and diffused. As light of particular wavelength is absorbed by the sample, the measurement of the diffuse reflectance light at different wavelength yields a spectrum called diffuse reflectance spectrum.

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. Diffuse reflectance data can be used for the Tauc plot using the Kubelka-Munk transformation [288,289], given by:

$$[\alpha h\nu]^{1/n} = A(h\nu - E_g) \quad (3.7)$$

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 [224].

According to Eqⁿ. 3.7, 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 (expressed in $h\nu$) of the material.

3.3.4 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 wavelength was from 400 to 600 nm.

3.3.5 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. The measurements were performed in a TecnaiG2 20 make TEM at 200 kV accelerating voltage. The powder samples was homogeneously dispersed in pure acetone by means of an ultrasonic bath and then deposited in the 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 XRD.

3.3.6 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_{α}) 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:

$$E_{KE} = h\nu - E_{BE} \quad (3.8)$$

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.

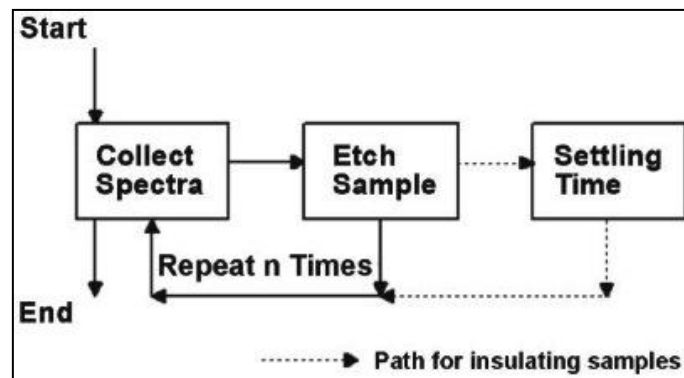


Figure 3.3: Summary of the experimental procedure for producing XPS depth profiles

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 interleaved 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 $MgK\alpha$ (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 12 mA. In ideal case (standard specimen), the surface of composites can be etched at about 7 \AA 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.

3.3.7 Temperature programmed oxidation (TPO)

This technique offers the ability to investigate the temperature-dependent properties of samples in an oxidative atmosphere in a specified temperature range.

In present study, TPO was carried out to investigate any strong interaction established between CdS and GO/rGO. The instrument for TPO experiments was a Micrometrics Pulse Chemisorb 2705 provided with TCD detector. Oxygen (5% by volume) in argon was used for oxidation and the temperature was raised linearly at a rate of 5 K per min from room temperature to 1173 K. The comparison of peak profiles gives an insight into nature of interaction between the CdS and alumina in the catalysts.

3.3.8 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance is the response of an electrochemical system (cell) to an applied potential. Electrical properties of materials as well their interfaces with surface-modified electrodes can be evaluated by this technique.

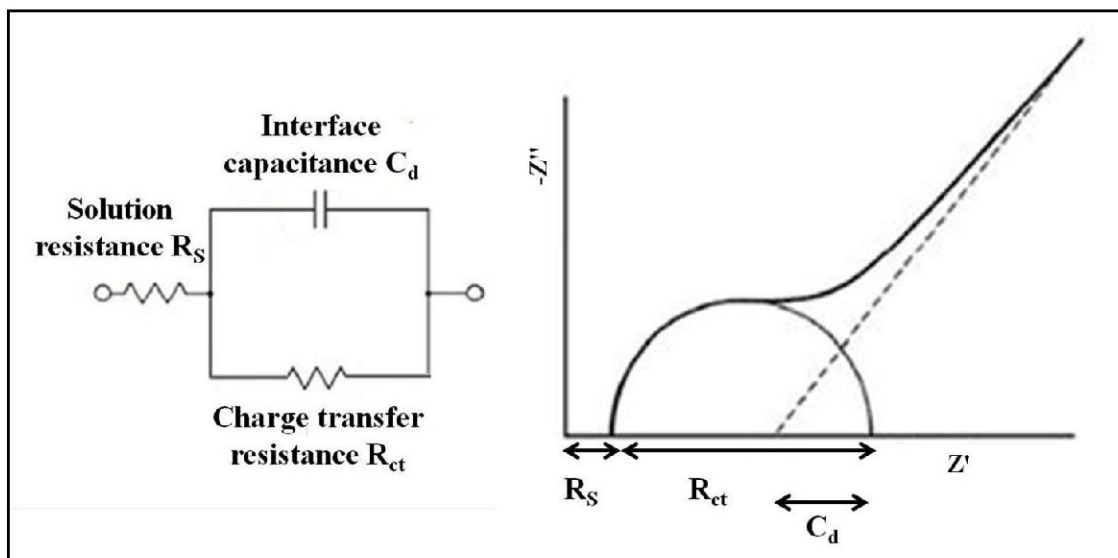


Figure 3.4: Basic components of Nyquist plot of electrochemical impedance spectroscopy [10].

The response of electrochemical systems is very nonlinear. The complex response of the system is usually displayed in Nyquist format [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 electrons 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 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 1 cm^2 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 uniformly spread on the carbon paper in the form of a continuous wet film using a brush. It was then dried in an oven for 4 h at 343 K. Before the impedance scanning experiments, the remaining surface was polished to minimize Ohmic effect. The electrolyte was a solution of sulphite and sulphide ions. The same solution was used for photocatalytic activity measurement.

3.4 Reaction set-up for photocatalysis with ultrasound

The experimental setup and procedure were same as mention in section 3.2. The reactor was typically a four necked flat bottomed flask with a vertical surface $\sim 7\text{ cm}$ was made flat for light to fall. Gas outlet of the reactor was connected to an inverted burette. The only modification was [as shown in Fig. 3.5], that it had a provision to insert an ultrasonic horn. Its tip was inside the electrolyte up to a depth 5 cm. The tip was made of stainless steel (SS304) having a diameter of 4 mm. The horn was connected to PZT transducer type ultrasound generator capable of generating ultrasound of 20 kHz frequency at different input powers from 10 to 40 W. Experiments were also carried out following same procedure as described above however, the magnetic stirrer was put off because the particles remained in suspension due to effect of ultrasound.

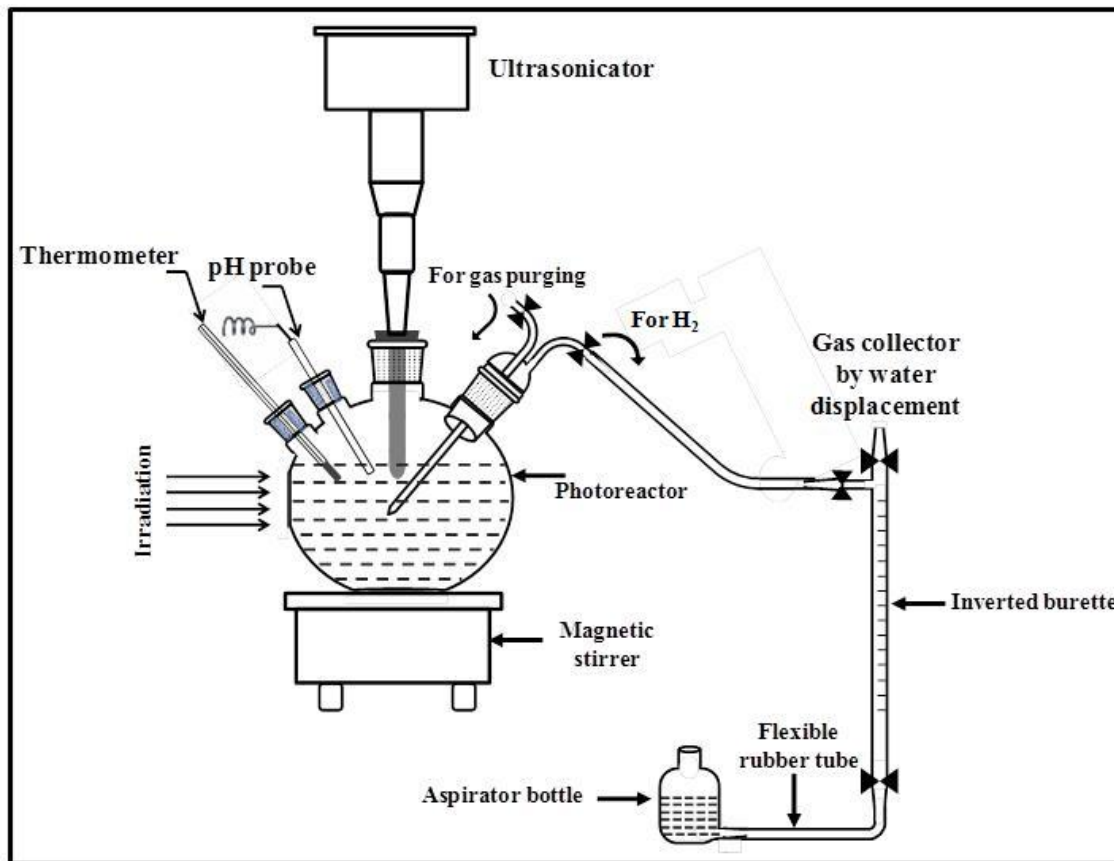


Figure 3.5: Schematic diagram of reaction set-up for photocatalysis with ultrasound.

3.5 Kinetic studies

The kinetics of dissociation of water for hydrogen production was studied in a same setup as discussed above for catalyst-3 which showed best activity. Before each run, the liquid having sacrificial agents was purged with N₂ gas for 1 h. For the deactivation studies, catalysts were tested for number of runs. At end of each run the light was put off and the liquid with catalyst was kept in dark for more than six hours & subsequently purged with N₂ and requisite amounts of electrolytes (sodium sulphide and sodium sulphite) was re-added to the electrolyte as calculated by the stoichiometric equation [Eqⁿ. 4.17, section 4.11] before the light was put on.

To see the effect of surfactant on hydrogen production rate, sodium dodecyl sulphate (a sulphur based surfactant) was added as 5 mmol/L. Similarly to study the effect of dissolved hydrogen, hydrogen gas was bubbled into the electrolyte solution. The effect of temperature was studied by putting heating cord around the reactor and the temperature was controlled by a variac.

