



**MARMARA UNIVERSITY**  
**INSTITUTE OF PURE AND**  
**APPLIED SCIENCES**



**CHALCOGENIDES IN**  
**PHOTOELECTROCHEMICAL HYDROGEN**  
**PRODUCTION APPLICATION AND**  
**CHARACTERIZATION**

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**RANA MUHAMMAD ZUNAIN AYAZ**

**MASTER THESIS**

Department of Chemical Engineering

**Thesis Supervisor**

Prof.Dr.Atif KOCA

ISTANBUL, 2019



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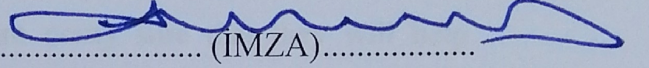
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**FEN BİLİMLERİ ENSTİTÜSÜ**

Marmara Üniversitesi Fen Bilimleri Enstitüsü Yüksek Lisans Öğrencisi Rana Muhammad Zunain AYAZ'ın “**Chalcogenides in Photoelectrochemical Hydrogen Production, Application and Characterization**” başlıklı tez çalışması, 17 Haziran 2019 tarihinde savunulmuş ve jüri üyeleri tarafından başarılı bulunmuştur.

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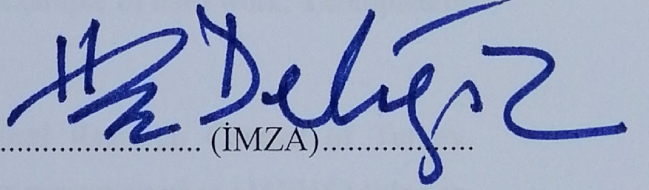
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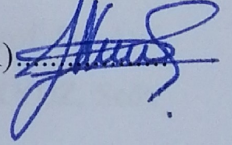
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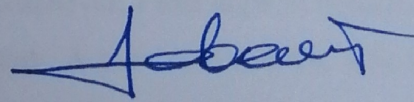


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Marmara Üniversitesi Fen Bilimleri Enstitüsü Yönetim Kurulu'nun 17/06/2019 tarih ve ..... sayılı kararı ile Rana Muhammad Zunain AYAZ'ın Kimya Mühendisliği Anabilim Dalı, Kimya Mühendisliği Programında Yüksek Lisans derecesi alması onanmıştır.

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**APPLIED SCIENCES**

Rana Muhammed Zunain AYAZ, a Master of Science student of Marmara University Institute for Graduate Studies in Pure and Applied Sciences, defended his thesis entitled “Chalcogenides in Photoelectrochemical Hydrogen Production, Application and Characterization”, on June 17, 2019 and has been found to be satisfactory by the jury members.

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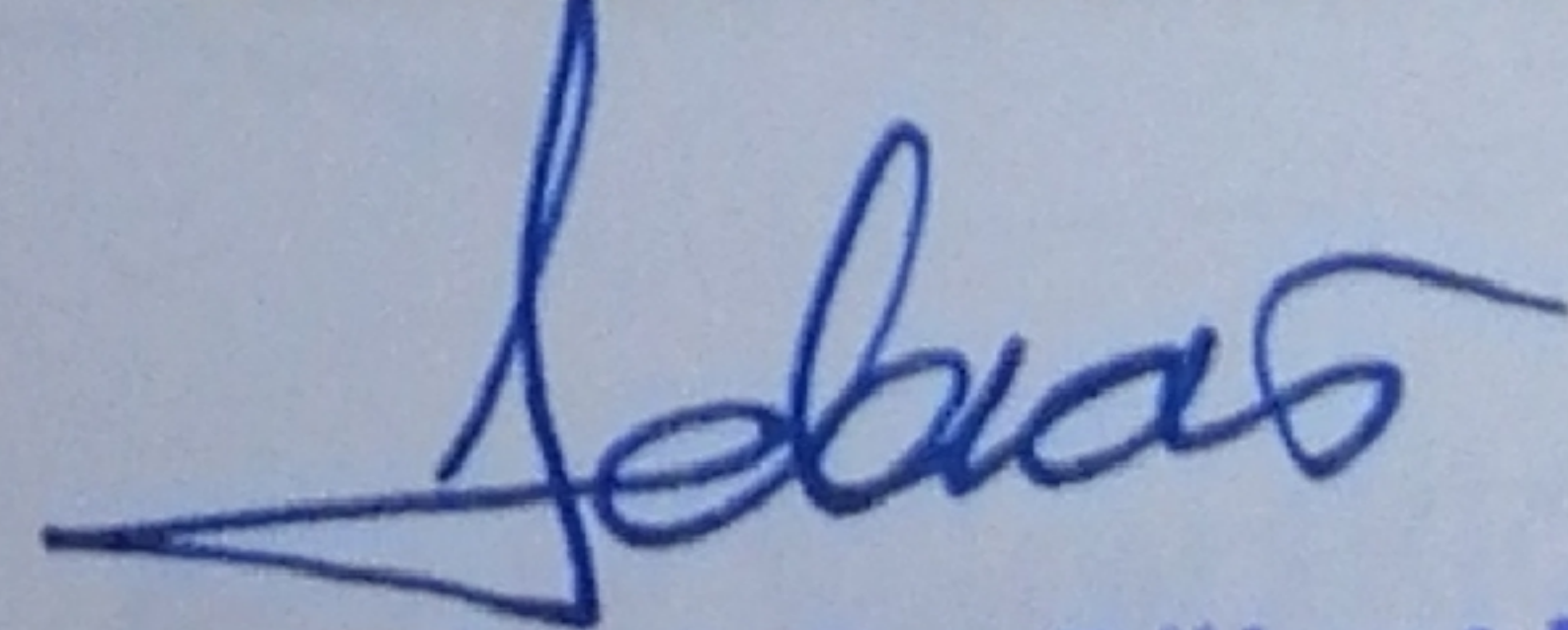
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**APPROVAL**

Marmara University Institute for Graduate Studies in Pure and Applied Sciences Executive Committee approves that Rana Muhammed Zunain AYAZ be granted the degree of Master of Science in Department of Chemical Engineering, Chemical Engineering Program on June 17, 2019. (Resolution no: .....).

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## SYMBOLS

|                           |                                                        |
|---------------------------|--------------------------------------------------------|
| <b>A</b>                  | : constant value                                       |
| <b>A<sub>s</sub></b>      | : surface area                                         |
| <b>C<sub>sc</sub></b>     | : capacitance of space charge layer                    |
| <b>d</b>                  | : inter-planer spacing                                 |
| <b>D</b>                  | : mean size of crystal particle                        |
| <b>E</b>                  | : charge on electron                                   |
| <b>E<sub>app</sub></b>    | : applied potential                                    |
| <b>E<sub>CB</sub></b>     | : conduction band edge potential                       |
| <b>E<sub>F</sub></b>      | : fermi level potential                                |
| <b>E<sub>fb</sub></b>     | : flat band potential                                  |
| <b>E<sub>VB</sub></b>     | : valance band potential edge                          |
| <b>f(R)</b>               | : K-M function                                         |
| <b>h</b>                  | : Planck's constant                                    |
| <b>K</b>                  | : Boltzmann constant                                   |
| <b>K</b>                  | : crystalline shape factor                             |
| <b>n</b>                  | : integer number                                       |
| <b>N<sub>Dopant</sub></b> | : free carrier density                                 |
| <b>R</b>                  | : absolute reflectance                                 |
| <b>T</b>                  | : temperature                                          |
| <b>v</b>                  | : frequency of light                                   |
| <b>V<sub>b</sub></b>      | : bias potential                                       |
| <b>ε<sub>0</sub></b>      | : permittivity in vacuum                               |
| <b>ε<sub>r</sub></b>      | : relative permittivity                                |
| <b>θ</b>                  | : diffraction angle                                    |
| <b>λ</b>                  | : wavelength                                           |
| <b>β</b>                  | : full width at half maximum of X-ray diffraction peak |

## **ABBREVIATIONS**

|                 |                                              |
|-----------------|----------------------------------------------|
| <b>ABPE</b>     | : applied bias photon-to-current efficiency  |
| <b>CA</b>       | : chronoamperometry                          |
| <b>CB</b>       | : conduction band                            |
| <b>EDS</b>      | : energy-dispersive X-ray spectroscopy       |
| <b>EIS</b>      | : electrochemical impedance spectroscopy     |
| <b>GO</b>       | : graphene oxide                             |
| <b>LSV</b>      | : linear sweep voltammetry                   |
| <b>M-S</b>      | : Mott-Schottky                              |
| <b>OCP</b>      | : open circuit potential                     |
| <b>PC (HER)</b> | : photocatalytic hydrogen evolution reaction |
| <b>PEC</b>      | : photoelectrochemical                       |
| <b>RGO</b>      | : reduced graphene oxide                     |
| <b>RHE</b>      | : reversible hydrogen electrode              |
| <b>SEM</b>      | : scanning electron microscopy               |
| <b>SR</b>       | : sacrificial reagents                       |
| <b>UV-vis</b>   | : ultraviolet-visible                        |
| <b>VB</b>       | : valance band                               |
| <b>XRD</b>      | : X-ray diffraction                          |

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## ABSTRACT

### CHALCOGENIDES IN PHOTOELECTROCHEMICAL HYDROGEN PRODUCTION APPLICATION AND CHARACTERIZATION

In this work, our main goal is to synthesize a photocatalyst for efficient hydrogen production. Although there is a huge variety of semiconducting photocatalyst materials for efficient hydrogen production but in most of the cases either because of photocorrosion or photogenerated charges recombination, photocatalyst loses its activity or a noble metal co-catalyst (doping, loading) is required to enhance the stability along with the activity of photocatalytic process.  $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ , a solid solution of CdS and ZnS, very famous photocatalyst has been synthesized through the process of thermal sulfurization. Furthermore, for the inhibition of photogenerated charge particles recombination and photocorrosion of photocatalyst, RGO is also decorated on the photocatalyst (RGO- $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ ) and electrolyte is supported with  $\text{S}^{2-}$ ,  $\text{SO}_3^{2-}$  sacrificial reagent. The process of thermal sulfurization used in this work is very novel of its own kind in which metal oxides are produced in first step and metal sulfides in the other step. By using different ratio of Cd and Zn, ten different samples have been synthesized as  $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ , RGO- $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ ,  $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ , RGO- $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ ,  $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}$ , RGO- $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}$ ,  $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{S}$ , RGO- $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{S}$ , CdS, and RGO-CdS. For the preparation of photoelectrode, spin coating technique was employed. After optimizing the annealing temperature, number of coating layers, and RGO contents, prepared photoelectrodes are characterized with X-ray diffraction analysis XRD, Raman spectroscopy, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), UV-Vis diffusive reflectance spectroscopy. After characterization, prepared photoanodes were tested photoelectrochemically. Incredible photo-activity along with photostability is very prominent in all tests. However, it is seen that with the increase in Cd-contents, the photo-activity (photocurrent density, hydrogen production rate) and photo-stability of photocatalysts increases remarkably. Out of all the synthesized and prepared samples, RGO-CdS exhibit the highest photocurrent density of  $6.5 \text{ mAcm}^{-2}$  and reaches almost 89% of its theoretical value. The applied bias photon-to-current efficiency (ABPE) appears to be 2.67% at 0  $V_{\text{bias}}$  (vs. Pt) which is the highest obtained photocurrent value and yield of RGO-CdS as compared to literature. The rate of hydrogen production for RGO-CdS comes out to be  $551.1 \mu\text{mol s}^{-1}$ . As a result of this work, we proposed RGO-CdS as an efficient photocatalyst possessing excellent photostability and has a potential for the use in the future researches and applications.

## ÖZET

### FOTOELEKTROKİMYASAL HİDROJEN ÜRETİMİNDE KALKOGENİDLERİN UYGULAMALARI VE KARAKTERİZASYONLARI

Bu çalışmada, temel amacımız verimli hidrojen üretimi için fotokatalizör sentezlemektir. Etkili hidrojen üretimi gerçekleştirebilmek için çok çeşitli yarı iletken malzemeler olmasına rağmen çoğu durumda fotokorozyon ya da ışık etkisiyle oluşan yüklerin geri reaksiyonu sebebiyle fotokatalizör aktivitesi düşer veya bir asil metal yardımcı katalizörü ile (katkılama, yükleme) fotokatalitik aktiviteyi ve kararlılığı arttırmak gereklidir. CdS ve ZnS'in katı çözeltisi olan çok bilinen bir fotokatalizör olan  $Cd_xZn_{1-x}S$ , termal sülfürizasyon yöntemi ile üretilmiştir. Ayrıca, ışık etkisiyle üretilen taşıyıcı yüklerin geri reaksiyonunun ve fotokorozyonun engellenmesi için, RGO fotokatalizör üzerine (RGO- $Cd_xZn_{1-x}S$ ) dekore edilmiştir ve elektrolit  $S^{2-}$ ,  $SO_3^{2-}$  kurban ajanları ile desteklenmiştir. Bu çalışmada kullanılmış olan termal sülfürizasyon işlemi, ilk aşamada metal oksitlerin üretimi ve diğer aşamada metal sülfürlerin üretimi ile kendi türünde çok yenidir. Farklı Cd ve Zn oranları kullanılarak, on farklı malzeme  $Cd_{0.3}Zn_{0.7}S$ , RGO- $Cd_{0.3}Zn_{0.7}S$ ,  $Cd_{0.5}Zn_{0.5}S$ , RGO- $Cd_{0.5}Zn_{0.5}S$ ,  $Cd_{0.7}Zn_{0.3}S$ , RGO- $Cd_{0.7}Zn_{0.3}S$ ,  $Cd_{0.9}Zn_{0.1}S$ , RGO- $Cd_{0.9}Zn_{0.1}S$ , CdS, ve RGO-CdS sentezlenmiştir. Fotoelektrotların hazırlanması için spin kaplama tekniği kullanılmıştır. Tavlama sıcaklığı, kaplama katmanlarının sayısını ve RGO miktarı optimize edildikten sonra hazırlanan fotokatalizörler, X-ray kırınım analizi (XRD), Raman spektroskopisi, taramalı elektron mikroskobu (SEM), enerji dağılımlı X-ray spektroskopisi (EDS), UV-Vis difüzyon yansıma spektroskopisi analizi ile karakterize edilmiştir. Karakterizasyondan sonra, hazırlanan fotoelektrotlar fotoelektrokimyasal olarak test edildi. Yapılan tüm testlerde kararlılık ile birlikte yüksek fotokatalitik aktivite oldukça belirgindir. Bununla birlikte, Cd oranının artışı ile birlikte foto aktivite (foto akım yoğunluğu ve hidrojen üretim hızı) ve fotokatalizörlerin fotostabilitesinin önemli ölçüde arttığı görülmüştür. Sentezlenen ve hazırlanan tüm fotokatalizörlerden RGO-CdS  $6.5 \text{ mAcm}^{-2}$  foto-akım yoğunluğuna sahiptir ve teorik değerin neredeyse %89'una ulaşır. Uygulanan bias ışıktan akım eldesi verimi literature ile kıyaslandığında en yüksek fotoakım yoğunluğu eldesiyle  $0 \text{ V}_{\text{bias}}$  de % 2.67 olduğu görülmüştür. RGO-CdS için hidrojen üretim hızı  $551.1 \mu\text{mol s}^{-1}$  olarak elde edilmiştir. Bu çalışmanın sonucunda RGO-CdS, yüksek foto kararlılığa sahip ve gelecekteki araştırma ve uygulama alanlarında kullanım potansiyeli olan verimli bir fotokatalizör olarak önerdik.

## 1. INTRODUCTION

In this chapter, energy issues around the globe (demand-supply-danger), energy resources (reversible, irreversible), then hydrogen as an alternative source of energy, its production through different technologies and the parameters (pros and cons) will be discussed in details.

### 1.1. Effect of Human Activities on Resources

Almost ten thousand years ago, the environment of the earth was drastically unstable and unfavorable for development and growth of any living being. After that, the environmental conditions changed and became surprisingly stable for development and growth of living beings [1-3]. This stable era of earth climate is known as Holocene. Before the Holocene, all of the environmental changes were occurred naturally but after the industrial revolution a new era of instability came into being. This era is known as Anthropocene [4]. For last hundred years, earth's population increased exponentially with respect to which the demand for energy and fuels also increased tremendously. In past, the resources which were enough to meet the need of mankind are now starting exhausting. In this era of instability, all of basic system of the planet earth start collapsing because we the human being already start crossing the planetary boundaries (the safe operating space for humanity) as it can be seen in the Figure 1.1 and Figure 1.2.

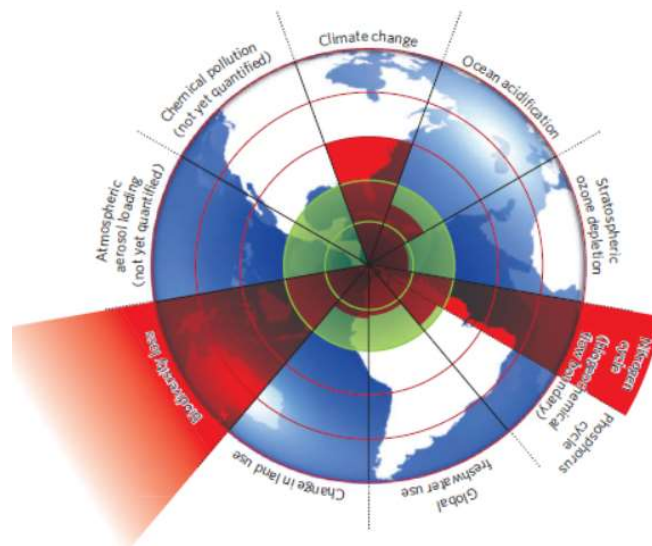


**Figure 1.1:** The exemplary diagram for nine different basic system and their boundaries [5].

| PLANETARY BOUNDARIES                                          |                                                                                                                                                                                                                                                   |                   |                |                      |
|---------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------|----------------|----------------------|
| Earth-system process                                          | Parameters                                                                                                                                                                                                                                        | Proposed boundary | Current status | Pre-industrial value |
| Climate change                                                | (i) Atmospheric carbon dioxide concentration (parts per million by volume)                                                                                                                                                                        | 350               | 387            | 280                  |
|                                                               | (ii) Change in radiative forcing (watts per metre squared)                                                                                                                                                                                        | 1                 | 1.5            | 0                    |
| Rate of biodiversity loss                                     | Extinction rate (number of species per million species per year)                                                                                                                                                                                  | 10                | >100           | 0.1-1                |
| Nitrogen cycle (part of a boundary with the phosphorus cycle) | Amount of N <sub>2</sub> removed from the atmosphere for human use (millions of tonnes per year)                                                                                                                                                  | 35                | 121            | 0                    |
| Phosphorus cycle (part of a boundary with the nitrogen cycle) | Quantity of P flowing into the oceans (millions of tonnes per year)                                                                                                                                                                               | 11                | 8.5-9.5        | -1                   |
| Stratospheric ozone depletion                                 | Concentration of ozone (Dobson unit)                                                                                                                                                                                                              | 276               | 283            | 290                  |
| Ocean acidification                                           | Global mean saturation state of aragonite in surface sea water                                                                                                                                                                                    | 2.75              | 2.90           | 3.44                 |
| Global freshwater use                                         | Consumption of freshwater by humans (km <sup>3</sup> per year)                                                                                                                                                                                    | 4,000             | 2,600          | 415                  |
| Change in land use                                            | Percentage of global land cover converted to cropland                                                                                                                                                                                             | 15                | 11.7           | Low                  |
| Atmospheric aerosol loading                                   | Overall particulate concentration in the atmosphere, on a regional basis                                                                                                                                                                          | To be determined  |                |                      |
| Chemical pollution                                            | For example, amount emitted to, or concentration of persistent organic pollutants, plastics, endocrine disruptors, heavy metals and nuclear waste in, the global environment, or the effects on ecosystem and functioning of Earth system thereof | To be determined  |                |                      |

**Figure 1.2:** The ecosystem resources and their boundaries. The red shaded area represent the resources whose boundaries has already been crossed [5].

So, with the increase in human population, the consumption of fuels also increases which shares a huge part in pollution. But the hydrogen when produced through the renewable energy source for example sun which is the gigantic source of energy is use to break the water which is also present in the immensely huge amounts, the only byproduct that can be produced during its consumption will be water vapor. The comparison of the amount of pollutants produced by different fuels has been shown in the Figure1.3.

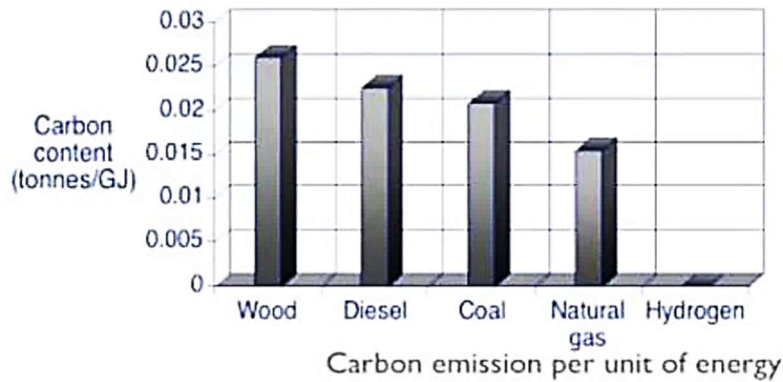


**Figure 1.3:** The comparison between different fuels on the basis of carbon emissions.

## 1.2. Hydrogen Energy

Global warming is one of the burning issues of the modern world. With the raising in temperature of earth, the glaciers are melting and sea levels are rising and it is believed that globally, and by the year 2080, because of rise in sea level nearly 20% coastal wetlands will be vanished. So, to summarize it can be said that there is two type of energy threats that world is facing right now;

- Scarce and diffident supplies
- Environmental mutilation which includes climate change

With the ever growing demand for fuels, now it is necessary to break the grounds and device new techniques to find the solution to this problem. The only solution to this problem is to

- Focus on the carbon-free energy systems
- Make use of renewable and clean energy alternatives

For recent past as a fuel has got a lot of attentions. Compared to energy sources for example, coal, oil and gas (primary energy sources), hydrogen is regarded as a secondary energy source which states that first it must be produced by using energy from any other primary energy source and after that it is sent for consumption where the latent chemical energy that it carries can be fully grasped [6]. Before going into details lets discuss the silent features that hydrogen as a fuel carries;

- Highest energy content
- Burning process is non-polluting as it is carbon free fuel
- Heating value is almost three times grander (28000 kcal/kg) than that of hydrocarbon.

- Easy in production
- Highly flammable.
- At ordinary temperature-pressure (T-P) conditions, exists as light gas, have a density only one fourteenth of the air and 11% of natural gas keeping the same T-P conditions.
- Cooling of hydrogen to -253 °C, causes condensation of gas to a fluid having specific gravity of roughly (1/10) that of gasoline.
- To initiate combustion, comparatively lesser amount of energy is required, and in the air burning flame of hydrogen has speed which remarkably greater than natural gas.
- Combustible composition ranges of hydrogen and air are extremely wide as compared to any other fuel while at ordinary temperature, flammability has a range of 4% to 74% by volume.

There are some other characteristics of hydrogen gas as a fuel and are enlisted in Table 1.1.

**Table 1.1:** A brief comparison of fuels and their properties.

| S.NO. | Material  | Auto ignition temperature      | Flash Point | Exposing range vol.% in air    | lower limit upper limit |
|-------|-----------|--------------------------------|-------------|--------------------------------|-------------------------|
| 1     | Crude oil | Depends on the nature of crude | 19          | Depends on the nature of crude |                         |
| 2     | Hydrogen  | 585                            | Gas         | 4.1                            | 74                      |
| 3     | Methane   | 538                            | Gas         | 5                              | 15                      |
| 4     | Ethane    | 514                            | Gas         | 3                              | 12.5                    |
| 5     | Propane   | 466                            | Gas         | 2.4                            | 9.5                     |
| 6     | Butane    | 430                            | Gas         | 1.5                            | 9                       |
| 7     | Benzene   | 563                            | -11         | 1.3                            | 7.1                     |
| 8     | Toluene   | 536                            | 4.5         | 1.2                            | 7.2                     |
| 9     | Naphtha   | 288                            | -18         | 1.1                            | 5.9                     |
| 10    | Gasoline  | 245                            | -7          | 1.4                            | 7.6                     |
| 11    | ATF       | 254.4                          | 38          | 0.7                            | 5                       |
| 12    | SKO       | 254                            | 35          | 0.7                            | 5                       |

Additionally, when hydrogen gas in internal combustion engine is used as fuel, the only by-product that it produces, is water and as a waste it produces NO<sub>x</sub> whose proportion can also be reduced by making minor changes in engine settings and nevertheless when hydrogen

production is done through renewable energy sources, it fulfills the requirements of a sustainable fuel which states that

- Protects the environment
- Protects the biodiversity
- Save the resources
- Helps achieving the high quality of life, cut down the poverty and increases the living standards.

A little comparison of emissions have been made and shown in Table 1.2.

**Table 1.2:** A Comparison of pollutant emissions between fossil fuel, coal and solar hydrogen system.

| Sr.NO. | Pollutant             | Fossil fuel system<br>(kg/GJ) | Coal<br>(kg/GJ) | Solar-Hydrogen System<br>(kg/GJ) |
|--------|-----------------------|-------------------------------|-----------------|----------------------------------|
| 1      | CO <sub>2</sub>       | 72.4                          | 100             | 0                                |
| 2      | CO                    | 0.8                           | 0.65            | 0                                |
| 3      | SO <sub>2</sub>       | 0.38                          | 0.5             | 0                                |
| 4      | NO <sub>x</sub>       | 0.34                          | 0.32            | 0.1                              |
| 5      | HC                    | 0.2                           | 0.12            | 0                                |
| 6      | Particulate<br>matter | 0.09                          | 0.14            | 0                                |

So, by seeing these statistics and characteristics that hydrogen gas possesses, it can be stated that hydrogen has a potential to be called as the fuel of future as it helps achieving the stability.

### 1.3. Routes to Hydrogen

Irrespective of the fact hydrogen is the richest element in monoatomic in the whole universe and constitutes almost 75% of all baryonic mass. However, in the earth's crust, it is not present freely but bounded up with other chemical species invariably into different chemical compounds. So, by using energy such as, heat or electricity, hydrogen can be obtained from other hydrogen-containing species. In common, for hydrogen production processes shown in Table 1.3 are being used.

**Table 1.3:** Routes to hydrogen.

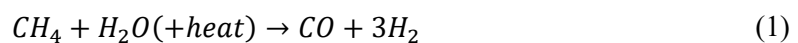
| Sources             | Production Process                          |
|---------------------|---------------------------------------------|
| <b>Fossil fuels</b> | Steam reforming of natural gas              |
|                     | Catalytic decomposition of natural gas      |
|                     | Partial oxidation of heavy oil              |
|                     | Coal gasification                           |
|                     | Steam-iron coal gasification                |
| <b>Water</b>        | Water electrolysis                          |
|                     | Thermochemical cycle                        |
|                     | Photochemical process                       |
|                     | Photoelectrochemical processes              |
|                     | Photobiological processes                   |
| <b>Biomass</b>      | Thermochemical (gasification and pyrolysis) |
|                     | Biologocal (fermentation and                |
|                     | Photobiological                             |

Presently, fossil fuels are the main sources for the production of hydrogen in the larger quantities such as, by steam reforming of natural gas and partial oxidation of coal or other heavy hydrocarbons [7]. A brief discussion of all methods have been in following paragraphs.

## 1.4. Hydrogen from Non-Renewable Energy Sources

### 1.4.1. Steam Reforming of Natural Gas

Steam reforming is the endothermic process in which a very high temperature steam, having temperature 700-1000 °C under the pressure of 3-25 bar, is utilized to produce hydrogen from natural gas such as methane. Along with hydrogen, carbon monoxide and relatively lesser amount of carbon dioxide is produced as byproducts. Finally, through the “pressure-swing-adsorption” all other impurities along with carbon dioxide are removed leaving behind pure hydrogen. The reactions that occur during the steam reforming process are given as follow;



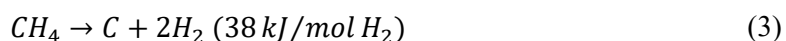
Gas shift reaction:



Still during the hydrogen production by the steam reforming of natural gas, CO<sub>2</sub> is produced which is one of its demerits and economically very expensive, and hence raises the question on the feasibility of hydrogen a fuel when it is produced through this process.

#### **1.4.2. Catalytic Decomposition of Natural Gas**

This is a process in which under air/water-free condition and in the existence of carbon-based catalysts the thermal decomposition of natural gas happens.



As there is very strong C-H bonds present in methane molecules (440 kJ/mol), so for its decomposition to happen, a very high temperature is required (> 1200°C). There is variety of transition metal is present to reduce the temperature for the thermal decomposition of methane but the dilemma of these metal catalysts is their deactivation due to the carbon deposition on the surface active sites and difficulties with metal-carbon separation.

#### **1.4.3. Partial Oxidation**

This is the exothermic process in which methane and other hydrocarbons present in natural gas reacts with the amount of oxygen which is less than the stoichiometry amount of oxygen required for the reaction to happen and it does not allow hydrocarbons to completely oxidize to CO<sub>2</sub> and water. So, the products only contains the hydrogen, carbon monoxide (and nitrogen if the reaction is happening in the presence of air rather than pure oxygen environment) small amount of CO<sub>2</sub> and other impurities. At the final stage, with the help of water shift reaction carbon monoxide yields carbon dioxide and more hydrogen gas.

#### **1.4.4. Coal Gasification**

This is cost affective process in which large quantity of hydrogen gas is produced when the coal gasification followed by the chemical conversion of fuel gas happens. The whole process comprises of four stages. In the very first stage, when pulverized coal is treated with an oxidant for example, steam, air or oxygen, coal is turned into a very high temperature synthesis gas (1800°C). The composition this syngas is carbon monoxide, hydrogen and carbon dioxide along with minute amount of some other gases and particles. In the next stage, the syngas is cooled and cleaned and then sent for the shift reaction where syngas reacts with steam where carbon monoxide get separated as carbon dioxide and pure hydrogen is sent for use.

#### **1.4.5. Hydrogen from Nuclear Energy**

Thermochemical water splitting cycles can be used for hydrogen generation. These reactions, by using nuclear reactor, operates at a temperature around ( $\geq 500^{\circ}\text{C}$ ). By the series of thermally driven chemical reaction, water is broken/converted into hydrogen and oxygen. In spite of the fact that a large amount of thermochemical reactions are present for hydrogen production by splitting water but the main challenge in this field is by lowering the temperature level increasing the efficiencies. However, the promising results of thermochemical cycles for thermochemical hydrogen production make this method a potential source for hydrogen production [8, 9].

### **1.5. Hydrogen from Renewable Energy Sources**

Hydrogen can also be generated by the utilization of renewable energy sources (for example wind, geothermal, ocean thermal, tidal and wave, and hydro energy) by using the electricity produced by them. This calls for the hydrogen production through the water electrolysis. As compared to convention hydrogen production methods, these are more environmental friendly and cost effective.

#### **1.5.1. Wind Energy**

The basic concept of wind energy is to translate the kinetic energy of the wind into mechanical energy, which in turns rotate the coil of the generator and produces electrical energy. This electricity can be used directly by sending it to the commercial supply chain or delivered to electrolyzer for electrolytic hydrogen production. Wind energy is a potential source for hydrogen production as this is pollution-free technology and has simple assembly.

#### **1.5.2. Geothermal Energy**

Geothermal energy is also an full of potential technology for hydrogen production as it produces electricity which can be used for electrolysis as well as also provided energy to water which in turns reduces the demand for energy required to produce hydrogen from it. For the storage motivations of hydrogen in the liquefied form, power from geothermal may also be used for the liquefaction of hydrogen gas. So, geothermal energy has a great future for sustainable and stable hydrogen economy [10].

### **1.5.3. Ocean Thermal Energy**

This system operates by employing the temperature difference that is present among the upper layer and the bottom of the sea. At the normal sunny day, the top layer of the sea surface becomes hot having temperature of 25 to 30 C. While the bottom of it, almost 1000 m down it, remains at 5 or less than 5 C. By harvesting the vapor-power cycle that utilizes or extracts the energy from this temperature difference by building the hot and cold reservoirs.

### **1.5.4. Tidal and Wave Energy**

Tidal and wave energy system is one of the mature and oldest systems to obtain energy that can be utilized in many areas. When it comes to hydrogen production, the scenario is very simple, in which the energy obtain from the tidal waves can directly be used to generate electricity which can be used for the electrolytic hydrogen production. This is the pollution-free technique but has the lower capacity as compare to other renewable energy sources.

## **1.6. Hydrogen Production by Solar Energy**

On the bases of temperature requirements, hydrogen production by utilizing the solar radiations can be classified into two classes; low temperature (0-200°C) and high temperature (200-2500°C). This classification has been explained in the table 1.4.

**Table 1.4:** Hydrogen production from thermochemical cycle.

| Technique                         | Temperature requirement       | Process               | Explanation                                                                |
|-----------------------------------|-------------------------------|-----------------------|----------------------------------------------------------------------------|
| <b>Concentrated solar thermal</b> | High temperature (200-2500 C) | Thermochemical cycles | Thermochemical cycles using metal oxides                                   |
|                                   |                               | Thermolysis           | Thermal disassociation of water                                            |
|                                   |                               | Gasification          | Steam gasification of coal                                                 |
|                                   |                               | Electrolysis          | Electrolysis of water using high temperature and solar thermal electricity |
|                                   |                               | steam reforming       | Steam reforming of natural gas                                             |
|                                   |                               | Cracking              | Thermally breaking of natural gas and hydrocarbons                         |
| <b>Photobiological</b>            | Low                           | Photo biolysis        | Plant and algal photosynthesis                                             |
| <b>PV</b>                         | Temperature (0-200°C)         | Electrolysis          | Water electrolysis                                                         |
| <b>Photocatalytic</b>             |                               | Photocatalysis        | Water photocatalysis                                                       |
| <b>Photoelectrochemical</b>       |                               | Photoelectrocatalysis | Water photoelectrolysis                                                    |

Here the two out of the mentioned processes that is, photocatalysis and photoelectrolysis will be explained in details. But before that the photocatalysts have to be discussed in details in order to get proper understanding of the concept.

### 1.6.1. Photocatalyst

Photocatalyst is a semiconductor material which has a specific band gap for example for efficient splitting of water it should have band gap between 1.2 (the thermodynamically required potential for water splitting) and 2.0 eV (the theoretically required band gap after including over potentials). The electrons, in a semiconductor are held by the valance band of atoms in crystal. When the photons of energy having energy larger and/or equal to the band gap of semiconductor, electrons use that energy to reach the energy levels of conduction band by going across the forbidden band gap.

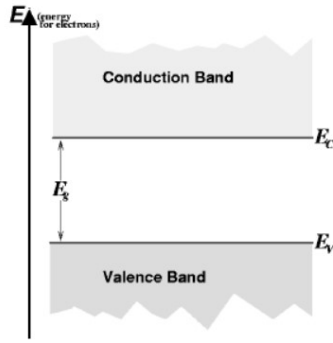


**Figure 1.4:** Simple example of band structure for semiconductor photocatalyst [11].

When the electrons excites to the energy levels of conduction band, they leave behind the vacancy or empty state available for another electron in the energy levels of valance band. This empty state or vacancy is known as hole. With the application of external electric field, at the same level due to the existence of a number of states around them, electrons in the conduction band move freely in reverse direction of the field. Under the action of same electric field, the electrons in valance band can also move, if at their energy level there are available states. So it can be said that there is also conduction with the application of electric field in valance band if holes are present there. But here is one important thing to remember that the motion of holes in valance band [11] has the same direction as that of applied electric field as it is evident from the Figure 1. 5.

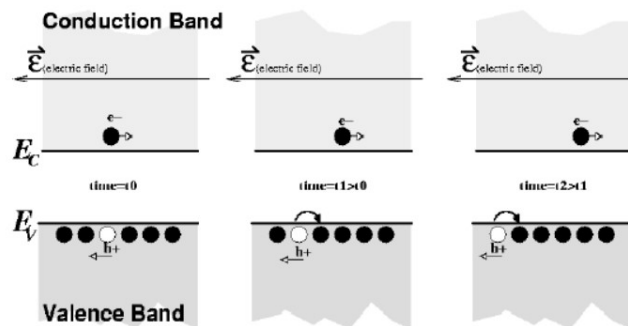


**Figure 1.5:** The drift of charges during the application of electric field in their respective energy levels [11].

Generally, semiconductors are divided into three basic classes such as, intrinsic semiconductors, and extrinsic semiconductors (n-type semiconductors, and p-type semiconductors). Before going into details of extrinsic semiconductors, first let us have a look on the fermi level.

**Fermi level:** At absolute zero temperature, the top of the collection of electron energy level is known as fermi level. So, at absolute temperature electrons pack themselves in the form of pool at the lowest available energy states, known as Fermi-sea. None of the carries enough energy to go up the surface

**Intrinsic Semiconductors:** A semiconductor in its purest form is known as intrinsic semiconductor. The band structure of intrinsic semiconductor at absolute zero temperature can is shown in Figure 1.6.

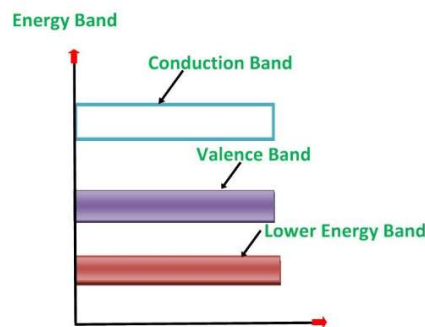


**Figure 1.6:** The band structure of an intrinsic semiconductor at absolute temperature [11].

At the absolute temperature, the conduction band is completely empty while the valance band is completely filled. With the increase in temperature, the excited electrons jumps to conduction band leaving behind holes in the valance band as it can be seen in Figure 1.7.

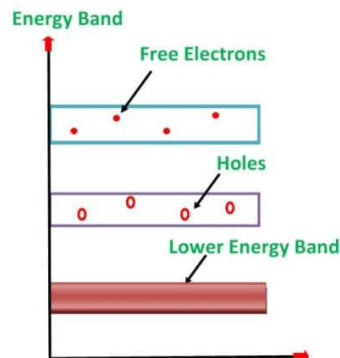


**Figure 1.7:** The band structure of an intrinsic semiconductor at higher temperature [11].

The charge carrier species (electrons and holes) have free random motions in their respective bands, and thus have a negative temperature coefficient of resistance. So, by increasing the temperature the material's resistance decreases and conductivity increases.

For intrinsic fermi level [11];

$$E_i = E_C - E_g/2 = E_V + E_g/2 \quad (1.1)$$

**Extrinsic semiconductors:** When an impurity is added to semiconductor material with the motivation of increasing its conductivity, this is known as extrinsic semiconductor. On the bases of impurity added to semiconductor, extrinsic semiconductors have been divided to two categories, n-type semiconductors, p-type semiconductors.

**N-type semiconductor and its Fermi level:** When a pentavalent impurity is added to semiconductor, it provides the large number of electrons and thus this type of semiconductor is known as n-type semiconductor. So, the count of electrons will be greater in conduction band as compared to valance band and hence there will be higher probability of finding an electron near the conduction band edge as compared to finding a hole at the valance band edge. As a result of that, in n-type semiconductors, fermi level comes closer to conduction band as it can be seen in Figure 1.8.

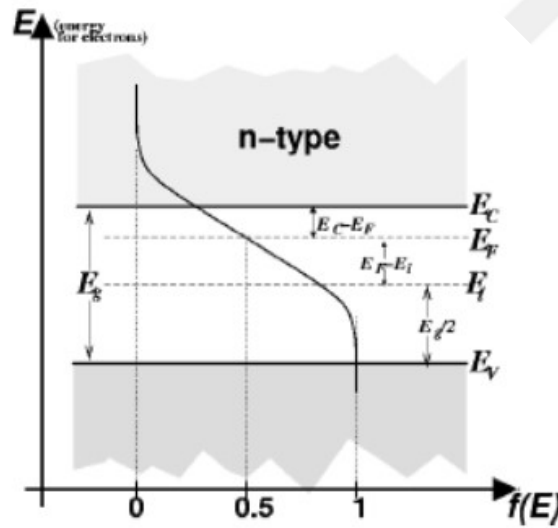


**Figure 1.8:** The band structure of n-type semiconductor photocatalyst [11].

$$f(E_C) > (1 - f(E_V)) \Rightarrow |E_C - E_F| < |E_F - E_V| \Rightarrow E_F > E_i \quad (1.2)$$

**P-type semiconductors:** When a semiconductor is doped with trivalent impurity, the semiconductor has a large number of holes and in that state, an intrinsic semiconductor is known as p-type semiconductor. So, count of holes in valance band is greater than the count of electrons in conduction band and hence there will higher probability of finding a hole near the valance band edge as compared to find electron near conduction band edge. Resultantly, fermi level goes near to the valance band in p-type semiconductors as it can be seen in Figure1.9.

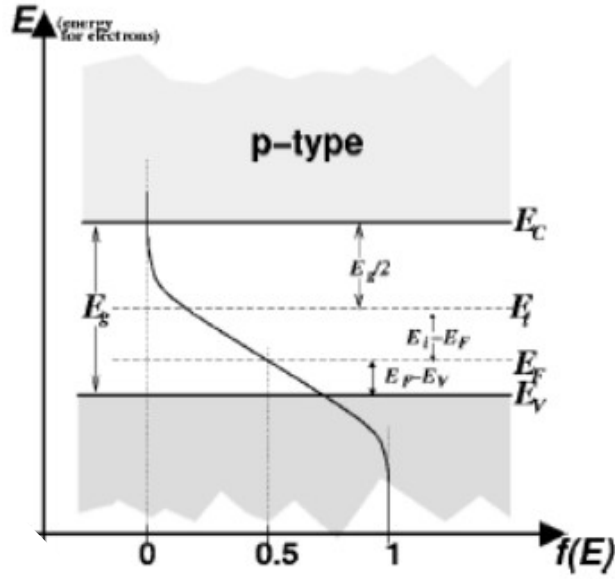


**Figure 1.9:** The band structure of a p-type semiconductor [11].

$$f(E_C) < (1 - f(E_V)) \Rightarrow |E_C - E_F| > |E_F - E_V| \Rightarrow E_F < E_i \quad (1.3)$$

In equations 1.2 and 1.3,  $f(E_C)$  represents the possibility of finding electron in CB while  $(1 - f(E_V))$  shows the possibility of finding hole in VB and  $E_i$  denotes the Intrinsic fermi level. For photocatalytic (PC) and/or photoelectrochemical hydrogen production, a large number and whole variety of photocatalytic materials have been discovered. Generally, photocatalysts are the different types of semiconductor materials which are employed in different photocatalytic and photoelectrolysis applications. Conventionally, semiconductor materials possess a sort of empty energy region in which there are energy levels no energy levels present that can allow or encourage the recombination of photogenerated charge carriers that is, electron and hole. The one of the most important considerations for a semiconductor for being a photochemically active, the photogenerated conductance electrons must have the redox potential sufficiently negative that  $O_2$  can be converted to superoxide by these electrons and the redox potential of the photogenerated valance band holes have to be highly positive to that extant where the can produce the  $OH^\cdot$  radicals [12-15].

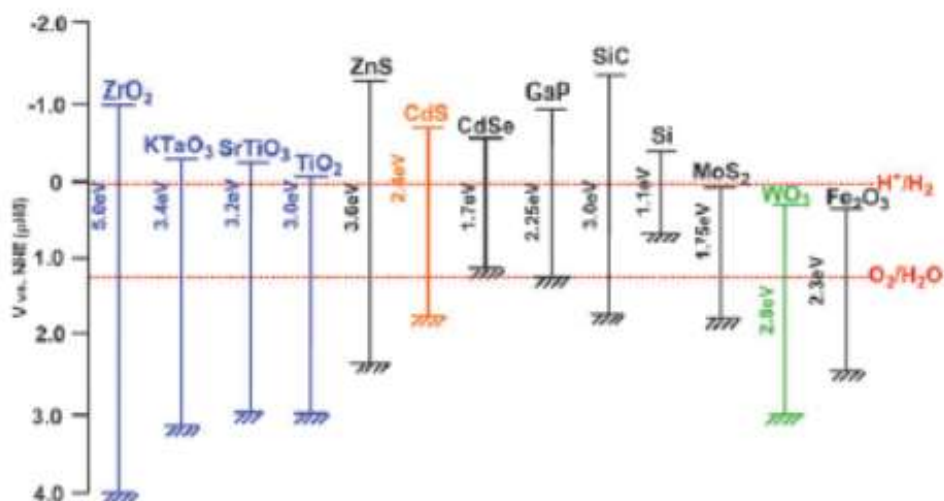
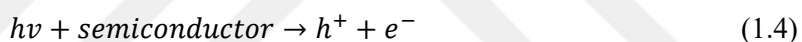


**Figure 1.10:** Variety of photocatalyst for hydrogen production and their band gap structure related to water splitting [12].

Furthermore, when the photons of light having energy ( $h\nu$ ) greater than or equal to the band gap of semiconductor, the photons of light get absorbed in the semiconductor material. As the absorption happens, excitation of electron happens in the valance band to the conduction band leaving behind the hole in valance band. As schematically it is shown in Figure 1.11.



To summarize it can be said that, a good photocatalyst material possesses the following characteristics;

- Have band gap energy between 1.2-2.0 eV
- The conduction band and valance band positions must be in accordance with the reduction and oxidation potential of water
- For hydrogen or oxygen evolution, it should have well catalytic activity
- Under the illumination in the aqueous solution, it should be stable for years.
- It should be cheaper and economical than solid state solar cell connected to an electrolyzer.

### 1.6.2. Photocatalytic Hydrogen Production

To explain the PC HER, in the simple words it can be described as having a photocatalyst in water, and when the photons of light having energy equal to or greater than the band gap of semiconductor absorbed by the surface of semiconductor, they produce photogenerated

electrons and holes in conduction and valance band respectively schematically has been shown in Figure 1.11.

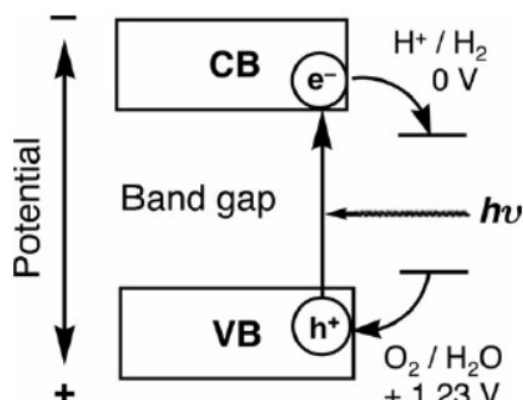


**Figure 1.11:** Principal of water splitting using semiconductor photocatalyst [16].

Electrons at conduction band pioneer the reduction reaction of water molecule there, as a result of which  $H_2$  evolution takes place at conduction band. Oxidation of water, on the other hand, happens at the valence band to form  $O_2$  for overall water splitting. The whole phenomena has been shown in Figure 1.12.

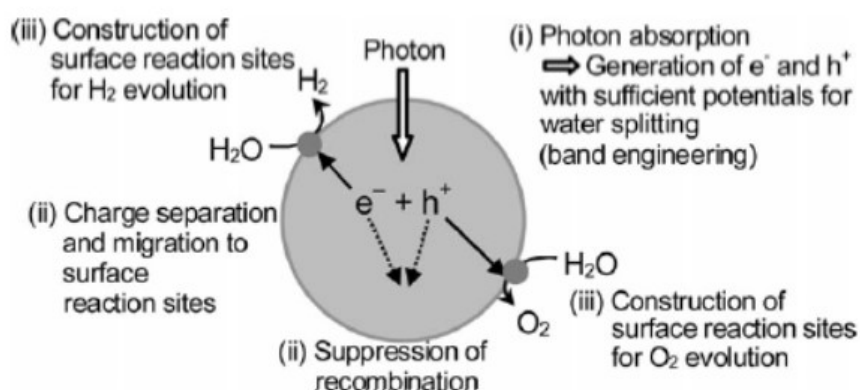


**Figure 1.12:** Main process in photocatalytic water splitting [16].

From Figure 1.12, step (i) is explained briefly in above paragraph. At the stage (ii), the charge separation and the migration to surface reaction sites takes place. The most important parameters that strongly affect this stage (ii) are size of particle, crystal structure and crystallinity as can be seen in Figure 1.13.

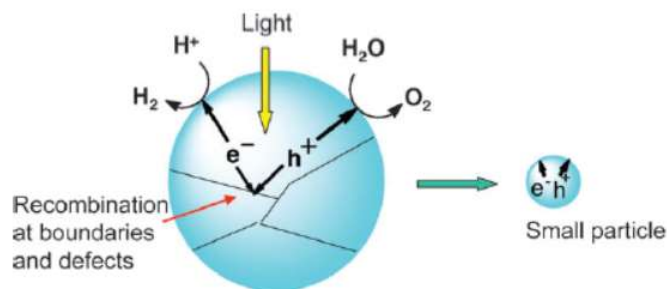


**Figure 1.13:** Effects of particle size and boundary on photocatalytic activity [16].

There is categorically inverse relation between the crystalline quality and defects amounts that is, as the crystalline quality rises the amount of defects decreases. These defects play a major role in decreasing the photocatalytic activity of a photocatalyst by providing the sites that act as trapping and recombination centers between the photogenerated charge carriers. On the same grounds, if photocatalyst has a smaller diameter, then the distance travelled by the photogenerated electrons and holes to migrate and reach the reaction site will be smaller which in turns reduces the possibilities for recombination. While in final step, the two important characteristics that play a vital role in PC activity are active sites (surface character) and surface area (quantity). If these active sites do not exist on the surface, the photogenerated charge carriers (electrons and holes) will recombine irrespective of that they have sufficient thermodynamic potentials for water splitting. To introduce active sites to the photocatalysts, photocatalysts are loaded with co-catalysts such as  $\text{RuO}_2$ ,  $\text{NiO}$  and  $\text{Pt}$ . Because in many cases the positions of conduction bands of many oxide photocatalysts are not negative sufficiently to reduce water for  $\text{H}_2$  production.

### 1.6.3. Photoelectrochemical (PEC) Hydrogen Production

The main difference between PEC and PC system is that in PC system both oxidation  $\text{H}_2\text{O}/\text{O}_2$  and reduction  $\text{H}^+/\text{H}_2$  reactions happen on the surface of photocatalyst. But in photoelectrochemical cell (PEC) the oxidation  $\text{H}_2\text{O}/\text{O}_2$  happens on the surface of photoanode and reduction reaction  $\text{H}^+/\text{H}_2$  happens at the counter electrode (Pt-wire) separately. The simple working of PEC cell containing  $\text{S}^{2-}$ ,  $\text{SO}_3^{2-}$  SR, is explained with steps in Figure 1.14.

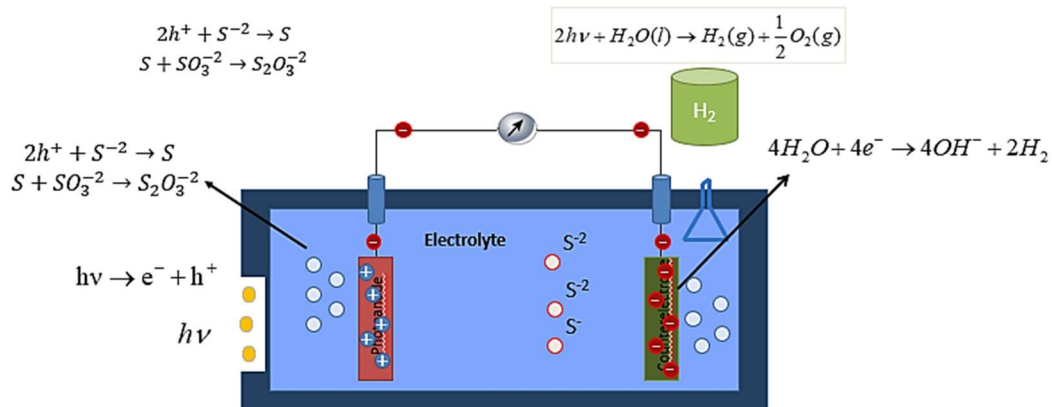
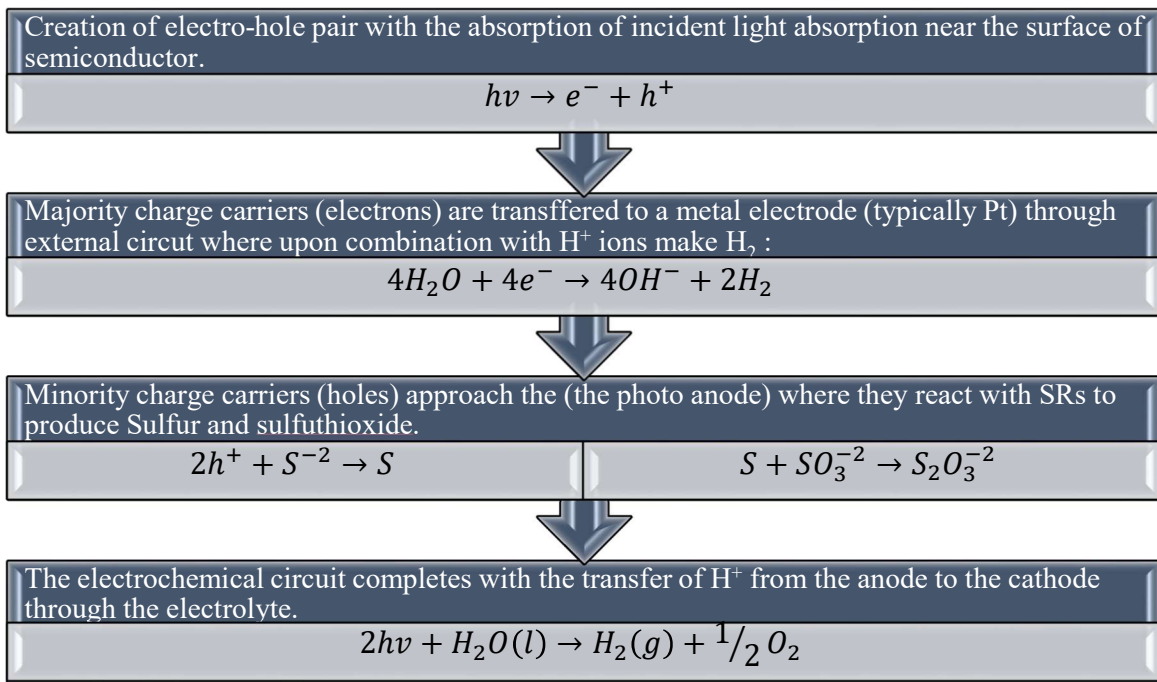


**Figure 1.14:** The principal of photoelectrochemical activity for hydrogen production.

In the very first step, the absorption of light happens near the surface of semiconductor that produce photogenerated electrons in conduction band while photogenerated holes in valance band. These photogenerated electrons as a majority charge carrier travel through the external circuit to the counter electrode where they come in contact with  $H^+$  and by reducing them produce hydrogen. On the other hand, holes as a minority charge carriers drift to the surface of the semiconductor (the photoanode) where they oxidize the SRs to produce Sulfur and sulfuthioxide.

## 1.7. Parameters Affecting the PEC

PEC is very sensitive analysis and there are number of factors that affect the PEC activity for hydrogen production. Some of very important parameters are discussed in the following paragraph.

### 1.7.1. Sacrificial Reagents

When it comes to affective and efficient PC or PEC hydrogen production, it demands for the almost negligible or no merits for recombination of photogenerated charge species otherwise it cut downs the quantum, solar-to-hydrogen and/or applied biased photon to current efficiency (ABPE). According to literature, it has been proved and confirmed that in the case of PC activity, SRs play an important role and retards this recombination activity for photogenerated charges and improves the quantum efficiency [17-19]. In spite of that, the SRs also possess the some other important features which are explained as follows,

- Inhibit and deter the photocorrosion of photocatalyst such NaInS<sub>2</sub>[20] and CdS [21, 22]
- Prove whether or not band positions of photocatalyst are suitable for oxidation (valance band H<sub>2</sub>O-to-O<sub>2</sub>) and reduction (conduction band H<sub>2</sub>O-to-H<sub>2</sub>) for water [23, 24].
- For overall water splitting, in Z-scheme photocatalysis systems, can be employed as redox couple, for example, Fe<sup>3+</sup>/Fe<sup>2+</sup>[25] and IO<sub>3</sub><sup>-</sup>/I<sup>-</sup> [26].

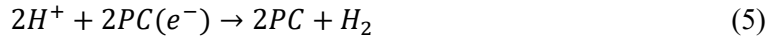
In addition, for the recent past, water splitting reactions that is, the overall water splitting [27] hydrogen evolution (HER) [24, 28, 29] and oxygen evolution reaction [30, 31] studies have gained a lot of attentions. HER studies became quite interesting with use of low band gap photocatalyst along with the controlling of oxidation potential with the usage of a variety of SRs. With introduction of the idea of SRs, now there is a huge library of photocatalysts is present for HER, such mesoporous TiO<sub>2</sub> loaded with Au, Pd, and Cu [32], hydrogen evolution activity of ZnS-CuInS<sub>2</sub>-AgInS<sub>2</sub> in solar light driven water splitting reaction [29], nano-particles of MoS<sub>2</sub> grown on graphene [33], (AgIn)<sub>x</sub>Zn<sub>(1-x)</sub>S<sub>2</sub>[34], ZnO-CdS coreshell nanorods [35], and last but not least enhanced photocatalytic activity of hydrogen production on CdS/MoS<sub>2</sub> [36].

Moreover, among the variety of SRs,  $S^{2-}/SO_3^{2-}$  as an oxidizing species have a considerable importance in PC water splitting reactions [24, 28, 29]. As when  $S^{2-}/SO_3^{2-}$  is used as sacrificial reagent the following reaction takes place;

The absorption of light by photocatalyst;



The proton-reduction by PC activity



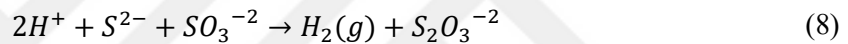
By the electron transfer to the hole of PC from SR regenerates PC



Thiosulfate formation



Overall solar light driven HER



It is well-known that depending on the solutions sulfur contents and pH,  $SO_3^{2-}$  can easily oxidize to  $S_4O_6^{2-}$ , by introducing the different ions of sulfur, the potential of this reaction can be adjusted [37]. Similarly, the use of redox mediators is one of the useful strategies that helps us to lower down the hydrogen evolution reaction for electrolysis of water molecule. The mediators sacrificially oxidize before reaching the oxidation potential of water [38, 39]. Taking Sayama K. et al. work as an example here who by using  $Fe^{2+}$ , which oxidizes to  $Fe^{3+}$ , as a redox mediator in PC system, lowered the oxidation potential of water electrolysis below 1 V bias potential [40].

By taking the above mentioned idea and work into considerations, in this work  $S^{2-}/SO_3^{2-}$  based SR has been used to lower the oxidation potential of water and to get 99.99% pure hydrogen gas evolution.

### 1.7.2. Electrode Preparation Techniques

After the selection of photocatalyst material, the next and the most important step the deposition of photocatalyst. The manner use to deposit photocatalyst on the electrode directly effects the overall PC activity. The optimal thickness of film is desirable for many reasons. For example catalyst films greater than a few monolayers that is, making overloaded films

excessively thick films creates the shadowing effect and hence decrease the light utilization of ability of photocatalyst. With extraordinary increase in film thickness, at the interface and surface of the films, the distance between electron-hole pair increases and as a results recombination of the charge carriers (distance longer than electron-hole life times) take place. So, in order to avoid the shadowing effect and to minimize the recombination of charge carriers the catalyst films should be of the order of few nanometers having the enough active sites or areas for the evolution of gas to happen. There some of the important deposition methods are explained in the following section:

### 1.7.3. Chemical Vapor Deposition

The solution of the catalyst is first needed to be vaporized. This demands for the application of very high temperature and/or very low pressure (vacuum) in the chamber. The substrate remains at the room temperature. As the solution reaches the chamber, it vaporizes and by the process of condensation reaches the surface of substrate, which upon reaction or decomposition at the substrate surface generates required deposit. Frequently, gas flow is utilized to purge the byproduct gases produced during the process from the reaction chamber.

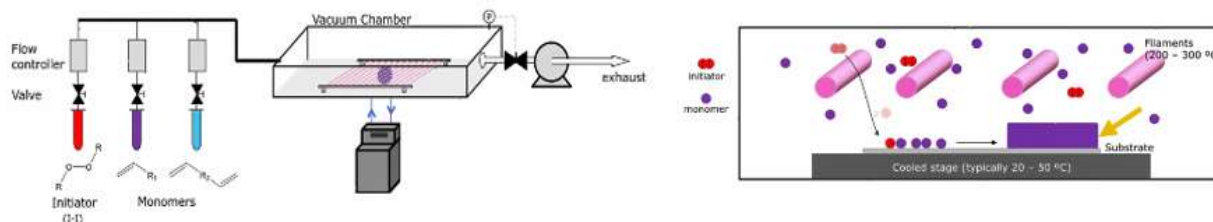


**Figure 1.15:** The scheme for CVD for electrode preparation.

### 1.7.4. Dip Coating

Dip coating is a very simple coating technique for the electrode preparation. In the gist of the dip coating, it can be described as a process in which a well-cleaned substrate which is needed to be coated is dipped into a beaker or liquid photocatalyst container. Upon the withdrawal of substrate from the container creates a film on the surface of substrate. The thickness of the film depends on the speed of withdrawal, temperature conditions and the particle size and viscosity of liquid.

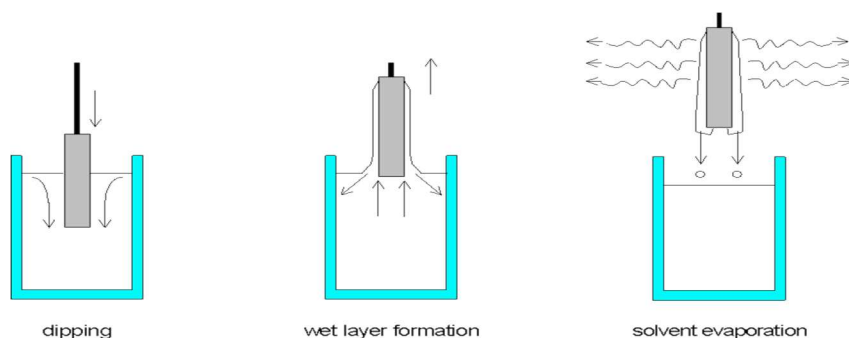


**Figure 1.16:** Dip coating for electrode preparation.

### 1.7.5. Physical Vapor Deposition

Physical vapor deposition (PVD) can be described as a process in which material which is needed to be coated is first vaporized from condensed state. Then transferred substrate in the form of vapors which condense and deposit there in the form of thin film. Actually it includes the series of deposition techniques which make use of vacuum to produce coatings and films.

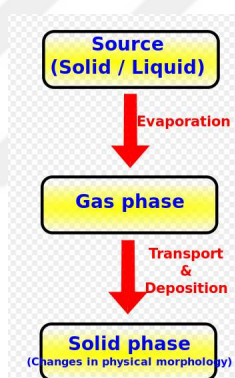


**Figure 1.17:** Stepwise process for PVD for electrode preparation.

### 1.7.6. Spin Coating

A process in which solution of photocatalyst and solvent (ethanol, water etc.) is poured on substrate. The substrate being placed on the disk of spin coater rotate about its own axis at a defined RPM. With action of centrifugal force, the solution spread on substrate uniformly. Generally, spin coating results films having specific thickness with relatively uniformity.



**Figure 1.18:** Spin coating steps for photoelectrode preparation.

### 1.7.7. Electro Deposition

The process which utilizes the electrochemical reactions to generate the thin films on the surface of substrate materials. A well-defined potential range is applied to the electrolyte containing desired material, occurring of the redox reaction direct the process of film generation.

Interesting Features

- Very Low cost as compared to CVD or PVD
- For the production of thin films, a very efficient method
- the composition and crystalline structure of catalyst materials needed to be coated can be controlled by adjusting the electrodeposition parameters

## 1.8. Characterization Techniques

In this section, all of the techniques that have been employed to characterize the prepared samples will be explained in details.

### 1.8.1. X-Ray Diffraction Analysis (XRD)

In the field of material sciences, the identification and recognition of unknown materials is a major issue. XRD is the technique that help us to identify and understand the crystalline materials by determining their compound formula, unit cell dimension, crystal system and sometimes the space group as well. The device use for this analysis is known as X-Ray diffractometer which mainly consist of three parts; an X-ray tube, a sample holder, and an X-ray detector as it can be seen in Fig 1.19.

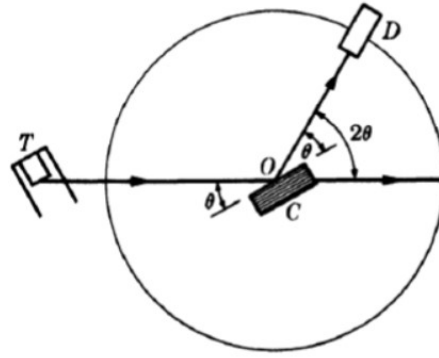


**Figure 1.19:** Scheme of X-Ray diffractometer [41].

The working starts with producing electrons by heating the filament in cathode ray tube, with the application of voltage the electrons moves toward the target material and bombardment happens on the target material. The X-ray spectra is produced when the incident beam possesses the sufficient energy to dislodge the electrons of the inner shell of targeted material. The X-ray beam after getting diffracted from the sample detected and counted by the detector. The sample under consideration is scanned in the range of  $2\theta$  angles which is very important as it helps us to obtain the diffractions coming from the sample at the random orientations. There is another important thing to note that if the diffracted rays are in the same phase, XRD utilizes the constructive interference of the diffracted X-rays as it can be seen in Fig 1.20.

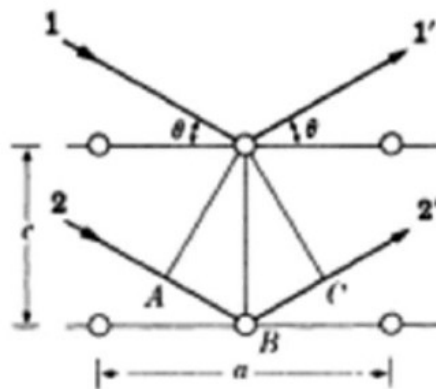


**Figure 1.20:** Schematic representation of X-ray diffraction from crystal [42].

The first and foremost condition for constructive interference is the path difference that exists between the reflected X-rays (reflected from the surface of sample and from the inter-layers of the sample) must be integer number of wavelength [41, 43]. For the two waves having

interference, their path difference can be given by  $2d\sin\theta$ , where  $\theta$  represents the angle of scattering as it can be seen in Figure 1.21.

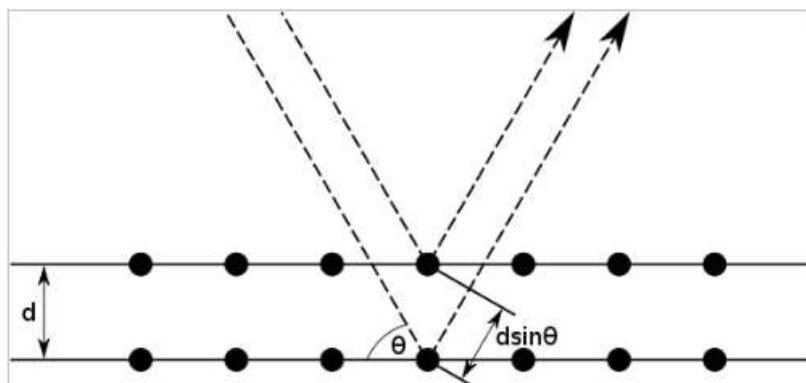


**Figure 1.21:** Schematic representation of Bragg diffraction [44].

In the successive crystallographic planes of crystalline lattice, the cumulative effect of reflection intensifies the destructive or constructive interference. This concept enforces the Bragg's law, which, for the constructive interference, states the condition on  $\theta$  as:

$$2d\sin\theta = n\lambda \quad (1.5)$$

Where  $n$  is the positive integer and  $\lambda$  is the wavelength of incident ray [44].

### 1.8.2. Raman Spectroscopy

For the study of inelastic scattering of light, Raman spectroscopy is employed. In contrast to Infrared spectroscopy, for a molecule to exhibit Raman effect, it is necessary to show a alteration of polarization potential that is, distortion of electronic cloud. The intensity of scattered light has a direct relationship with the magnitude of polarization potential change. Raman is a very useful technique which can be applied to small amount of samples with no sample preparation required and it is non-destructive. Absorption of photon having the energy greater than the energy difference of two vibrational states, causes the excitation of molecule. So, the incident light excites the system from the lower to higher energy state and the scattering reaction occurs while recovering system from this state. However, when the light is scattered elastically, it has the same energy as that of incident light which is also known as Rayleigh scattering. On the basis of energy losses with respect to system, scattering is divided into two classes; Stokes scattering and Anti-Stokes scattering as can be seen in Figure 1.22.

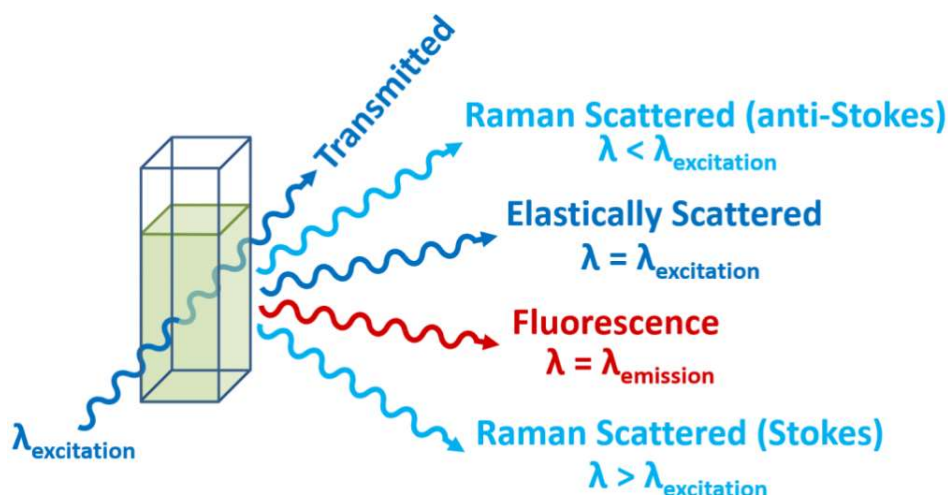


**Figure 1.22:** Types of scattering taking place during the absorption-scattering reactions in Raman [45].

- Stokes Scattering

During the process of scattering reactions, if the system reaches higher energy state than the former one, by gaining the energy, the scattered light also loses this amount of energy and is known as Stokes scattering.

- Anti-Stokes Scattering

For the system vibrating already is excited, system loses its energy and reaches energy state which is lower than it had before. This is known as Anti-Stokes scattering.

Plot of Raman spectrum consist of two axis, vertical axis represents the energy intensity (counts, counts per second and/or arbitrary units) while the horizontal axis depicts the light frequency wavenumber). The Raman spectrometer used for analysis in this work has been shown in Figure1.23.



**Figure 1.23:** Raman apparatus used for Raman analysis.

A Raman spectrum has three parts, a very intense Rayleigh line, Raman bands present in Stokes (low energy, red shifted) and are less intense. While the third one is Anti-Stokes (high energy, blue shifted). Because of ease in detection and higher intensity only the Stokes bands are recorded. The location of Rayleigh line is at zero, while wavenumbers of Anti-Stokes lines are negative and positive for Stokes lines. Every material has its own special wavenumber shifts.

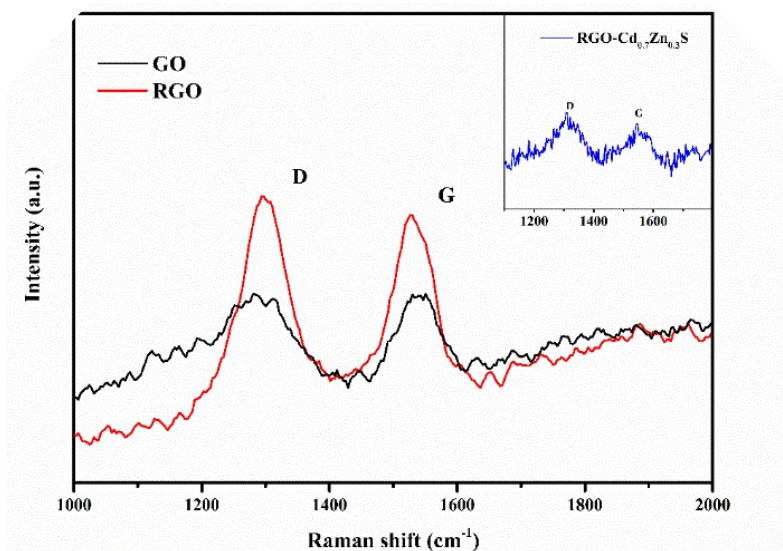


**Figure 1.24:** Representation of Raman spectrum.

### 1.8.3. Ultraviolet-visible Diffusive Reflectance Spectroscopy

Since the opacity of solid materials does not allow the light to pass through them, so the incident light is reflected from the surface of the material sample. On the bases of reflection, the reflections in UV-Vis diffusive reflectance spectroscopy in two classes; specular reflection and diffusive reflection. Specular reflection is happens when the incident light has reflection symmetrically regarding to the normal line. On the other hand, diffusive reflection happens when the incident light scatters in different directions as it can be seen in Figure 1.25.0

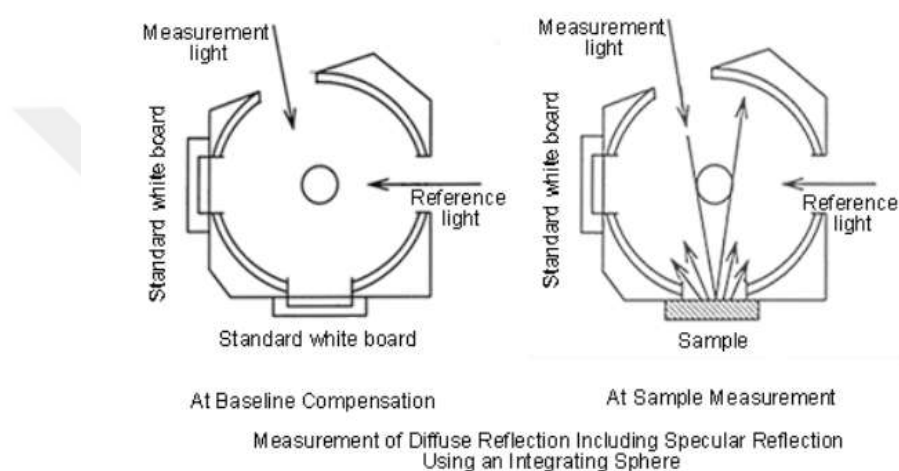


**Figure 1.25:** The working principal of UV-Vis diffusive reflectance spectroscopy [139].

Briefly working can be explained as sample is placed in the front of incident light window. This concentrated incident after being reflected from the sample detected and value obtained pronounced as reflectance which in simple words is relative reflectance regarding the white powdered standard reference material whose reflectance is considered as 100%. So, UV-Vis diffusive reflectance spectroscopy is the powerful tool to characterize sample on the bases of their light absorbing or reflecting properties.

### 1.8.4. Scanning Electron Microscopy (SEM)

To understand the surface topography and composition of the sample, scanning electron microscopy is of the powerful tools which is a type of electron microscope. Its working principle is very simple in which sample is scanned by sending a beam of electrons to the sample which produces its image. This incident beam of electrons interact with atoms of sample and produce various signals that have information about surface topography and composition.

The beam of electrons is produced by an electron gun provided with a suitable cathode. Normally, Tungsten filament is employed as lowest vapor pressure and highest melting point as compared to all metals. The energy range of produced electron beam is normally 0.2-40 keV. This beam is focused to a spot having diameter of about 0.4-5 nm with help of one (or sometimes two) condenser lenses. The primary electron beam upon interaction with sample, due to scattering and absorption within the volume of sample, electrons lose energy. Because of this energy exchange between the sample and beam of electron, elastic scattering causes the reflection of high energy electrons while the inelastic scattering causes the emission of secondary electrons and electromagnetic radiations. A very specialized detector is used to detect any of these beam and to generate image of sample [46]. A very simple diagram showing the basic components of SEM in Figure 1.26.

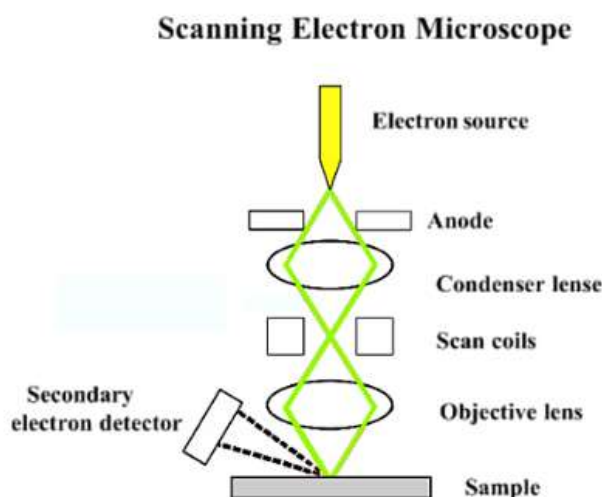


**Figure 1.26:** Schematic representation of SEM components [46].

#### **1.8.5. Energy Dispersive X-Ray Spectroscopy (EDS)**

Energy dispersive X-Ray spectroscopy is a chemical microanalysis technique to analyze the sample composition. It works with detection of X-rays emitted from the given sample as a result of electron bombardment on the sample.

## 2. EXPERIMENTAL CONSIDERATIONS

In this chapter all of the materials that have been used throughout the experimentation, synthesis of photocatalyst and the preparation of photoanode from it, and the characterization techniques that have been used to characterize the as produced samples will be discussed in details. Furthermore, a formal detailed explanation of optimization of system along with the electrochemical measurements and their results will be discussed.

### 2.1. Literature Review

When it comes to water splitting by utilization of solar light irradiation, the very first activity of that kind was performed by Honda-Fujishima in 1970s. As he successfully split the water molecule into its constituents (hydrogen and oxygen) by using  $\text{TiO}_2$  as photoelectrode. Under the illumination of UV-light and with some bias from external power source, photogenerated electrons from  $\text{TiO}_2$  travelling through external circuit reach Pt-counter electrode where they reduce  $\text{H}^+$  to  $\text{H}_2$  while holes on  $\text{TiO}_2$  reach the surface of photoanode and oxidize the water to  $\text{O}_2$ [47] as it can be seen in Figure2.1.

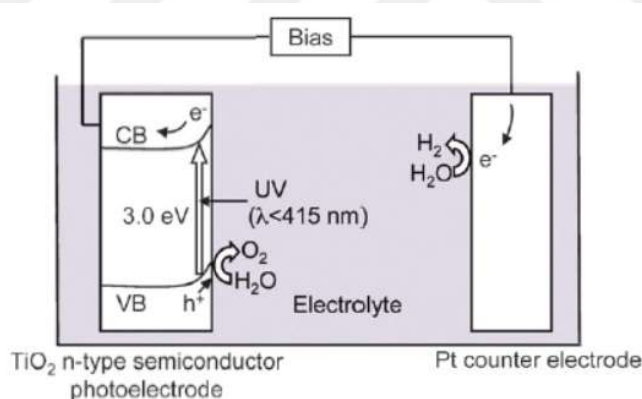


**Figure 2.1:** Honda-Fujishima effect-water splitting using a  $\text{TiO}_2$  photoelectrode [16].

Since that finding, a huge number of semiconductor materials have been used as photocatalyst in photocatalytic and photoelectrochemical hydrogen production. In the recent past, more attentions have been given to heterogeneous photocatalyst materials which generally includes metal oxide based, metal (oxy)sulfide based, metal chalcogenides based and metal (oxy) nitrides based photocatalyst[48-52]. The addition of co-catalysts (loading and doping) and sacrificial reagents also improve the photostability of photocatalyst, increase the life time of photogenerated charges which in turns enhances the photocatalytic activity of photocatalyst. Recently, for  $\text{H}_2$  production by light driven photocatalytic water splitting

reactions, chalcogenides based semiconducting photocatalysts have gained a remarkable attention[53-57]. For example, CdS is a very effective and active sulfur-based photocatalyst among the IIB-VIA having direct band gap of 2.4 eV and remarkably active in visible region of solar spectrum. It has a considerably high negative conduction band and has efficient absorption in visible region for HER [58-60]. However, being n-type semiconductor, CdS in aqueous solutions is prone to photocorrosion in which  $S^{2-}$  ion separates from CdS and oxidizes by the photogenerated holes leaving behind the  $Cd^{2+}$  and the fast recombination of photogenerated charge particles reduces its scope as an efficient photocatalyst[61, 62]. One of the possible solutions to this problem is to couple CdS with semiconductors having wide band gaps such as ZnS [63]. But as far as it is concerned with ZnS, it is only active in the UV region of solar spectrum which is only 3-5% of the whole solar spectrum. Similarly, it is also reported in literature that to avoid photocorrosion and to have an efficient photogenerated charge reaction in n-type chalcogenides semiconductors, it is necessary to combine or couple the semiconductor specie with charge carrier transfer catalyst such as, Pt, Pd, Rh, Ni,  $RuO_2$ , and WC etc [64, 65].

A solid solution of CdS and ZnS that is,  $Cd_xZn_{1-x}S$  has become very famous and got a lot of attention since recent past because of its moldable and controllable band structure, very efficient absorption in visible region of solar spectrum, active and effective photocatalytic performance for hydrogen production [66-77]. Although it's optical absorption can be improved and band gap can be optimized by varying the percentage of ZnS in solid solution, but the fast recombination of photogenerated charge carriers is still a dilemma. The problem can be addressed by changing different parameters, one of which is synthesis method. For the synthesis of this solid solution, there are number of methods are present in the literature such as, co-precipitation [70, 78], microemulsion [79], chemical bath deposition [80], cation exchange [69], hydrothermal treatment [81, 82] and thermolysis [83]. In spite of these methods that have been reported here for the synthesis of  $Cd_xZn_{1-x}S$ , thermal sulfurization seems to be a very effective method as it has been employed by our group in their previous work [84].

Furthermore, the Jing DW et. al. also utilized the same method to synthesize CNT- $Cd_{0.1}Zn_{0.9}S$ , reported and elaborated the advantages of this method in their work [82]. Additionally, Kai Zhung et. al. synthesized  $Cd_xZn_{1-x}S$  by utilizing different methods, tested and analyzed the synthesized sample from various structural analyses and photoelectrochemical tests. It has been reported that  $Cd_xZn_{1-x}S$  that has been prepared by

sulfurization technique possesses very sharp and only hexagonal phase with remarkably good crystallinity. Similarly, having absorption edge at the longest wavelength and without the presence of noble metal co-catalysts relatively higher photocatalytic activity are also the characteristics that might be rooted from thermal sulfurization[68].

## 2.2. Introduction to Graphene:

Graphene have 2D structure which is compose of carbon atoms that are  $Sp^2$  hybridized and arranged in hexagonal pattern. This type of arrangement is called honeycomb structure. Graphene exhibit extraordinary mechanical, electric properties and very high specific surface area. High mechanical strength is due to covalent nature of bonding and small bond length. High electric conductivity and low electrical noise is because of very no band gap between valance and conduction band [15].

### 2.2.1. Graphene Crystal Structure:

Carbon atoms in graphene are  $Sp^2$  hybridized,  $Sp^2$  hybridization yield three  $Sp^2$  orbitals that are arrange at  $120^\circ$  degrees and one un-hybridized orbital which form delocalized electronic cloud just like benzene that is why we can say “graphene is a polycyclic aromatic hydrocarbon of quasi infinite size”[85] as it can be seen in Figure 2.2.

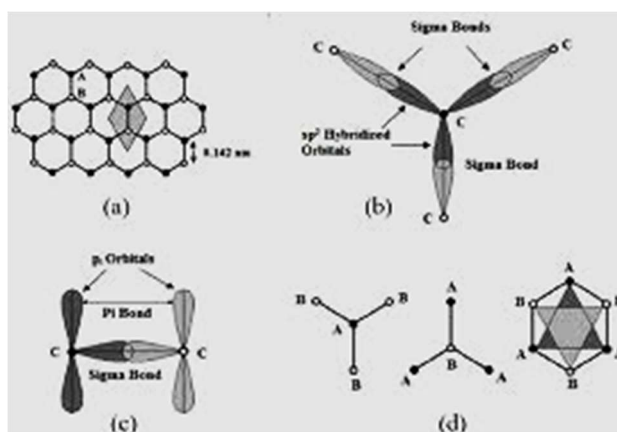


**Figure 2.2:** Structure of Graphene [85].

### 2.2.2. Routes for Graphene Preparation:

In 1859, Benjamin Brodie provided the base for graphene synthesis by chemical method, he studied the reaction of graphite with oxidizing agent such as chlorates [86]. In 1898 L. Staudenmaier rendered the reaction time by using sulfuric acid in reaction mixture of Brodie.

In 1958, Hummers and Offeman published graphite oxide preparation using Potassium permanganate instead of chlorate which produce toxic ClO [87]. About 90 year after Brodie, Vogt studied the exfoliation of graphene oxide and found cracked sheets using transmission electron microscopy [88]. In 1986 by Boehm et al. labeled these bodies as “graphene” [89]. Geim and Novoselov isolated single layer of carbon atoms by mechanical exfoliation by scotch tape and they received Noble Prize for their work [90] and studied the electric properties of graphene which set off a large number of research to work on graphene.

Graphene can be synthesized by using graphite as raw material (Graphite is layered, planar structure each layer consist of carbon atoms arranged in a honeycomb lattice with bond distance of 0.142 nm and separation between planes is 0.335 nm) or by using any carbon material (methane, ethane, acetylene).

The exfoliation method of graphite includes;

- Mechanical cleavage
- Liquid-Phase Exfoliation
- Electrochemical methods.

Using Carbon precursor, following methods can give graphene;

- Chemical Vapor Deposition
- Thermal Decomposition of SiC.

**Chemical Vapor Deposition CVD:** In this process transition metal substrate put in a closed chamber and gradually heated to 1000<sup>0</sup>C with the continuous flow of feed gas, the carbon atom from hydrocarbon nucleate on the substrate and nuclei grow to give a larger film. After the formation of film, substrate is rapidly cool to room temperature[91].

**Thermal decomposition of silicon carbide:** This method utilized the segregation of SiC. This method has the ability to produce large films of graphene. This process involve two steps; annealing of SiC at above 800<sup>0</sup>C under continuous flow of H<sub>2</sub> or Argon, which cause the sublimation of Si, in second step Carbon atoms arrange themselves to give graphene[92].

**Mechanical cleavage:** Mechanical Exfoliation is called the mother of graphene synthesis because in 2004 Geim at Manchester University isolated single-layer samples from graphite using scotch-tape. He stick graphite on a piece of tape and cleaved it with other sticky tape until invisible powder left on the starting tape and then transferred it to silicon dioxide substrate[90].

**Electrochemical method:** In this method boro-silicate glass pressed on graphite layer at 200°C, and the voltage of 1700-1800V is applied. The electric field pull the layers of graphite apart and deposited on glass plate[93].

**Liquid Phase Exfoliation of Graphite Oxide:** Chemical route of graphene synthesis by using graphite as starting material is most convenient method to produce graphene.

There are two ways of graphene synthesis by this method;

- a) Liquid Phase Exfoliation of Graphite.
- b) Exfoliation of Graphite by Oxidation.

**a. Liquid Phase Exfoliation of Graphite:** Process involves three step; In first step the graphite is mixed in a solvent that increase the distance between the graphite layers, in second step mixture is ultra- sonication to split graphite layer into individual platelets final step is the purification of the product by removing solvent [94].

**b. Exfoliation of Graphite by Oxidation:** Oxidation route of graphene synthesis by using graphite as starting material is largely used method. Oxidation of graphite is done by using strong oxidizing agent like  $\text{KMnO}_4$  and concentrated sulfuric acid followed by reduction using strong reducing agent like ascorbic acid or the salts of hydrazine to give graphene usually called reduced graphene oxide (RGO)[87].

### 2.2.3. Reduction of GO:

During oxidation of graphite different functional groups attached to GO sheets. These functional groups have different binding energies depending upon the type and location. To obtained graphene these functional group should be removed, the graphene obtained by the removal of functional groups from GO is called reduce graphene oxide (RGO). Many method are available to remove these groups, some important and vastly used are given in table 2.1.[95-114]. Thorough reduction of GO is very tough to attain, but for large scale synthesis and applications graphene production through GO is very attractive. The structure of RGO sheets is given in Figure 2.3.

**Table 2.1:** [95-114] Comparison of different methods of GO reduction

| Advantage                                                                    | Disadvantage                                                                    | Electric conductivity                                                                                                      | C/O Ratio                                                     |
|------------------------------------------------------------------------------|---------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------|
| <b>Thermal Reduction</b>                                                     |                                                                                 |                                                                                                                            |                                                               |
| <b>Different level of reduction can be achieve by varying temperature.</b>   | Small size, wrinkled graphene sheets.<br>30% yield.<br>Large energy consumption | Depend on reduction temperature, typical mean value is 10–23 S/cm.<br>500°C 50 S/cm,<br>700°C 100 S/cm<br>1100°C 550 S/cm. | Depend on the temperature.<br>At 500°C C/O=7<br>750°C C/O=13. |
| <b>Radiation Reduction</b>                                                   |                                                                                 |                                                                                                                            |                                                               |
| <b>Uniform and rapid reduction.</b>                                          | Expansive and not suitable for bulk production                                  | Photo-irradiation = 10 S/cm<br>Laser = 256 S/cm                                                                            | ----                                                          |
| <b>Photocatalytic Reduction</b>                                              |                                                                                 |                                                                                                                            |                                                               |
| <b>Green and Sustainable, Low waste production.</b>                          | High level of reduction cannot be not be achieved.<br>Use UV- light source.     | Electric resistance around 150 (k $\Omega$ /sq)                                                                            | ----                                                          |
| <b>Electrochemical Reduction</b>                                             |                                                                                 |                                                                                                                            |                                                               |
| <b>No special chemical agent<br/>Room temperature</b>                        | Large scale synthesis is costly and difficult.                                  | 85 S/ cm                                                                                                                   | C/O = 23.9                                                    |
| <b>Chemical reagent reduction</b>                                            |                                                                                 |                                                                                                                            |                                                               |
| <b>Mass production, cheaper and easily available</b>                         | Chemical waste is produced                                                      | Hydrazine 99.6 S/ cm<br>NaBH <sub>4</sub> 16.6 S/cm.<br>Ascorbic acid 77 S/cm<br>Hydroiodic acid 300 S/cm                  | C/O = 13<br>C/O = 8.6<br>C/O = 12.5<br>C/O = 15               |
| <b>Solvothermal Reduction</b>                                                |                                                                                 |                                                                                                                            |                                                               |
| <b>Green, less toxic and produce a stable and well dispersion rGO sheets</b> | Time consuming, high pressure and less reduction than other methods.            | Electric resistance depend on solvent used<br>DMF 10 <sup>5</sup> –10 <sup>6</sup> $\Omega$ /sq<br>NMP 3.74 S/cm           | C/O = 14.3<br>C/O = 5.15                                      |

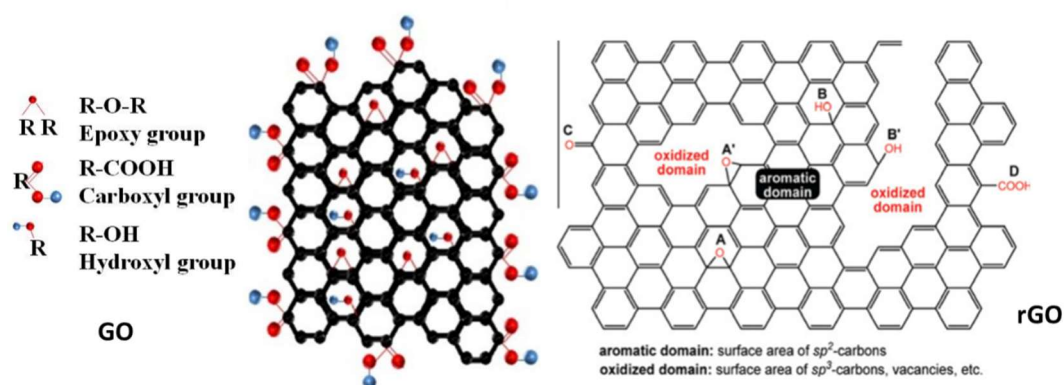


**Figure 2.3:** Structure of GO and RGO sheet [85].

## 2.3. Experimentation

### 2.3.1. Materials

All experimental measurements were carried out with highly pure chemicals. Indium tin oxide glass (ITO), cadmium acetate dihydrate, zinc acetate dihydrate, elemental sulfur, ethanol, acetone, graphite, sodium sulfide, sodium sulfite, sulfuric acid ( $\text{H}_2\text{SO}_4$ ), potassium permanganate, hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), hydrochloric acid (HCl) and hydrazine hydrate were purchased from Aldrich and used without any further purification. All electrochemical measurements were carried out at standard temperature and pressure conditions (STP) i.e. at 25 °C and 1 atm.

### 2.3.2. Preparation of Reduced Graphene Oxide (RGO)

Hammer's method have been practiced for the synthesis of RGO. However, here briefly hummer's method can be described as fellow;

### 2.3.3. Hammer's Method

*Preparation of graphene oxide (GO):* For the preparation of GO, 1 g of graphite powder was mixed with 23 ml of  $\text{H}_2\text{SO}_4$  and a homogeneous solution obtained by stirring the spices with the help of magnetic stirrer. Then 3 g  $\text{KMnO}_4$  added to the solution gradually in ice bath because the reaction is exothermic. Then mixer stirred again for 30 min in sand bath at 40 °C 50 ml ultrapure water is added to stirring mixture. While adding water, temperature rises to 98 °C. After 15 min, mixture of 5 ml of 30% HCl and 167 ml ultrapure water added to reaction mixture and left on the stirrer for 2 hr. Later on reaction mixture was filter and rinsed

with 10% HCl solution. At the final stage, filtrate left for drying at 50 °C for 12 hr and as an end product brown colored powder of graphene oxide was obtained.

*Preparation of reduced graphene oxide (RGO):* For preparation of RGO, 0.2 g as obtained GO and 200 ml ultrapure water were mixed in a flask. For proper dissolution of reactant in water, reactant mixer was put in ultrasonic bath for sonication and remains there until particles cannot be seen from naked eye. Then with the gradual addition of 2 ml water to the reaction solution, solution was heated to 100 °C in water cooled condenser for 24 hr. during this process conversion of GO to RGO happens and appeared as black colored solid which was then filtered and rinsed with 250 ml water and 250 ml methanol. The final product was then left at room temperature for drying and stored under vacuum.

#### **2.3.4. Preparation of Photocatalyst**

Preparation of photocatalyst happened in two stages; preparation of metal oxides followed by preparation of metal sulfides.

#### **2.3.5. Preparation of Metal Oxides**

At the first stage of preparation of photocatalyst, thermal cracking method has been used to produce metal oxides. For this purpose, tube furnace was used and figure of its cross-section have been shown in figure 2.4. Cadmium acetate dihydrate  $[\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$  and zinc acetate dihydrate  $[\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$  were mixed in different weight ratios and underwent thermal cracking process which happened in tube furnace to get five different compositions of metal oxides i.e.  $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{O}$ ,  $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{O}$ ,  $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{O}$ ,  $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{O}$  and  $\text{CdO}$ . For the synthesis of RGO decorated photocatalysts, then mixture of RGO,  $[\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$  and  $[\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$  was used as reactant mixture. These weight ratios are given in following Table 2.2.

**Table 2.2:** Weight ratios for  $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  and contents of RGO for each corresponding photocatalyst sample.

| Photocatalyst                            | Wt% Cd | Wt% Zn | Cd content<br>(g) | Zn content<br>(g) | RGO<br>(g) | S content<br>(g) |
|------------------------------------------|--------|--------|-------------------|-------------------|------------|------------------|
| $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ | 30     | 70     | 0.474             | 2.68              | 0.034      | 0.258            |
| $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ | 50     | 50     | 1.499             | 1.23              | 0.031      | 0.353            |
| $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}$ | 70     | 30     | 1.365             | 1.423             | 0.031      | 0.358            |
| $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{S}$ | 90     | 10     | 1.755             | 0.474             | 0.031      | 0.358            |
| $\text{CdS}$                             | 100    | 0      | 1.95              | —                 | 0.031      | 0.358            |

For thermal cracking mixture of solids was placed, one at a time, at 500 °C for 3 hr in argon atmosphere. The assembly of tube reactor is given in Figure 2.4.

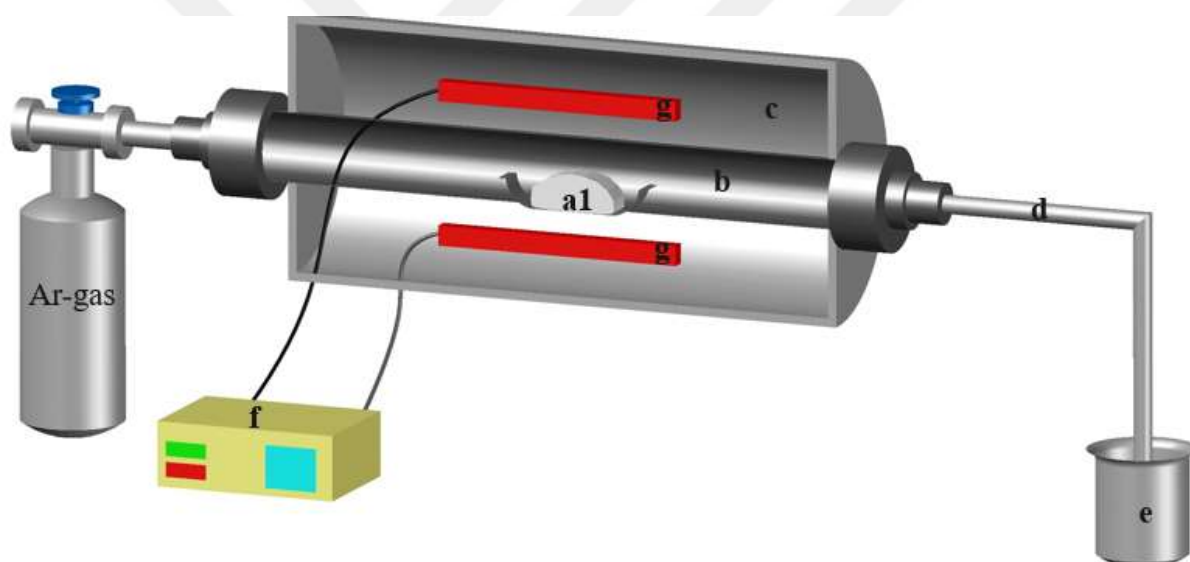


**Figure 2.4:** Structure and arrangement of tube furnace for thermal cracking of metal dihydrates into metal oxides.

Mixer of  $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  labeled as **a1** was poured to alumina crucible and placed at the center of quartz tube labeled as **b** which was afterwards placed in tube reactor **c**. One end of tube was connected to argon supply to create Ar-atmosphere inside the reactor and the other end **d** i.e. purge end was put into the water beaker **e** with help of rubber pipe to incarcerate the hazardous gases in the water produced during the thermal cracking process. Reaction lasts for 3hr at 500 °C under Ar-atmosphere and reaction conditions were controlled with panel **f**. At the end of the reaction, product remains in the

reactor until it reaches room temperature 25 °C. The reactant material and the end product has been given in Figure 2.5.



**Figure 2.5:** The physical appearance of reactants before and after the thermal cracking.

### 2.3.6. Preparation of Metal Sulfides

Preparation of metal sulfides was done with Sulfurization method. For this process, the end product from thermal cracking i.e. metal oxides grinded into powder and again pour in alumina crucible were placed at the center of the quartz tube while on the other end of tube elemental sulfur was placed with help of alumina crucible. That end of tube connected to Ar-gas supply while the other end was linked to the pipe going into the water beaker. Before starting the reaction, Ar gas flowed through the system for 30 min to remove all unwanted residual gases. As tube reactor has different temperature zones at different positions, the reactant mixture experienced 700 °C (as temperature was set to 700°C) while elemental sulfur had 200 °C zone. Sulfurization lasted for 6hr at 700°C. The apparatus arrangement can be seen in Figure 2.6. After the reaction completion, end product remained inside the reactor and cooled to room temperature slowly.

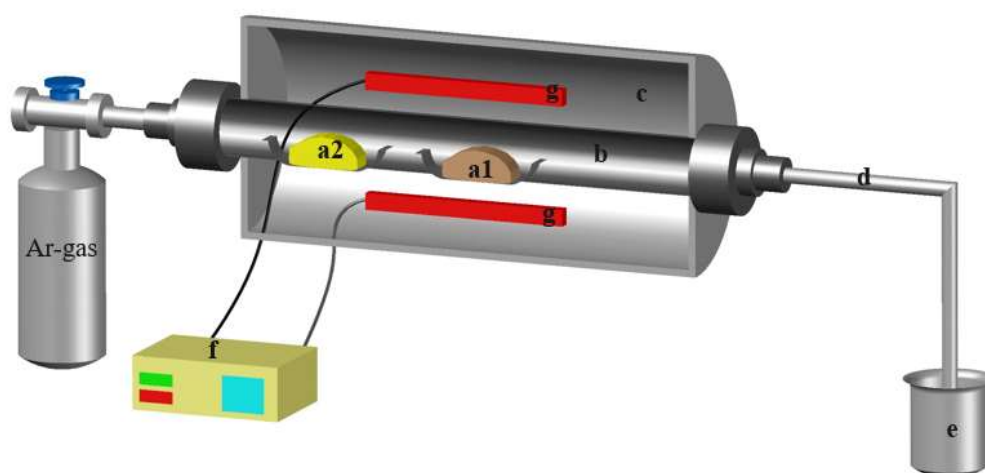


**Figure 2.6:** The arrangement of reactant materials in tube furnace during thermal sulfuration process.

At the final stage, product taken out of the quartz tube, was grinded to a very fine powder and ready for further analysis. Same procedure was repeated for RGO-decorated metal oxides for the preparation of metal sulfides. After completion the synthesize ten photocatalysts different in compositions were prepared as  $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ ,  $\text{RGO-Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ ,  $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ ,  $\text{RGO-Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ ,  $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}$ ,  $\text{RGO-Cd}_{0.7}\text{Zn}_{0.3}\text{S}$ ,  $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{S}$ ,  $\text{RGO-Cd}_{0.9}\text{Zn}_{0.1}\text{S}$ ,  $\text{CdS}$  and  $\text{RGO-CdS}$ .

### 2.3.7. Preparation of Photoanodes

For the preparation of photoanodes, an ITO glass sheet with the dimensions of  $0.8 \times 1$  cm used as substrate. In this work, spin coating technique was employed for preparing photoanodes by using Model p6700 series spin coater. For this purpose, suspension was prepared with 20 mg photocatalyst material in 1.5 ml ethanol. Then suspension was sonicated with ultrasonic bath to dissolve the solid solute in solvent until material's particle cannot be seen through naked eye. Before coating on ITO, ITO glass was cleaned ultrasonically with acetone, ethanol and then with ultrapure water.

While coating photocatalyst material on ITO with spin coater, RPM was set to 4000 for 30 sec with intermediate heating at  $150^\circ\text{C}$  in air after deposition of each coat. For every layer, 15  $\mu\text{l}$  suspension was poured drop-wise on the surface of ITO-substrate. After coating, photoanode was annealed at  $550^\circ\text{C}$  for 1 hr in air and left unattended until it reaches the room temperature. This picture of final product is given in Figure 2.7.

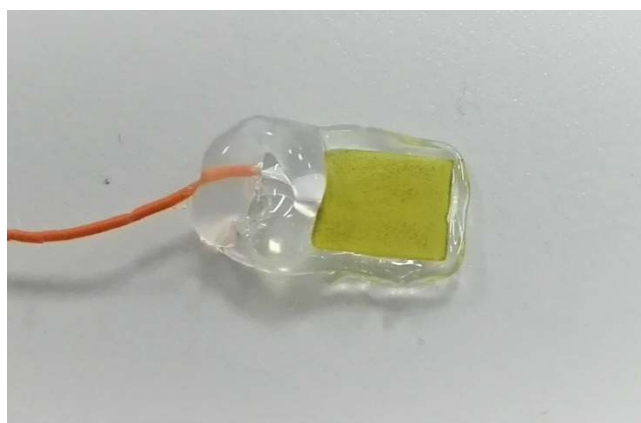


**Figure 2.7:** The physical appearance of photoelectrode ( $\text{RGO-Cd}_{0.7}\text{Zn}_{0.3}\text{S}$ ) prepared by spin coating and annealed at  $550^\circ\text{C}$ .

### 3. RESULTS AND DISCUSSION

In this chapter all of the materials that have been used throughout the experimentation, synthesis of photocatalyst and the preparation of photoanode from it, and the characterization techniques that have been used to characterize the as produced samples will be discussed in details. Furthermore, a formal detailed explanation of optimization of system along with the electrochemical measurements and their results will be discussed.

#### 3.1. Optimization

For last ten years or more, there have been lot of research work started related to solid solution of CdS and ZnS having in mind that CdS has band gap 2.42 eV and very active in visible region while ZnS has 3.66 eV and has activity in UV-region of solar spectrum. Therefore, by changing the weight percentages of CdS and ZnS, band gap of this solid solution i.e.  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  can be controlled. On the other, method of synthesis also plays an important in defining the band gap. Having the ability of modifiable and controllable band gap makes  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  exceptionally an excellent photocatalyst for photocatalytic hydrogen production and photoelectrochemical hydrogen production reactions.

CdS alone however, is also an amazing photocatalyst but the only problem is its photostability under visible light irradiation. CdS being an n-type semiconductor, is prone to photocorrosion in the aqueous solutions and reduces its scope as an efficient photocatalyst [61, 62]. Brad et al., [64, 65] confirmed that combination of electron or hole transfer catalysts for example Pt, Pd, Rh, Ni, RuO<sub>2</sub> and WC etc. with n-type semiconductors increase their life span by rendering the photocorrosion and promotes the efficient charge transfer reactions [115-118]. Taking this into the considerations, in this present work RGO decorated CdS has been synthesized, characterized and analyzed photoelectrochemically where RGO not only increases the life span of photogenerated charged carriers by shuttling and transporting but also enhance the absorption by the photocatalyst scattering the incident light[119].

Furthermore, sulfurization provides the photocatalyst very sharp, hexagonal phase with good crystallinity and also allows photocatalyst to absorb longer wavelengths[120]. As mentioned above, after the completion of sulfurization process, ten photocatalytic material samples varying in composition ( $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ , RGO- $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ ,  $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ , RGO- $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ ,  $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}$ , RGO- $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}$ ,  $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{S}$ , RGO- $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{S}$ , CdS and RGO-CdS) have been prepared and before PC, PEC and surface/physical characterization, these samples underwent

series of PEC analysis to figure out the most optimized conditions for the system. In other words before any other sort of characterization, system parameters such as annealing temperature, number of layers of photocatalyst on the ITO-substrate, and weight percentage of RGO in the sample were optimized and used during the whole experimentation and experimentation.

### 3.1.1. Film Thickness optimization

Firstly, number of layers of photocatalytic material on the ITO-substrate were optimized as number of layers has direct relation with thickness of deposition and in simple words also directly effects the efficacy of system as explained in the Figure 3.1.

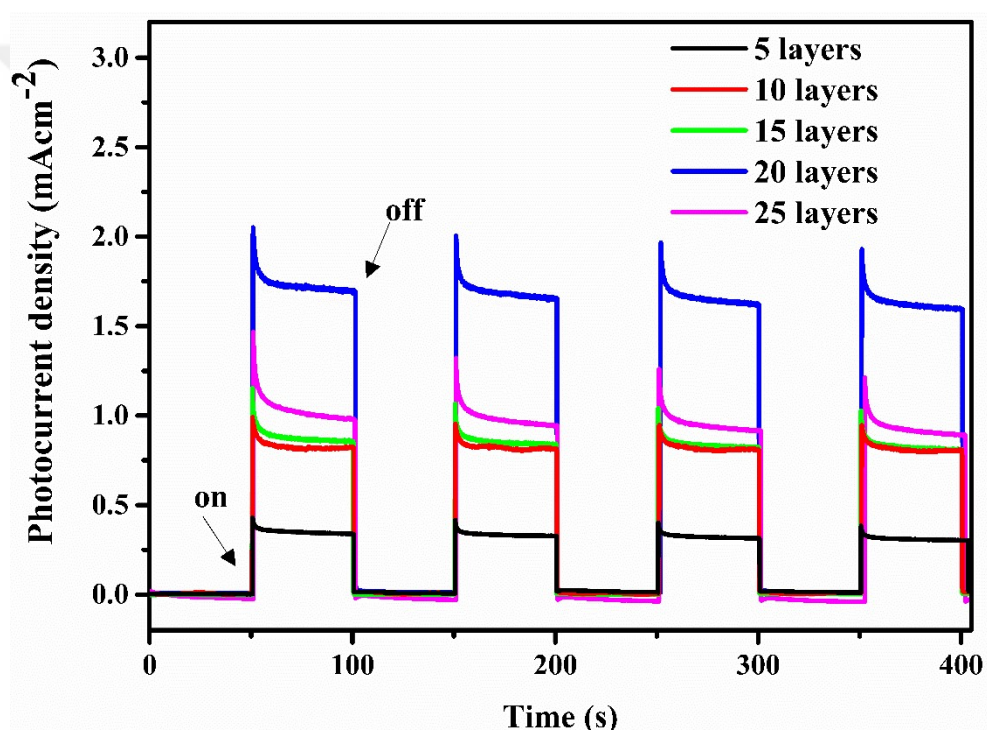


**Figure 3.1:** Photocurrent response of ITO/RGO-Cd<sub>0.7</sub>Zn<sub>0.3</sub>S photocatalyst with 5, 10, 15, 20, and 25 layers. Electrolyte used for electrochemical measurements, contained 0.35 M Na<sub>2</sub>S and 0.25 M Na<sub>2</sub>SO<sub>3</sub> at 0.25 V versus RHE.

From our previous work [84], Cd<sub>0.77</sub>Zn<sub>0.23</sub>S photocatalyst sample had the highest photocatalytic hydrogen production. So taking it as an example here in this work and by decorating it with RGO, RGO-Cd<sub>0.7</sub>Zn<sub>0.3</sub>S was prepared and used as an example photoanode for initial optimization of the system. It can be seen that the variations in photoelectrochemical activity of for example RGO- Cd<sub>0.7</sub>Zn<sub>0.3</sub>S photoanode with varying the number of layers for example, with the increase in the number of layers photocurrent density

also increases until it becomes  $2.1 \text{ mAcm}^{-2}$ , the maximum value, at 20 layers. It establishes that the photoanode prepared with this optimized number of layers exhibits the highest activity and photostability among the other electrodes prepared with any other count. It can be attributed that with the increase in the number of layers, the absorption of incident light by the photoanode also increases. On the other hand, with the further increase in the number of layers photocurrent density decreases drastically along with gradual decrease in stability. The possible explanation to this behavior is that with extraordinary increase in thickness of film on ITO-substrate, the increased distance between electron-hole pair at the interface and the surface of the film provides the electron-hole recombination centers and resultantly suppress the electron transfer.

### 3.1.2. Annealing Temperature Optimization

The another important system parameter was also optimized by annealing the same photoanode as mentioned above at three different temperatures such as  $450^\circ\text{C}$ ,  $550^\circ\text{C}$ , and  $650^\circ\text{C}$  and results of photoelectrochemical behavior are presented in Figure 3.2.

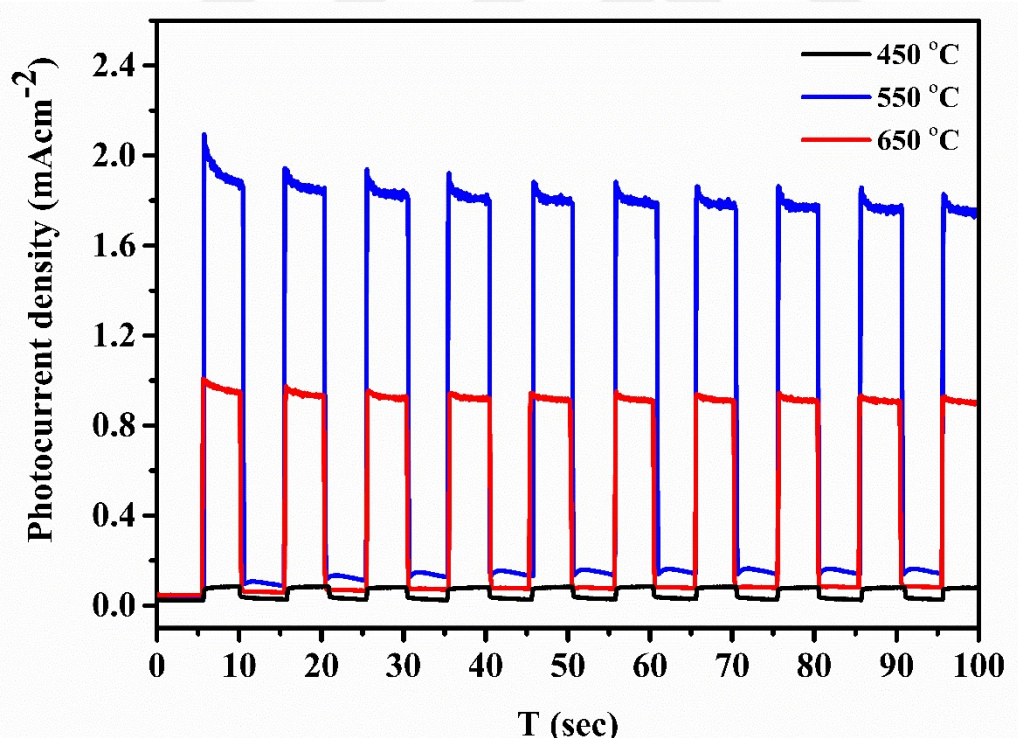


**Figure 3.2:** The effect of annealing temperature on Photo-response of ITO/RGO- $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}$ .

As it can be seen from the plot that photocurrent density increases enormously for example from  $0.09$  to  $1.02 \text{ mAcm}^{-2}$  at  $450$  and  $650^\circ\text{C}$  respectively, to  $2.1 \text{ mAcm}^{-2}$  at  $550^\circ\text{C}$ . This

improved behavior of photoanode can be explained in terms of better adhesion and continuity of  $\text{Cd}_x\text{Zn}_{1-x}\text{S}$  and  $\text{RGO-Cd}_x\text{Zn}_{1-x}\text{S}$  and ITO materials because of their sintered film structure avoiding the degradation of ITO. As reported in the literature [121], degradation of ITO occurs at the temperatures above  $650^\circ\text{C}$ . Thus, it is probable that considering sulfurization atmosphere this degradation could be more significant at  $650^\circ\text{C}$  even though the sintering of film is greater at this temperature.

Similarly, the wt% of RGO in nanocomposites was also optimized to find the best wt% of RGO in order to prepare efficient photocatalyst. RGO-CdS photocatalyst was prepared with 4 different wt% of RGO such as 0.1 wt% RGO-CdS, 0.3 wt% RGO-CdS, 1.0 wt% RGO-CdS, and 3.0 wt% RGO-CdS. These example samples were tested photoelectrochemically and results are explained in Figure 3.3.

As it can be seen from the figure, 0.3 wt% RGO-CdS yielded the highest photocurrent density  $6.5 \text{ mAcm}^{-2}$  as compared rest of the samples that is, 0.1 wt% RGO-CdS, 1.0 wt% RGO-CdS, and 3.0 wt% RGO-CdS. Redundancy of RGO in 1.0 wt% and 3.0 wt% nanocomposite reduces the available amount of incident light to photocatalyst. So, after finding the optimize values for system parameters i.e. 20 layers for coating,  $550^\circ\text{C}$  temperature for annealing of photoanode and quantity of RGO i.e. 0.3 wt%, these parameters have been taken into the considerations while performing the whole experimentation and photoelectrochemical analysis.

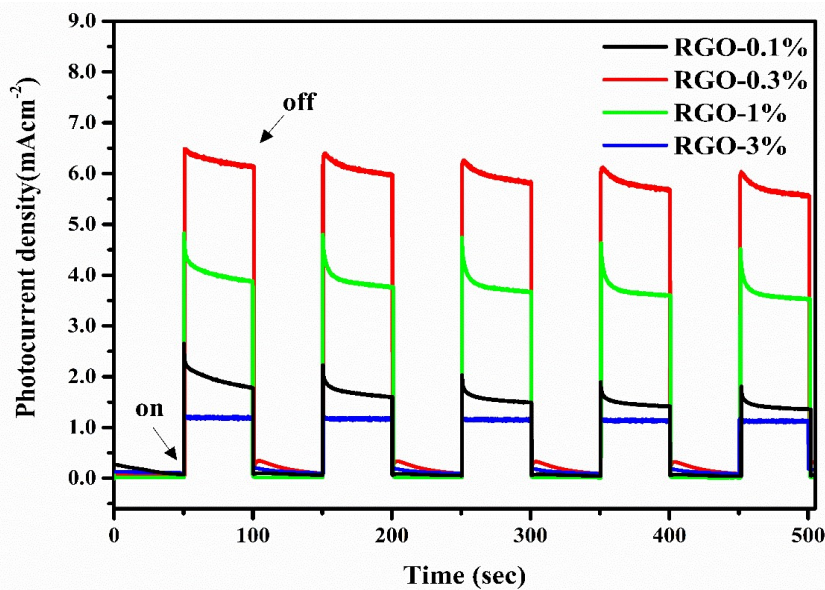


**Figure 3.3:** The effect of RGO quantity (0.1 wt%, 0.3 wt%, 1 wt% and 3 wt%) in CdS on photocurrent density.

### 3.1.3. Characterization of Photoanodes

All the prepared Photoanodes after annealing were characterized by using different techniques to confirm the various characteristics of photocatalyst for example, phase, crystal system, size of particles, vibrational energy, band gap and composition of substrate etc. For this purpose different characterization techniques have been used and results are explained in the following paragraphs.

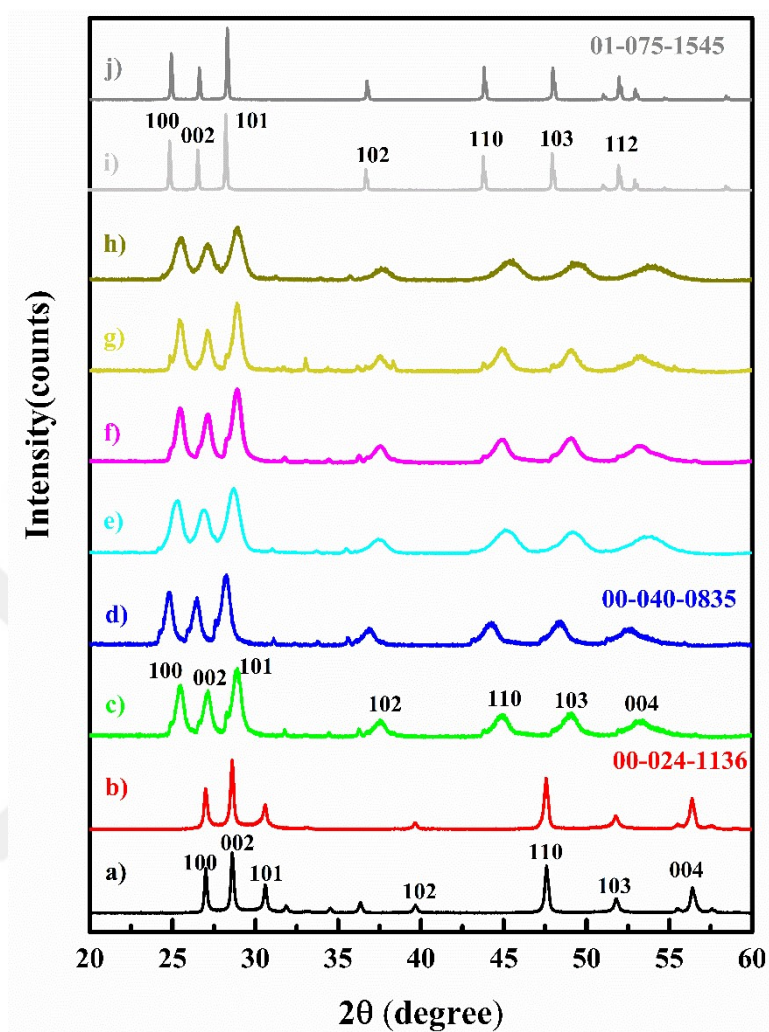
### 3.1.4. X-Ray Diffraction (XRD) Analysis

XRD is one of the powerful and fast tools to estimate the dimension of unit cell, crystal system and the compound formula of provided photocatalyst. In this work, for XRD analysis, Bruker D2 Phaser was used and results were recorded over the range of  $20^\circ < 2\theta < 60^\circ$  under Cu K $\alpha$  radiation having wavelength 1.541 Å. According to the relevant literature, particle size of the photocatalyst has a vital importance for the activity of photocatalyst [122]. The determine the particle size Debye Scherrer equation have been used which is;

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (3.1)$$

Where, D is the mean size of crystal particle, K is the crystalline shape factor whose value is taken as 0.9,  $\lambda$  is the wavelength of X-Ray,  $\beta$  is full width at half maximum (FWHM) of X-ray diffraction peak and calculated from Origin Program and measured in radians while  $\theta$  is Braggs angle (degree). Taking ITO/CdS and ITO/RGO-CdS (the most efficient photoanode in this study) as an example and its XRD analysis results are displayed in Figure 3.4. There are 7 major peaks obtained for each of the samples. These peaks correspond to the Hexagonal crystal system with lattice parameters  $a=4.132$  Å,  $b=4.132$  Å and  $c=6.734$  Å. In Figure xx. pattern a and b represents the Cd<sub>0.3</sub>Zn<sub>0.7</sub>S and RGO-Cd<sub>0.3</sub>Zn<sub>0.7</sub>S respectively. For both of the samples major characteristic peaks are located at  $27.02^\circ$ ,  $28.6^\circ$ ,  $30.6^\circ$ ,  $39.6^\circ$ ,  $47.6^\circ$ ,  $51.8^\circ$ , and  $56.4^\circ$  which correspond to (100), (002), (101), (102), (110), (103), and (004) planes of hexagonal structure. With respect to reference code 01-024-1136, these XRD patterns of Cd<sub>0.3</sub>Zn<sub>0.7</sub>S, RGO-Cd<sub>0.3</sub>Zn<sub>0.7</sub>S photoanodes are quite consistent with the hexagonal structure of respective reference code. In the same way, the major peaks of Cd<sub>0.5</sub>Zn<sub>0.5</sub>S, RGO-Cd<sub>0.5</sub>Zn<sub>0.5</sub>S, Cd<sub>0.7</sub>Zn<sub>0.3</sub>S, RGO-Cd<sub>0.7</sub>Zn<sub>0.3</sub>S, Cd<sub>0.9</sub>Zn<sub>0.1</sub>S and RGO-Cd<sub>0.9</sub>Zn<sub>0.1</sub>S can be seen in patterns c, d, e, f, g and h having positions at  $24.02^\circ$ ,  $26.45^\circ$ ,  $28.2^\circ$ ,  $36.8^\circ$ ,  $44.2^\circ$ ,  $48.3^\circ$ , and  $52.5^\circ$ . These  $2\theta$  values of respective samples correspond to (100), (002), (101), (102), (110), (103), and (004) planes of hexagonal structure. Furthermore, for these photoanodes the

obtained XRD patterns have consistency with the hexagonal structure with respect to reference code 00-040-0835.



XRD patterns, a)  $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ , b)  $\text{RGO-Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ , c)  $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ , d)  $\text{RGO-Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ , e)  $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}$ , f)  $\text{RGO-Cd}_{0.7}\text{Zn}_{0.3}\text{S}$ , g)  $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{S}$ , h)  $\text{RGO-Cd}_{0.9}\text{Zn}_{0.1}\text{S}$ , i)  $\text{CdS}$ , j)  $\text{RGO-CdS}$  for composite powders.

Moreover, patterns i and j represent the XRD-patterns of  $\text{CdS}$  and  $\text{RGO-CdS}$ . The major peaks of these photocatalysts appeared at  $24.8^\circ$ ,  $26.6^\circ$ ,  $28.4^\circ$ ,  $36.7^\circ$ ,  $43.9^\circ$ ,  $48.1^\circ$ , and  $51.9^\circ$  which correspond to the hexagonal structure planes (100), (002), (101), (102), (110), (103), and (112). The presence of RGO in samples confirmed by the small peak at  $24.8^\circ$  which can be attributed to (002) plane of RGO, confirming its presence in the photocatalyst. By utilizing the above mentioned equations, the particle sizes estimated for all of the prepared samples and has been given in the Table 3.1.

Table 3.1: Crystalline sizes of photocatalysts estimated from XRD analysis.

| Photocatalysts                               | Crystallinity sizes (nm) |
|----------------------------------------------|--------------------------|
| <b>Cd<sub>0.3</sub>Zn<sub>0.7</sub>S</b>     | 31.15                    |
| <b>Cd<sub>0.5</sub>Zn<sub>0.5</sub>S</b>     | 7.67                     |
| <b>Cd<sub>0.7</sub>Zn<sub>0.3</sub>S</b>     | 7.45                     |
| <b>Cd<sub>0.9</sub>Zn<sub>0.1</sub>S</b>     | 13.97                    |
| <b>CdS</b>                                   | 62.8                     |
| <b>RGO-Cd<sub>0.3</sub>Zn<sub>0.7</sub>S</b> | 24.16                    |
| <b>RGO-Cd<sub>0.5</sub>Zn<sub>0.5</sub>S</b> | 4.10                     |
| <b>RGO-Cd<sub>0.7</sub>Zn<sub>0.3</sub>S</b> | 7.90                     |
| <b>RGO-Cd<sub>0.9</sub>Zn<sub>0.1</sub>S</b> | 57.48                    |
| <b>RGO-CdS</b>                               | 62.8                     |

### 3.1.5. Raman Spectroscopy

To observe the rotation, vibrational and other low frequency modes in a system, Raman spectroscopy is used. It is a very powerful tool in chemistry to identify the molecule by the structural fingerprint given by this spectroscopy. For the present work, Raman spectra has been recorded for each photocatalyst sample and results are presented in Figure 3.5. Raman spectrum for Cd<sub>x</sub>Zn<sub>1-x</sub>S (x= 0.3, 0.5, 0.7, 0.9, and 1) consist of two major peaks, the stronger one having A1 longitudinal optical (1 LO) mode while the weaker one having overtone of LO (2 LO) mode. For each sample both of the modes can be seen in the figure

The presence of characteristic peaks of 1 LO and 2 LO modes at xx cm<sup>-1</sup> and yy cm<sup>-1</sup> confirms the presence of Cd<sub>x</sub>Zn<sub>1-x</sub>S as it is evident from the related literature. For reduced graphene oxide (RGO), two bands were observed named as D-band and G-band. D-band's intensities correspond to disordered sp<sup>3</sup> while G-band's intensities represent ordered sp<sup>2</sup> graphitic carbons [123]. Here, there is one term is of the great importance which helps us to understand degree of disorder and average size of sp<sup>2</sup> domain in provided sample, that is intensity ration of D and G band can be denoted as I<sub>D</sub>/I<sub>G</sub>. All the RGO-decorated photocatalyst RGO-Cd<sub>x</sub>Zn<sub>1-x</sub>S (x= 0.3, 0.5, 0.7, 0.9, and 1) sample possess the bands rooted from the presence of RGO. However, an overlap of D and G band of RGO has been observed in RGO-Cd<sub>0.5</sub>Zn<sub>0.5</sub>S, RGO-Cd<sub>0.9</sub>Zn<sub>0.1</sub>S and RGO-CdS Raman spectrum. One of the possible reasons to this behavior is that after the reduction process I<sub>D</sub>/I<sub>G</sub> ratio for GO increases which

as a result causes the elimination of oxygen moieties and hence as a result of enhancement in the number of  $sp^2$  domains alteration of GO happens [123].

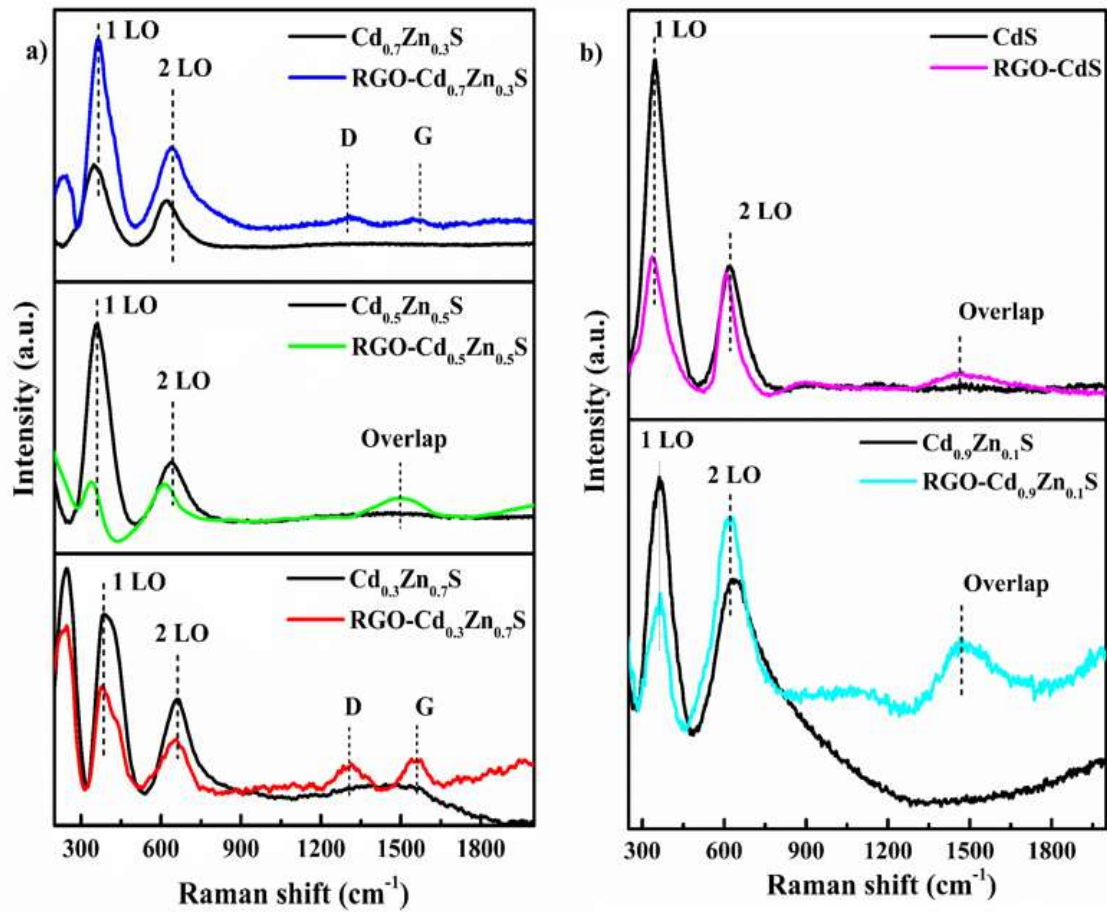


**Figure 3.4:** a) Raman spectra for Cd<sub>0.3</sub>Zn<sub>0.7</sub>S, RGO-Cd<sub>0.3</sub>Zn<sub>0.7</sub>S, Cd<sub>0.5</sub>Zn<sub>0.5</sub>S, RGO-Cd<sub>0.5</sub>Zn<sub>0.5</sub>S, Cd<sub>0.7</sub>Zn<sub>0.3</sub>S composite powders from bottom to top respectively. b) Raman spectra for Cd<sub>0.9</sub>Zn<sub>0.1</sub>S, RGO-Cd<sub>0.9</sub>Zn<sub>0.1</sub>S, CdS, RGO-CdS composite powders from bottom to top respectively.

Moreover, the D and G band signal intensities of RGO for Cd<sub>0.7</sub>Zn<sub>0.3</sub>S are lesser as compared to RGO-Cd<sub>0.3</sub>Zn<sub>0.7</sub>S which can be explained in the terms of quantity difference of RGO in both samples as RGO-Cd<sub>0.3</sub>Zn<sub>0.7</sub>S has high RGO content as compared to RGO-Cd<sub>0.7</sub>Zn<sub>0.3</sub>S. Another interesting has been seen during Raman measurements that is RGO causes red and/or blue shifts in 1 LO and 2 LO peaks of photoanodes. This can be attributed that this shifted may be rooted from the doping effect of RGO to the photocatalyst. Furthermore, to analyze the conversion of GO to RGO, Raman spectrum was measured for both samples and results are explained in Figure 3.5(d). The new positions of D and G band

in RGO with some shifting which is very close to the pristine graphene band of  $1586\text{ cm}^{-1}$  confirms the conversion of GO to RGO.

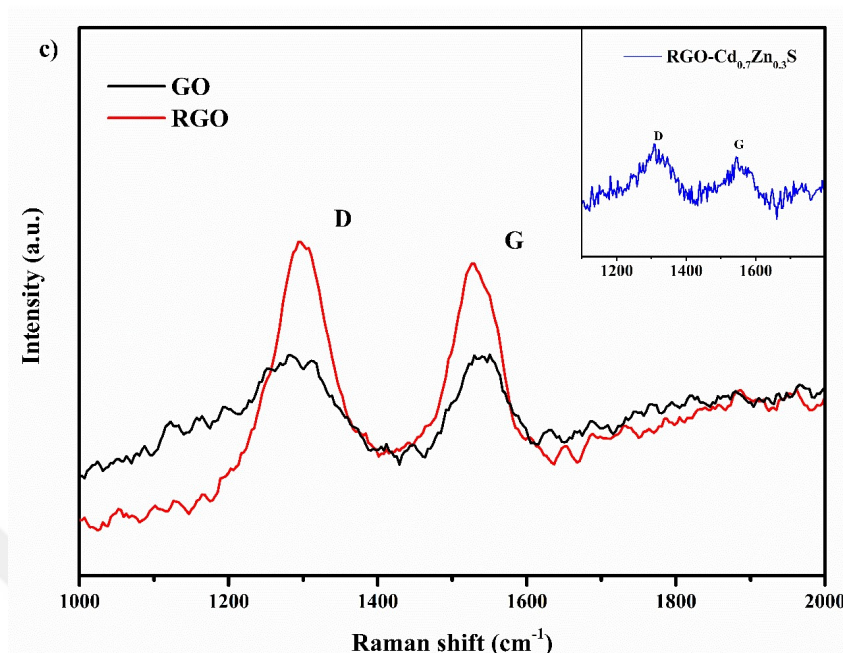


**Figure 3.5.1: c)** Raman spectra of GO and RGO. In inset image, D and G band of RGO in RGO- $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}$  can be seen.

### 3.1.6. Scanning Electron Microscopy (SEM)

As in the previous work of our team,  $\text{Cd}_{0.77}\text{Zn}_{0.23}\text{S}$  had been synthesized by the same method that is thermal sulfurization and tested photocatalytically for hydrogen production resultantly it gave the excellent results as compared to rest of the samples. So taking it as an example material here,  $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}$  and RGO- $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}$  were characterized by SEM and results are shown in Figure 3.6 a, b, c, and d. It can be seen from the figures that photocatalyst has a diameter of  $\sim 250\text{ nm}$  and possesses the spherical shape. There are some regions of agglomeration can be seen in the image. One of the possible reasons is densification of the films happened as a result of sintering. However, the particle estimated from XRD analysis comes out to be  $7.9\text{ nm}$  for ITO/ $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}$  and ITO/RGO- $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}$  which is different from what have been measured from SEM as SEM measures the particle size.

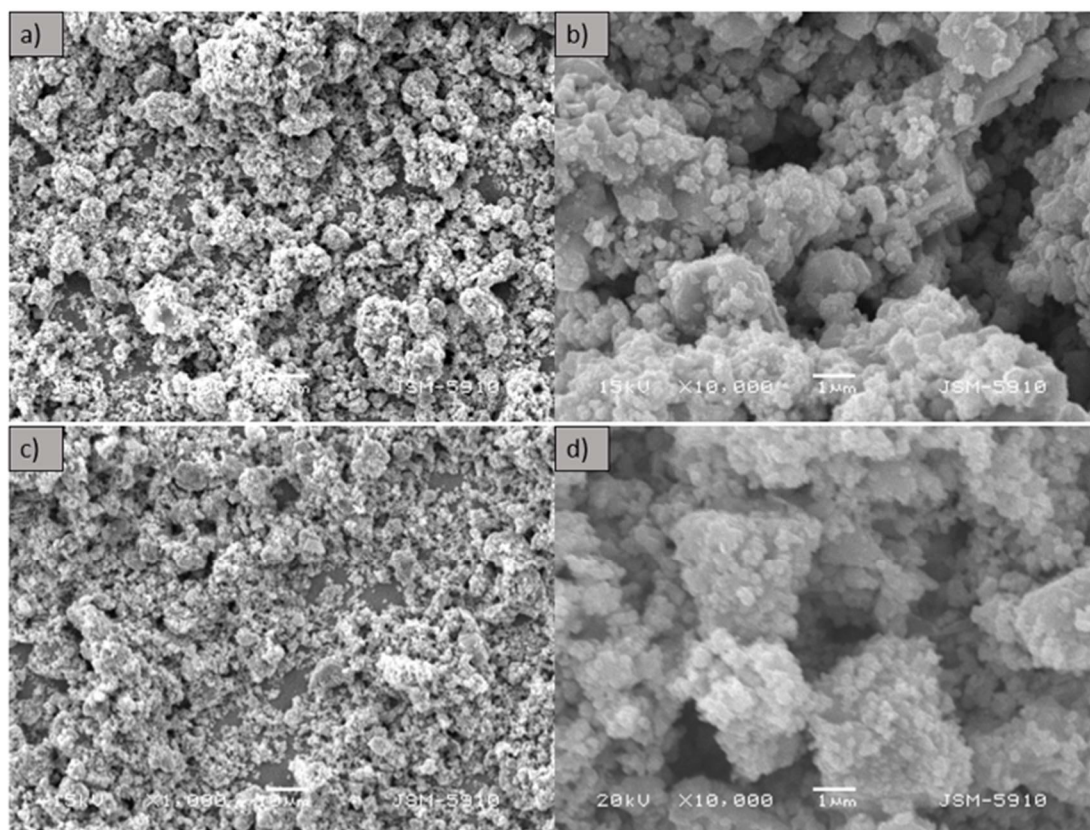


**Figure 3.5:** a,b) SEM image of ITO/Cd<sub>0.7</sub>Zn<sub>0.3</sub>S and c,d) ITO/RGO-Cd<sub>0.7</sub>Zn<sub>0.3</sub>S.

### 3.1.7. Energy Dispersive X-Ray Spectroscopy (EDS)

Energy dispersive X-Ray spectroscopy is a chemical microanalysis technique to analyze the sample composition. It works with detection of X-rays emitted from the given sample as a result of electron bombardment on the sample. Hence, for composition analysis, Cd<sub>0.7</sub>Zn<sub>0.3</sub>S and RGO-Cd<sub>0.7</sub>Zn<sub>0.3</sub>S photocatalysts were analyzed with EDS and results are given in Figure 3.7. Figure shows the strong signals of Cd: Zn: S with 0.7: 0.3: 1.0. Furthermore, the existence of C and O in the figure gives the confirmation of the presence of RGO in the photocatalyst.

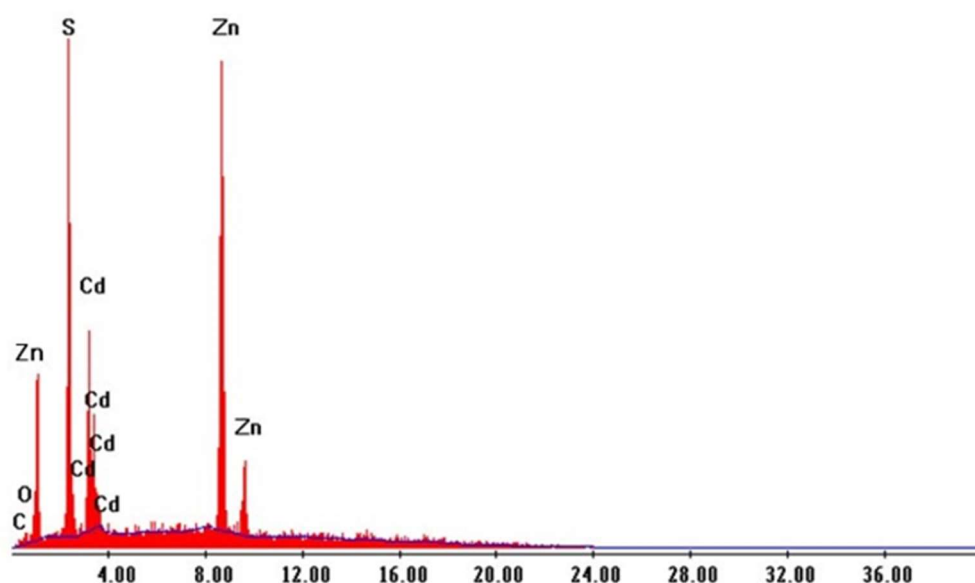


**Figure 3.6:** EDS of photocatalyst RGO-Cd<sub>x</sub>Zn<sub>1-x</sub>S, having the Cd, Zn and S signals representing the presence of Cd, Zn and S in 0.7: 0.3: 0.1 ratio in Cd<sub>x</sub>Zn<sub>1-x</sub>S while C and O signals shows the presence of RGO.

### 3.1.8. Ultraviolet-visible Diffusive Reflectance Spectroscopy

UV-vis diffusive reflectance spectroscopy was also used to analyze and characterize the prepared photocatalytic sample and results are explained in Figure 3.8. It can be seen from the figure, Cd<sub>1-x</sub>Zn<sub>x</sub>S photocatalyst materials have the higher relative reflectance R% as compared to RGO decorated Cd<sub>1-x</sub>Zn<sub>x</sub>S. It can be attributed that RGO decorated Cd<sub>1-x</sub>Zn<sub>x</sub>S photocatalysts have the higher extent of incident utilization as compared to Cd<sub>1-x</sub>Zn<sub>x</sub>S. This behavior possibly rooted from RGO as it has a property to scatter the incident light. In this way more light is available to photocatalyst for absorption as compared to Cd<sub>1-x</sub>Zn<sub>x</sub>S. So it is very obvious from the figure that RGO-Cd<sub>1-x</sub>Zn<sub>x</sub>S has higher extent of visible light utilization as compared to Cd<sub>1-x</sub>Zn<sub>x</sub>S for hydrogen production under solar light irradiation.

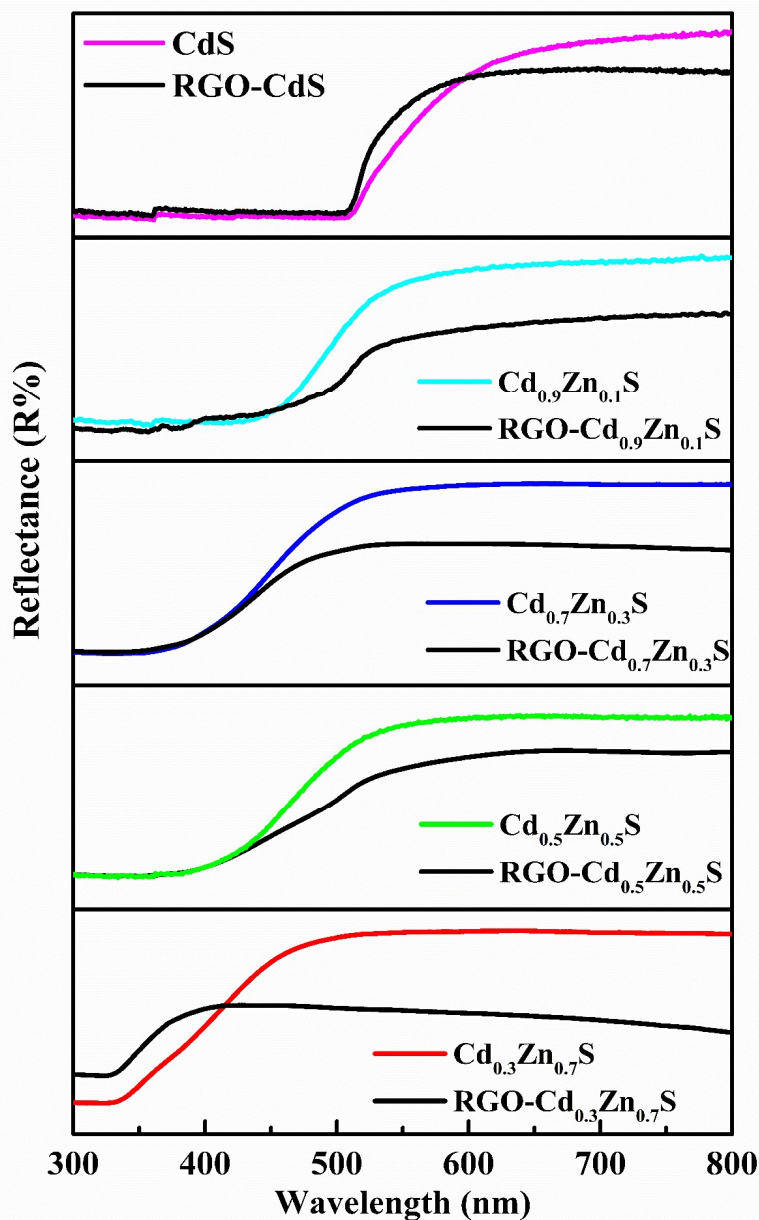


**Figure 3.7:** UV-vis diffusive reflectance spectra of  $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ ,  $\text{RGO-Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ ,  $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ ,  $\text{RGO-Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ ,  $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}$ ,  $\text{RGO-Cd}_{0.7}\text{Zn}_{0.3}\text{S}$ ,  $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{S}$ ,  $\text{RGO-Cd}_{0.9}\text{Zn}_{0.1}\text{S}$ ,  $\text{CdS}$ , and  $\text{RGO-CdS}$  composite powders from bottom to top respectively.

For determining the band gap energies of prepared samples, Kubelka-Munk function of Tauc-plot methods have been used and results are explained in Figure 3.9 and Table 3.2.

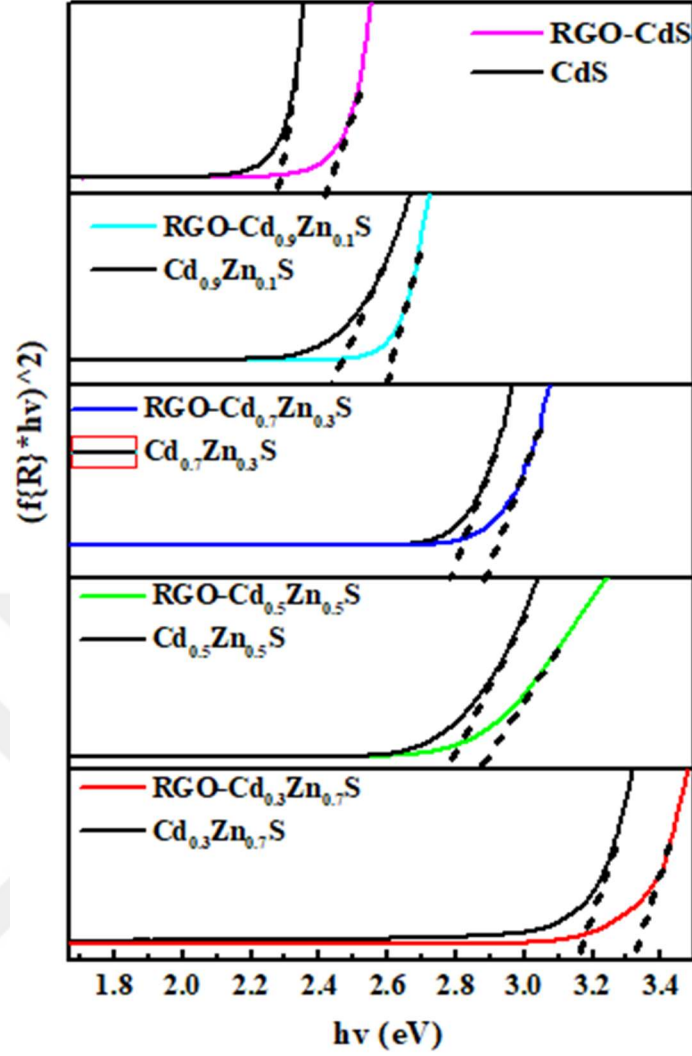


**Figure 3.8:** The band gaps of  $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ ,  $\text{RGO-Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ ,  $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ ,  $\text{RGO-Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ ,  $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}$ ,  $\text{RGO-Cd}_{0.7}\text{Zn}_{0.3}\text{S}$ ,  $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{S}$ ,  $\text{RGO-Cd}_{0.9}\text{Zn}_{0.1}\text{S}$ ,  $\text{CdS}$  and  $\text{RGO-CdS}$  by using Kubelka-Munk function from bottom to top respectively.

It can be seen in figure that with increase in Cd-contents, the band gap decreases. For example  $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$  has lower band gap as compared to  $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ ,  $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{S}$  has lower than  $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}$  and same effect can be seen for  $\text{CdS}$  and  $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{S}$ . The reason behind this could be lower band gap energy of Cd (2.42 eV) as compared to Zn (3.66 eV). With increase in Cd-contents, the effect of Cd becomes prominent on the sample's band gap. The opposite effect can be seen for RGO. The samples having RGO shows higher band gap as compared to ones which do not have RGO. This behavior also rooted from higher band gap energy of RGO.

**Table 3.2:** The band gap values of photocatalysts.

| Photocatalysts                               | Band gaps (eV) |
|----------------------------------------------|----------------|
| <b>Cd<sub>0.3</sub>Zn<sub>0.7</sub>S</b>     | 3.14           |
| <b>Cd<sub>0.5</sub>Zn<sub>0.5</sub>S</b>     | 2.90           |
| <b>Cd<sub>0.7</sub>Zn<sub>0.3</sub>S</b>     | 2.79           |
| <b>Cd<sub>0.9</sub>Zn<sub>0.1</sub>S</b>     | 2.42           |
| <b>CdS</b>                                   | 2.37           |
| <b>RGO-Cd<sub>0.3</sub>Zn<sub>0.7</sub>S</b> | 3.32           |
| <b>RGO-Cd<sub>0.5</sub>Zn<sub>0.5</sub>S</b> | 2.98           |
| <b>RGO-Cd<sub>0.7</sub>Zn<sub>0.3</sub>S</b> | 2.87           |
| <b>RGO-Cd<sub>0.9</sub>Zn<sub>0.1</sub>S</b> | 2.58           |
| <b>RGO-CdS</b>                               | 2.41           |

### 3.2. Photoelectrochemical Measurements

For photoelectrochemical measurements, a homemade three electrodes electrochemical cell was developed whose specifications are mentioned below;

#### 3.2.1. Electrodes

- Working Electrode

In this work, indium tin oxide (ITO) glass (0.8 × 1.0 cm) is used as substrate. Cd<sub>x</sub>Zn<sub>1-x</sub>S and RGO-Cd<sub>x</sub>Zn<sub>1-x</sub>S coated ITO glass electrode (ITO/RGO-Cd<sub>x</sub>Zn<sub>1-x</sub>S) serves as working electrode.

- Counter Electrode

Pt-wire was used as counter electrode as it has ability to absorb hydrogen and as an inert metal does not take part in redox reactions taking place in the cell.

- Reference Electrode

Ag/AgCl electrode was used as reference electrode. The measurements taken with Ag/AgCl reference electrode was converted to reduced hydrogen electrode (RHE) by using following conversion formula;

$$E_{(RHE)} = E_{Ag/AgCl} + 0.059 * pH + E_{Ag/AgCl}^{\circ} \quad (3.2)$$

- Light Source

Asahi Solar Simulator HAL-320 Compact Xenon Light Source was used as a light source. The sample was radiated with well-focused light having intensity of 1 sun ( $100 \text{ mWm}^{-2}$ ). After preparing the photoanodes from the catalytic material, these photoanodes have been tested and analyzed photoelectrochemically. For example, for analyzing the prepared photoanodes open circuit analysis (OCP), linear sweep voltammetry (LSV), chronoamperometry (CA), electrochemical impedance spectroscopy (EIS) and Mott-Schottky analysis was used and results are explained as follows;

### 3.2.2. Linear Sweep Voltammetry (LSV)

LSV is an important technique to find out the photocurrent generation by a photoelectrode in a specific applied potential window under the visible light irradiation. The linear sweep voltogram has been recorded for all prepared photoanodes and results are explained in Fig 3.10. As it can be seen in Fig 3.10 a), as compared to  $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ , RGO- $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$  produces higher photocurrent but just gives almost  $0.25 \text{ mAcm}^{-2}$  at 0 V (vs. RHE) but as the applied potential increases, the amount of produced photocurrent also increases until the applied becomes 0.75 V (vs. RHE) which is indeed a huge amount of applied potential however the photocurrent obtained at that potential. Same pattern can also be seen for RGO- $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ , RGO- $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{S}$  and RGO- $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{S}$  where RGO decorated photocatalyst produced higher photocurrent density as compared to photocatalyst without RGO. However, RGO- $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{S}$  yields the maximum photocurrent density as compared to rest which is almost  $4.3 \text{ mAcm}^{-2}$  at 0.37 V (vs. RHE) as it can be seen in Figure 3.10 d).

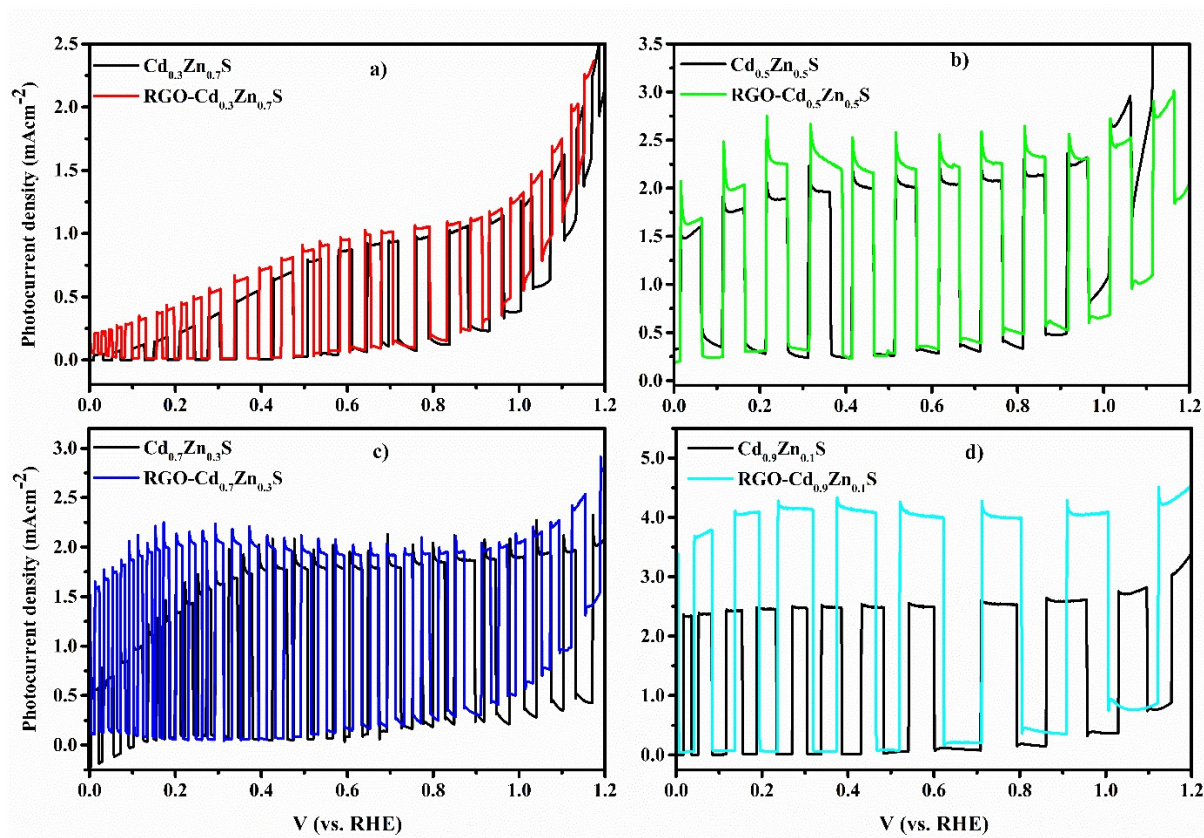


**Figure 3.9:** Linear sweep voltammetry for a) ITO/Cd<sub>0.3</sub>Zn<sub>0.7</sub>S, ITO/RGO-Cd<sub>0.3</sub>Zn<sub>0.7</sub>S, b) ITO/Cd<sub>0.5</sub>Zn<sub>0.5</sub>S, ITO/RGO-Cd<sub>0.5</sub>Zn<sub>0.5</sub>S, c) ITO/Cd<sub>0.7</sub>Zn<sub>0.3</sub>S, ITO/RGO-Cd<sub>0.7</sub>Zn<sub>0.3</sub>S, d) ITO/Cd<sub>0.9</sub>Zn<sub>0.1</sub>S, ITO/RGO-Cd<sub>0.9</sub>Zn<sub>0.1</sub>S.

So there is very interesting behavior can be observed from the figure that with the increase in Cd-contents of photocatalysts, photocurrent density also increases. For confirming this behavior, CdS and RGO-CdS have been tested and results are given in Figure 3.11. As it is clear from the RGO-CdS gave the highest photocurrent density as compared rest of the photocatalyst materials which is about 7.07 mAcm<sup>-2</sup> at 0.542 V (vs. RHE). To find the further confirmation of the behavior, chronoamperometry analysis was performed at the potentials learned from LSV.

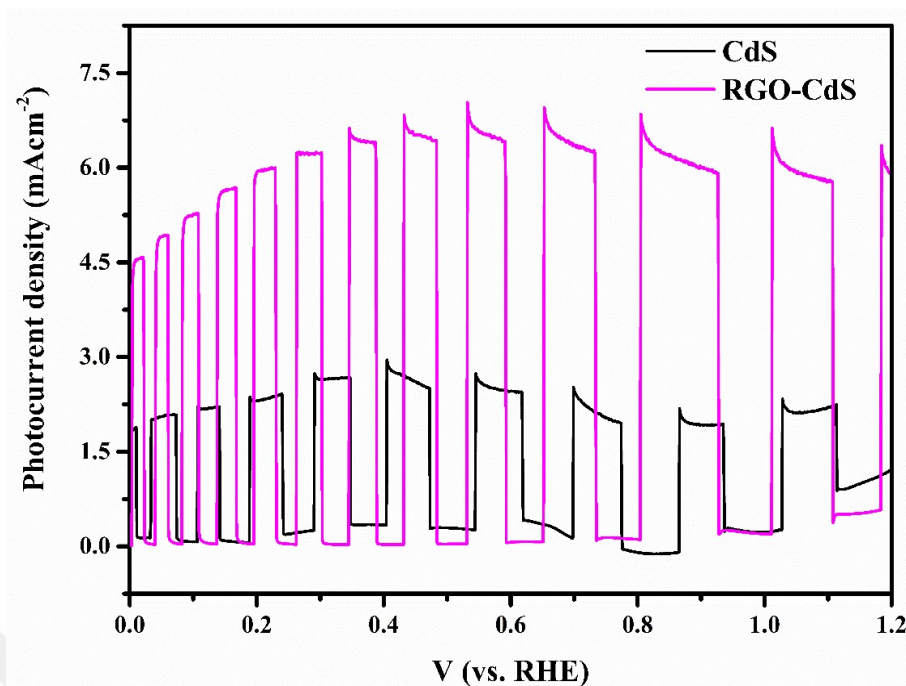


**Figure 3.10:** Linear sweep voltammetry for CdS, RGO-CdS.

The presence of RGO in the photocatalyst probably inhibits the dissolution of photocatalyst and shifts the flat band potential down with the help of sacrificial reagents in the electrolyte  $\text{S}^{2-}/\text{SO}_3^{2-}$  [124, 125]. The increase in the extent of light absorption of the catalyst may be another reason for the shift in the flat band potential. Therefore, as a combined effect of storage, shuttling, and increase in absorption, the presence of RGO makes RGO-CdS catalyst an excellent candidate for visible light driven PEC water splitting. The formation of extensive  $\text{H}_2$  bubbles on the surface of the counter electrode during the I-V curve analysis was also clear indication of high photocatalytic activity under visible light irradiation.

### 3.2.3. Open Circuit Potential (OCP)

Conductivity and flat band potential ( $E_{fb}$ ) are the important characteristics that have to be recognized before performing any photoelectrochemical analysis for photoelectrodes. As these terms play a vital role in understanding the band structure for a semiconductor which in turns directs the semiconductor's ability to undergo the efficacious water splitting under the solar irradiation[126]. OCP is the one of the commanding techniques for the estimation of  $E_{fb}$ . Similarly, the effect of RGO on the conductivity of photocatalyst  $\text{Cd}_x\text{Zn}_{1-x}\text{S}$  such as transportation of photogenerated charge carries, their storage and shuttling was also analyzed

by OCP analysis. All photoanodes have been undergone the OCP analysis and results are shown and compared in Figure 3.12.

As it can be seen in the figure, under the light irradiation condition, a fast generation and the movement of photogenerated charge carrier happens and voltage falls down towards more negative potential and reaches a steady value. This behavior gives a clear sign of n-type behavior of semiconductors. But when the light was turned off, the recombination and movement of charge carrier commenced and the potential returns to its initial steady value. Here is an interesting phenomenon was observed which was the low rate of recombination of charge carriers for RGO bearing photoanodes as compared to photoanodes that do not possess the RGO which can be seen in Figure 3.12 a, b and c. It can be attributed that RGO decorated  $\text{Cd}_x\text{Zn}_{1-x}\text{S}$  have much better transportation for photogenerated charge carriers as compared  $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ . As it was seen from LSV analysis that RGO-CdS appeared to be the most effective photocatalyst. So, ITO/CdS and ITO/RGO-CdS were also analyzed with OCP analysis here and results are given in Figure 3.12 (e). In the aqueous solution of sacrificial reagents under the light on conditions, the upper limit or value of potential under light, which is considered as flat band potential ( $E_{fb}$ ) came out to be -0.32 V (vs.RHE)[127]. The determination of  $E_{fb}$  here was a great development as according to literature, as if  $E_{fb}$  is known then positions of conduction and valence band can be determined by using band gap and these results are also supported by Mott-Schottky analysis as shown in Figure 3.13 whose one of the main purposes is to find  $E_{fb}$ .

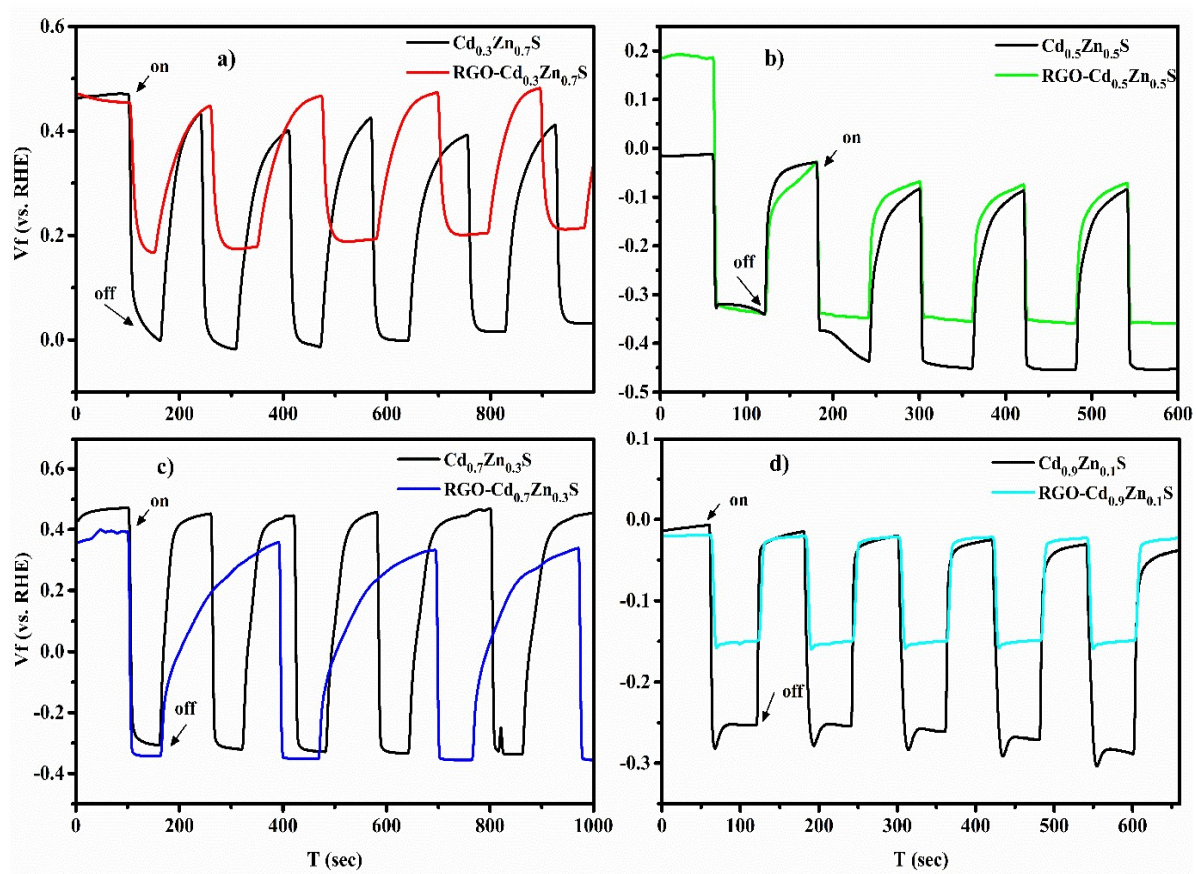


**Figure 3.11:** Open circuit potential of a) ITO/Cd<sub>0.3</sub>Zn<sub>0.7</sub>S, ITO/RGO-Cd<sub>0.3</sub>Zn<sub>0.7</sub>S, b) ITO/Cd<sub>0.5</sub>Zn<sub>0.5</sub>S, ITO/RGO-Cd<sub>0.5</sub>Zn<sub>0.5</sub>S, c) ITO/Cd<sub>0.7</sub>Zn<sub>0.3</sub>S, ITO/RGO-Cd<sub>0.7</sub>Zn<sub>0.3</sub>S, d) ITO/Cd<sub>0.9</sub>Zn<sub>0.1</sub>S, and ITO/RGO-Cd<sub>0.9</sub>Zn<sub>0.1</sub>S.

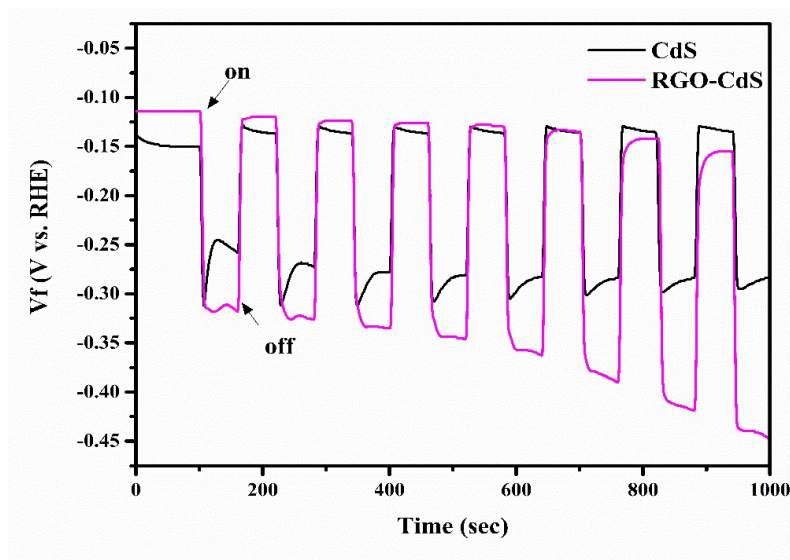


**Figure 3.12:** OCP for ITO/CdS and ITO/RGO-CdS.

### 3.2.4. Mott-Schottky Analysis,

To estimate the  $E_{fb}$  and free charge carrier density (donors or acceptors)  $N_{Dopant}$  of photoelectrodes, mott-schottky analysis enables us to do so. Here is the most important equation for this analysis which is used to determine the above mentioned terminologies,

$$\frac{1}{C^2} = \frac{2}{\epsilon_0 \epsilon_r e N_{Dopant} A_s^2} \left( E_{app} - E_{fb} - \frac{KT}{e} \right) \quad (3.3)$$

Where  $C_{sc}$  capacitance of space charge layer of photoelectrode,  $\epsilon_0$  represents permittivity in vacuum,  $\epsilon_r$  represents relative permittivity whose value normally somewhat above or below 10 so considered as 10,  $e$  represents the charge on electron,  $A$  represents the area of surface,  $E_{app}$  is the applied potential (vs. Ag/AgCl),  $E_{fb}$  is the flat band potential,  $K$  is the Boltzmann constant,  $T$  is the temperature and  $N_{Dopant}$  represents the free carrier density or donor density [128]. The term  $E_{fb} - \frac{KT}{e}$  is equal to the x-intercept determined from the Gamry achem. However, the value of  $N_{Dopant}$  considered equal to the slope of the system's plot. Here is one important thing to remember that the nature of slope dictates the conductivity type of semiconducting materials. For example, if the slope is positive then the semiconductor will be n-type or vice versa. Both of the photoanodes possess the n-type conductivity as slope is positive which is in agreement with linear sweep voltammetry is and open circuit potential measurements as expressed in Figure 3.11 and Figure 3.13.

Furthermore,  $N_{Dopant}$  plays a pivotal role in the width of the depletion layer and rate of recombination which also known as bulk and surface properties of semiconductor. So, by measuring the values of parameters, they were placed in above mentioned equation The ITO/RGO-CdS has higher value of  $N_{Dopant}$  as compared to ITO/CdS whose values are  $1.68 \times 10^{18}$  and  $2.42 \times 10^{18}$  carriers/cm<sup>3</sup> for ITO/CdS and ITO/RGO-CdS, respective. The more effectivity of RGO-CdS over CdS is also reinforced with the fact that the linear region of the slope for RGO-CdS is lower than that of CdS which in turns reason behind the higher donor density of RGO-CdS.

Moreover, the enhanced  $N_{Dopant}$  value for RGO-CdS can also be linked with doping effect which takes its roots from RGO which can be observed in shifts 1 LO and 2 LO peaks of Raman spectra of photoanodes which can be seen in Figure 3.5. When the M-S graph extrapolated and extended till it intersects the x-axis gives the value of flat band potential for the respective sample as it can be seen from Figure 3.14 where the  $E_{fb}$  value was found as -0.3 and -0.12 V vs. RHE for ITO/RGO-CdS and ITO/CdS, respectively which is the same value

that was found with the help of OCP analysis Figure 3.15. According to the literature, for n-type semiconductors the conduction band exists 0.1-0.2 V higher than  $E_{fb}$  that is, CB exists at more negative potentials than  $E_{fb}$  [129].

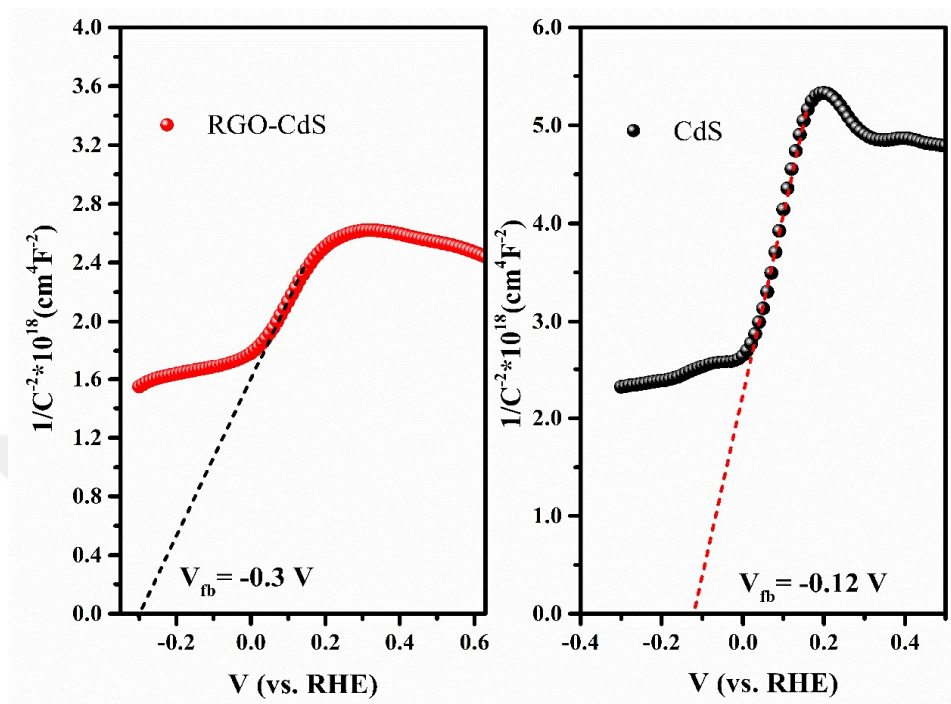


**Figure 3.13:** Mott-Schottky plots of ITO/CdS and ITO/RGO-CdS

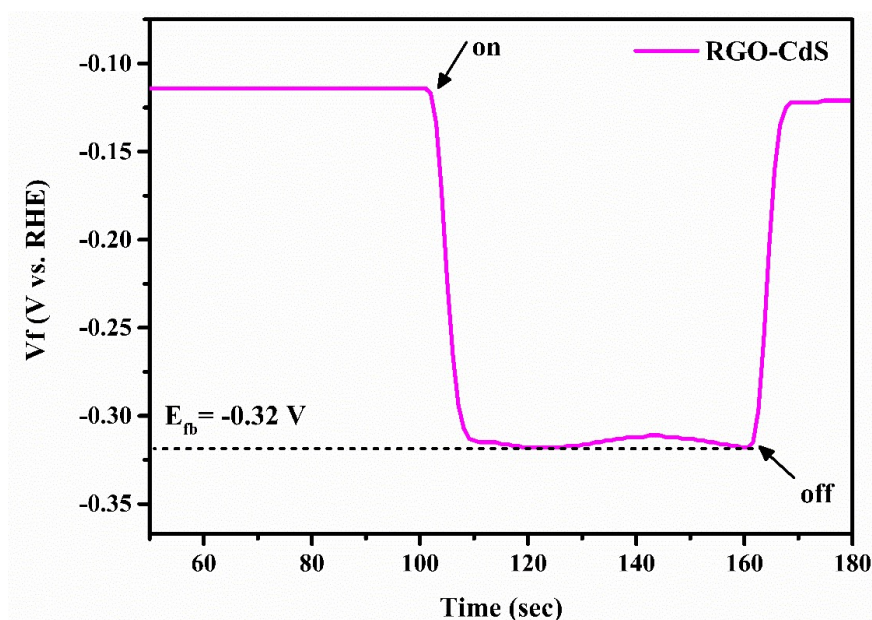


**Figure 3.14:** OCP response of RGO-CdS under light on and off conditions.

Generally, the difference between conduction band and flat band is considered to be 0.1-0.2 V for n-type semiconductors. By taking this into considerations, for RGO-CdS, CB estimated as -0.4 V and for CdS as -0.22 V. The schematic representation of the whole picture has been shown in Figure 3.16.

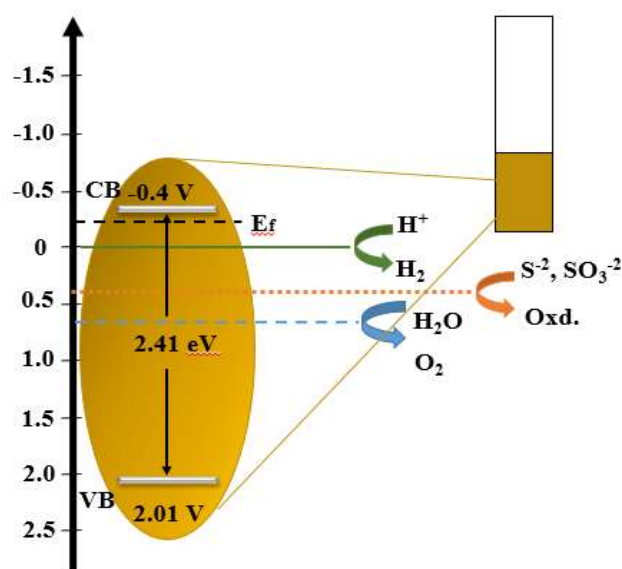


**Figure 3.15:** Schematic illustration of CB and VB positions of ITO/CdS and ITO/RGO-CdS.

### 3.2.5. Electrochemical Impedance Spectroscopy (EIS)

To evaluate the synergetic effects for ITO/RGO-CdS and ITO/CdS, electrochemical impedance spectroscopy was employed under light and dark conditions. The experimentation was performed with AC signal having amplitude of 10 mV having frequency ranged from 0.01 to  $10^5$  Hz. During experimentation, saturated calomel electrode (SCE) was used as reference electrode. The response of photoanodes under dark and illumination conditions have been recorded and results of the experimentation in the form of Nyquist plots have been given and explained in Figure 3.17 a, b, and c. The size of Nyquist arcs are smaller in size for ITO/RGO-CdS under the illumination as compared to ITO/CdS. This shows that under light conditions, RGO-CdS offers a least resistant path to the electron flow as compared to ITO/CdS.

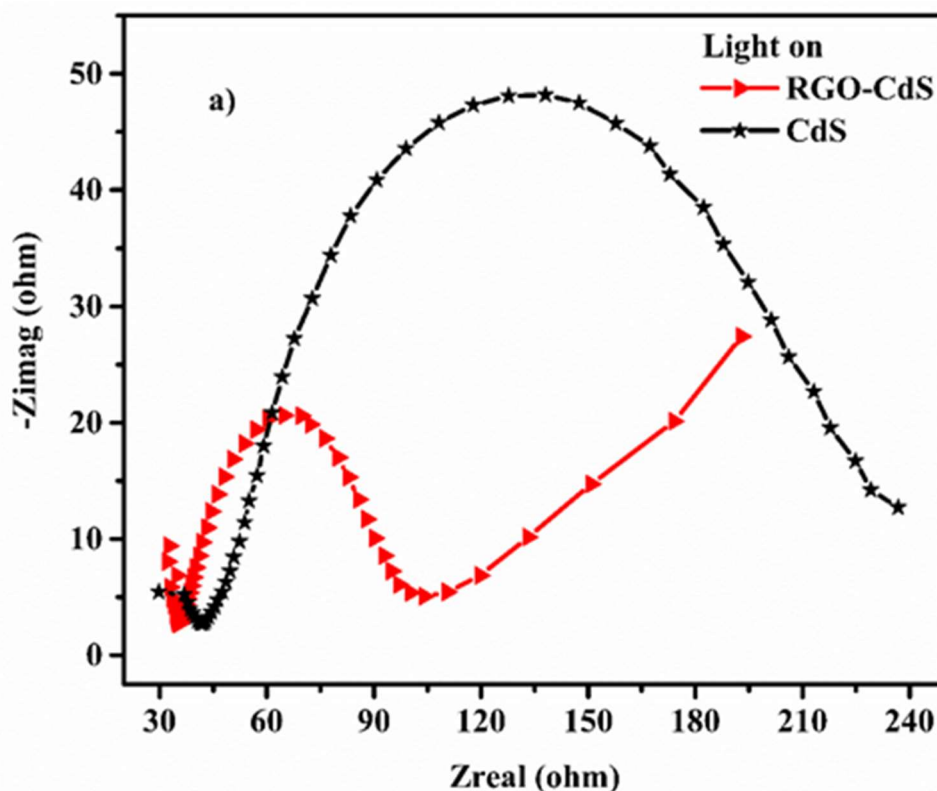


**Figure 3.16:** Potentiostatic EIS responses of ITO/RGO-CdS and ITO/CdS in light and dark conditions. a) Impedance of ITO/RGO-CdS and ITO/CdS under light irradiation.

The same phenomenon was also observed when ITO/RGO-CdS and ITO/CdS were tested under the dark conditions as shown in Figure 3.17 c. It can be seen from the Figure 3.17 c that RGO-CdS offers the more conductive path to photogenerated charges as compared to CdS even under the dark conditions which might be takes roots from the presence of RGO. When the comparison was made only for ITO/RGO-CdS itself under dark and illumination, it appears that under illumination RGO-CdS showed higher conductivity as compared to dark. Hence, the analysis proposes that there is highly visible drop in charge transfer resistance on the surface and solid-state interface layer resistance under the irradiation of visible light. While making comparison of the ITO/RGO-CdS photocatalyst with the rests, especially with ITO/CdS, it clearly put forward this idea that the ITO/RGO-CdS is remarkably a good photoactive catalyst because presence of RGO plays a vital part in charge separation and transfer because of its incredible characteristics of photogenerated charge collection and transferring, and consequently it offers less resistive path for charge movement.

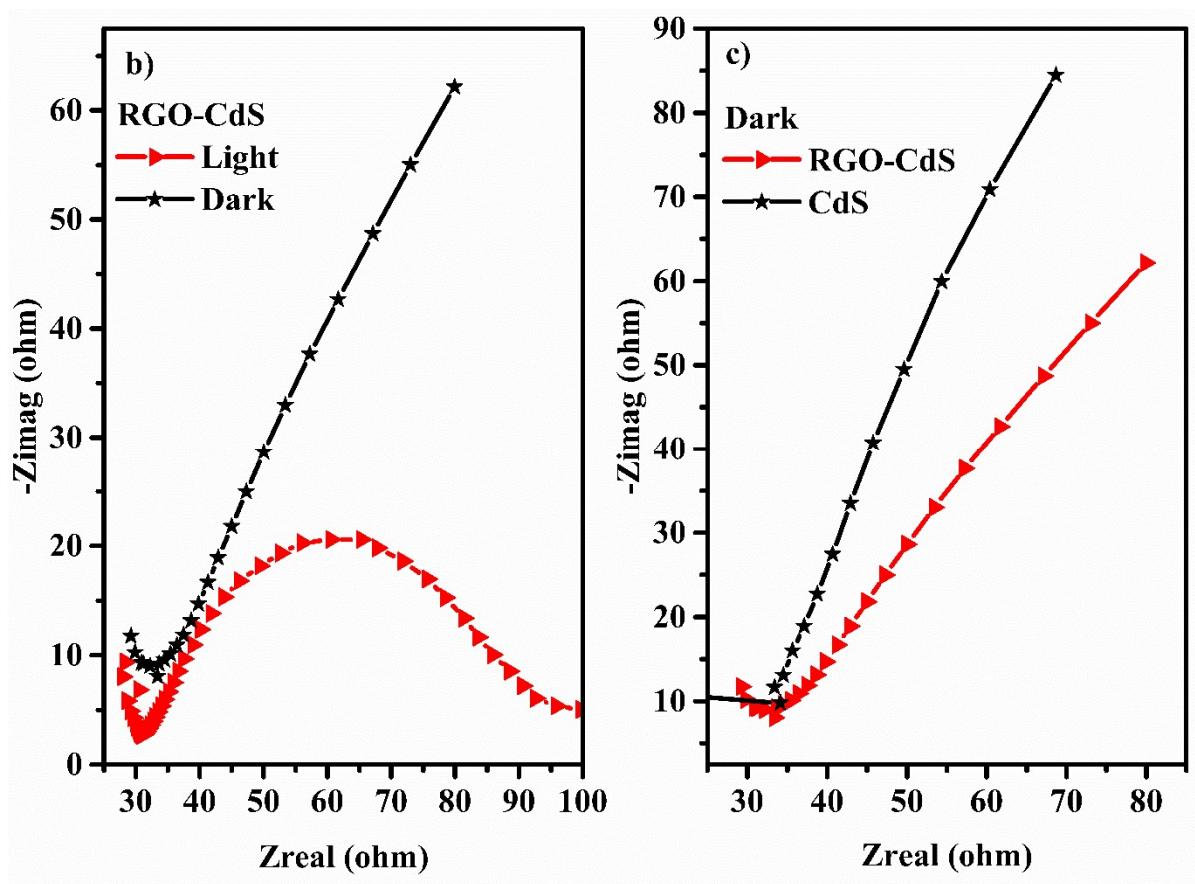


**Figure 3.17.1:** b) Impedance of ITO/RGO-CdS under dark conditions, c) Impedance of ITO/RGO-CdS and ITO/CdS under dark conditions.

### 3.2.6. Chronoamperometry:

After evaluating the activity and effectiveness of the photoanodes through LSV and OCP analysis, the photoanodes need to be compared on the basis of their output which calls for a technique known as chronoamperometry. Chronoamperometry is a technique in which a well-defined potential (determined from LSV analysis) is applied which remains constant throughout the analysis and the output of photoanodes along with their stability is directly observed with respect to time. The behavior of photoanodes in chronoamperometry analysis has been given in Figure 3.18.

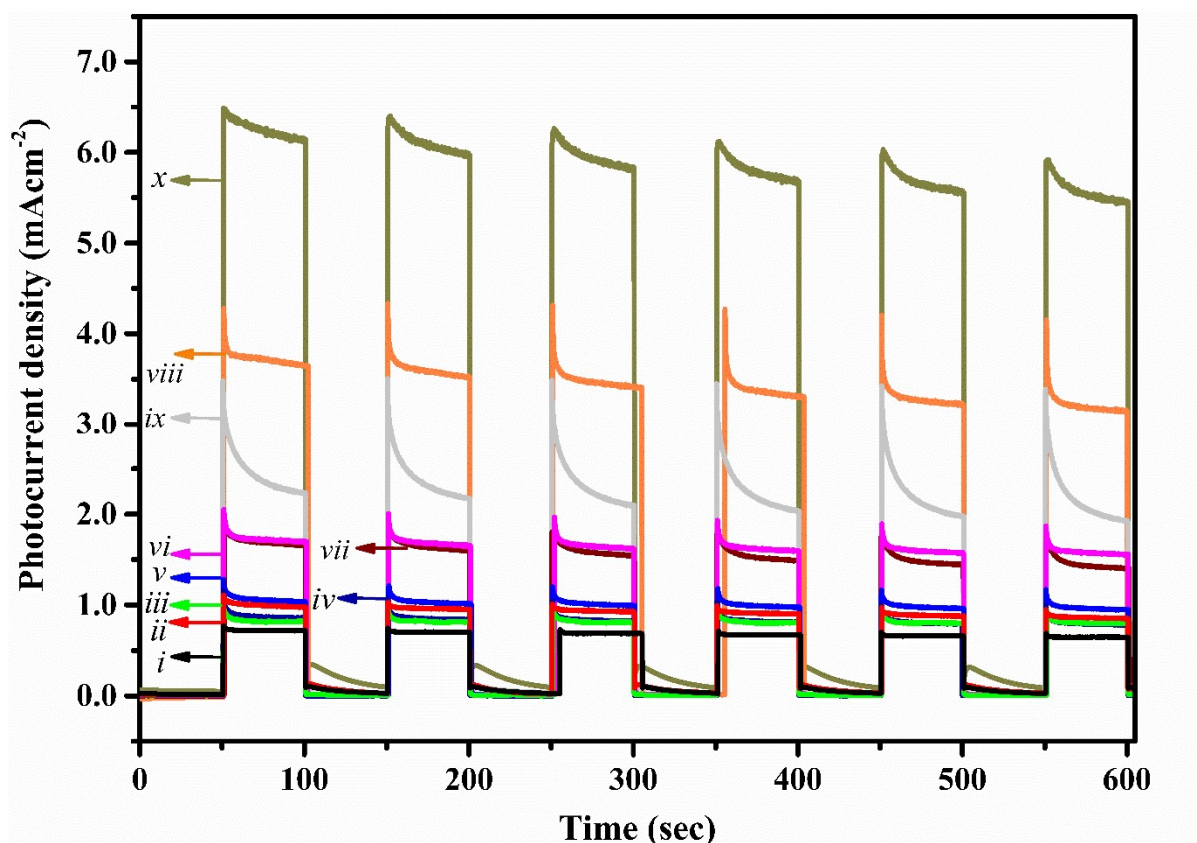


**Figure 3.17:** Photo-response vs. time for i) ITO/Cd<sub>0.3</sub>Zn<sub>0.7</sub>S, ii) ITO/RGO-Cd<sub>0.7</sub>Zn<sub>0.3</sub>S, iii) ITO/Cd<sub>0.5</sub>Zn<sub>0.5</sub>S, iv) ITO/RGO-Cd<sub>0.5</sub>Zn<sub>0.5</sub>S, v) ITO/Cd<sub>0.7</sub>Zn<sub>0.3</sub>S, vi) ITO/RGO-Cd<sub>0.7</sub>Zn<sub>0.3</sub>S, vii) ITO/Cd<sub>0.9</sub>Zn<sub>0.1</sub>S, viii) ITO/RGO- Cd<sub>0.9</sub>Zn<sub>0.1</sub>S, ix) ITO/CdS, and x) ITO/RGO-CdS under visible light irradiation.

As it was mentioned in linear sweep voltammetry that there are two kind of behaviors can be seen that is, on the bases of RGO decoration and on the basis of Cd-contents, there was a remarkable difference in photocurrent density produced. Every photocatalyst decorated with RGO gives the higher photocurrent density as compared to photocatalyst of its own kind with RGO decoration. For example ITO/RGO-Cd<sub>0.7</sub>Zn<sub>0.3</sub>S shows the higher photocurrent (1.0 mAcm<sup>-2</sup>) as compared ITO/Cd<sub>0.3</sub>Zn<sub>0.7</sub>S (0.9mAcm<sup>-2</sup>). The same behavior can be seen for the rest of the photoanodes where RGO decorated photoanode's photocurrent outweighs its counter-part i.e. without RGO decorated. The comparison is explained briefly in Table 3.2. Secondly, the just like it was proposed in LSV analysis that with increase in Cd-contents amount of photocurrent produced also enhances. The Figure 3.19.is the true picture of what we are proposing.

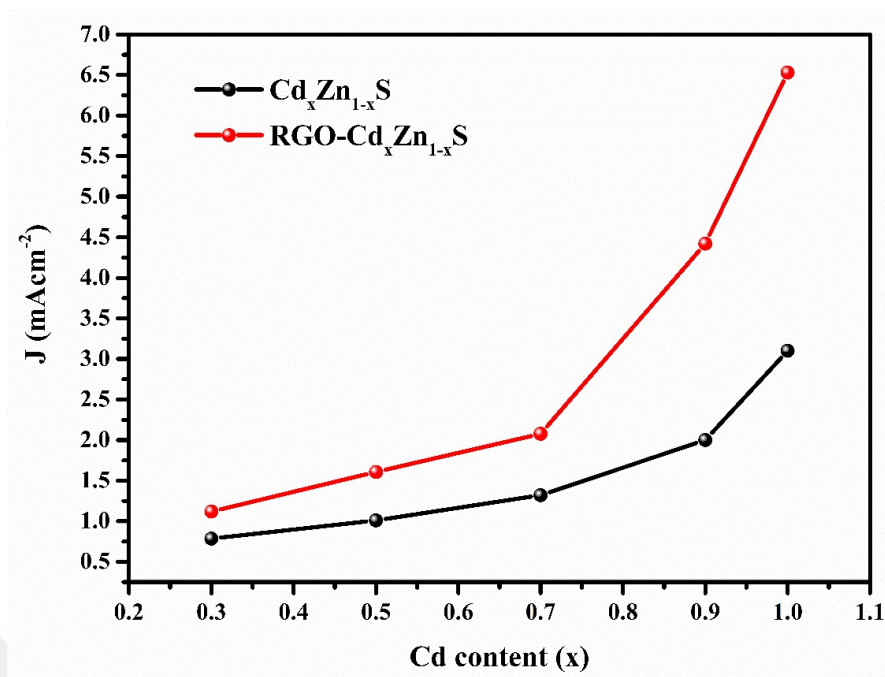


**Figure 3.18:** Relationship between Cd content in RGO-Cd<sub>x</sub>Zn<sub>1-x</sub>S vs photocurrent density at 0.545 V applied potential versus RHE.

The role of RGO is becoming very obvious in photocatalyst as RGO almost enhancing 2 times the photocurrent production capacity of photocatalyst as it can be seen from the figure. It can be attributed here that RGO by improving not only the photogenerated charges transportation and storage but also enhances the absorption capacity of photocatalyst which in turns augments the hydrogen production capacity of photocatalyst.

**Table 3.3:** Comparison of photocatalysts and their produced photocurrent.

| Photocatalysts                        | Photocurrent Density (mA/cm <sup>2</sup> ) | Photocatalysts                            | Photocurrent Density (mA/cm <sup>2</sup> ) |
|---------------------------------------|--------------------------------------------|-------------------------------------------|--------------------------------------------|
| Cd <sub>0.3</sub> Zn <sub>0.7</sub> S | 0.79                                       | RGO-Cd <sub>0.3</sub> Zn <sub>0.7</sub> S | 1.12                                       |
| Cd <sub>0.5</sub> Zn <sub>0.5</sub> S | 1.04                                       | RGO-Cd <sub>0.5</sub> Zn <sub>0.5</sub> S | 1.61                                       |
| Cd <sub>0.7</sub> Zn <sub>0.3</sub> S | 1.33                                       | RGO-Cd <sub>0.7</sub> Zn <sub>0.3</sub> S | 2.1                                        |
| Cd <sub>0.9</sub> Zn <sub>0.1</sub> S | 2.0                                        | RGO-Cd <sub>0.9</sub> Zn <sub>0.1</sub> S | 4.42                                       |
| CdS                                   | 3.5                                        | RGO-CdS                                   | 6.54                                       |

### 3.2.7. Applied Bias Photon-to-current Efficiency (ABPE)

It has been seen in the literature related to photoelectrochemistry while estimating efficiency of photoelectrodes or photocatalyst normally solar to hydrogen efficiency (STH) is used. But when it comes to the systems where electrolyte is based on sacrificial reagents then the validity of STH is compromised[130]. In this work, we worked on a kind of more authentic efficiency which is known as applied bias photon-to-current efficiency (ABPE). This efficiency also calculated on the principal that is, application of bias potential between working and counter electrode finds the efficiency of system. A point to remember that this efficiency is only applicable for two electrode systems.

It is given as

$$ABPE = \left[ \frac{j_{ph} \left( \frac{mA}{cm^2} \right) \times (1.23 - |V_b|)(V)}{P_{Total} \left( \frac{mW}{cm^2} \right)} \right] \quad (3.4)$$

Where  $j_{ph}$  represents the photocurrent density,  $V_b$  bias potential (vs. Pt electrode) and  $P_{total}$  is the power of incident light which was taken as 1 sun ( $100 \text{ mWcm}^{-2}$ ). Efficiency of each photoanode was calculated and compared. It was seen that RGO-CdS has yielded the maximum efficiency of 2.67% at  $V_{bias} = 0 \text{ V}$  (vs. Pt.). However, the behavior of efficiency change with respect different bias voltage was also recorded and results are explained in the Fig 3.20. As it can be seen in the figure that with the increase in bias potential, efficiency increases until it reaches the maximum value of 3.2% at  $V_{bias} = 0.36 \text{ V}$  (vs. Pt.). The comparison also was made between the theoretical ABPE and calculated ABPE. It was seen that with the present system, RGO-CdS has reached 29% of its theoretical ABPE, which indeed an excellent result itself. The comparison of ABPE calculated for this system is also made with the previous literature and can be seen in table 3.3. In the table it can easily be seen that our system had highest efficiency at the potential applied in each respective work. For example, the very first work CdS prepared by solvothermal method [124] has ABPE of 2.63% at 0.134 V (vs. RHE), while at the same potential (0.134 V) our system exhibits 2.96%.

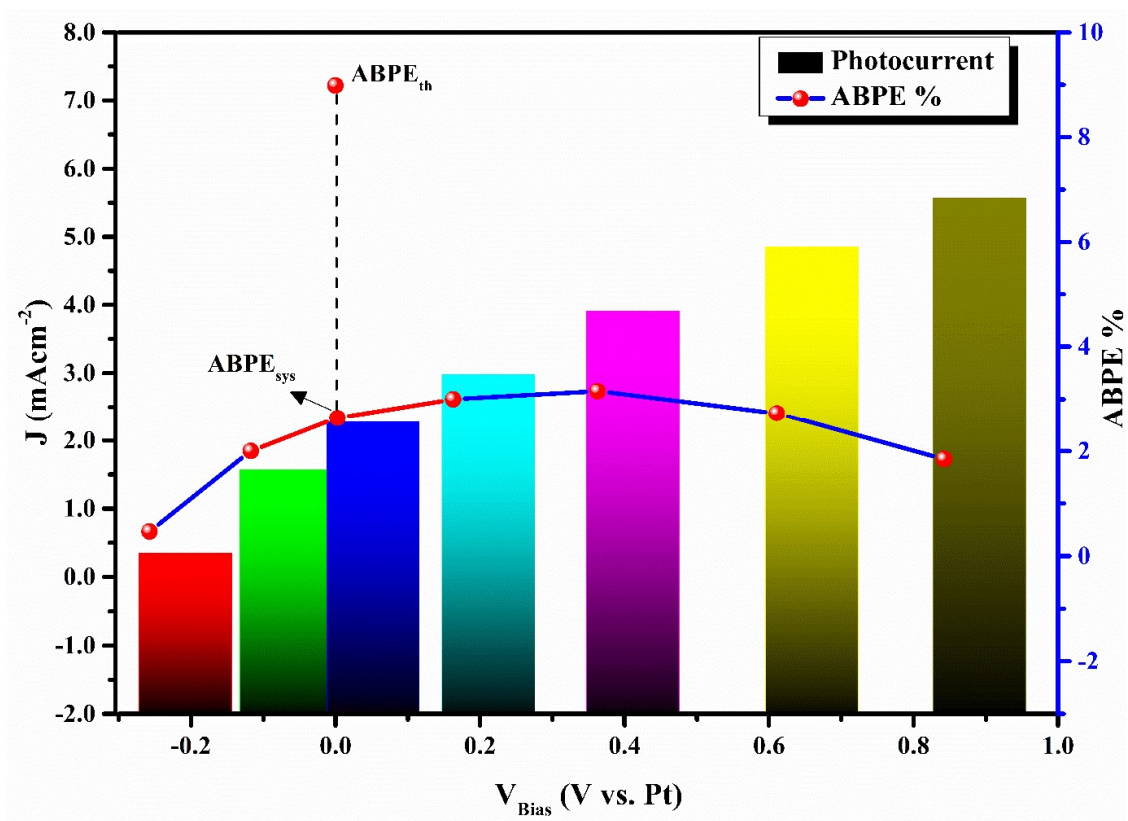


**Figure 3.19:** Comparison of photocurrent density and efficiency versus  $V_{bias}$  (V vs RHE) for RGO-CdS.

**Table 3.4:** Comparison of ABPE from previous literature to present work

| Photocatalyst                     | Sythesize method                                      | Electrolyte                                       | Photocurrent<br>( mAcm <sup>-2</sup> ) | ABPE %*<br>(litrature) | Bias Potential**<br>(Vs.RHE) | ABPE %<br>(this work)*** | Reference |
|-----------------------------------|-------------------------------------------------------|---------------------------------------------------|----------------------------------------|------------------------|------------------------------|--------------------------|-----------|
| CdS                               | Solvothermal                                          | Na <sub>2</sub> SO <sub>3</sub>                   | ~2.6                                   | 2.63                   | 0.134                        | 2.96                     | [131]     |
| 3D<br>bTiO <sub>2</sub> /RGO/CdS  | SILAR                                                 | Na <sub>2</sub> S                                 | ~3                                     | 1.80                   | 0.81                         | 2.00                     | [132]     |
| B-SnO <sub>2</sub> NF-CdS         | Sequential<br>chemical bath<br>deposition             | KOH                                               | 3.4                                    | 2.18                   | 0.32                         | 3.10                     | [133]     |
| CdS/TiO <sub>2</sub><br>nanowires | alkali<br>hydrothermal<br>growth process<br>and SILAR | Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub> | 3.6                                    | 2.30                   | -                            | -                        | [134]     |
| CdS@TiO <sub>2</sub>              | Hydrothermal<br>method                                | Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub> | 1.8                                    | 1.70                   | 0.05                         | 2.70                     | [135]     |
| Cd/CdO/CdS                        | Electrodeposition                                     | Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub> | 5.73                                   | 2.64                   | 0.57                         | 2.80                     | [136]     |

. \*ABPE% is the value obtained from respective literature at the bias potential mentioned in the next column.

\*\*Bias potential used in respective literature while calculating ABPE%.

\*\*\*Comparing ABPE% of this work with respective literature by using the same bias potential as used in respective literature.

### 3.3. Rate of Hydrogen Production

The rate of hydrogen has been calculated, compared for all photocatalysts and this comparison has been given in Figure 3.21. As it can be seen for all  $\text{Cd}_x\text{Zn}_{1-x}\text{S}$  photocatalysts, with the increase in the Cd contents, the rate of hydrogen production also increase and becomes maximum that is,  $214.4 \mu\text{molhr}^{-1}$  for CdS. However, when the results are compared with RGO-decorated  $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ , it can be seen that every RGO decorated  $\text{Cd}_x\text{Zn}_{1-x}\text{S}$  catalyst higher hydrogen production rate as compared to its counter-part. For example, RGO-CdS has almost two folds higher production rate ( $551.1 \mu\text{molhr}^{-1}$ ) as compared to CdS. Again, the main reason for RGO-CdS behind having this much higher production rate as compared to CdS is the role of RGO as RGO enhances the life-time of photogenerated charge particles by shuttling, storing and transporting them, and also increases the absorption ability of photocatalyst by scattering the incident light.

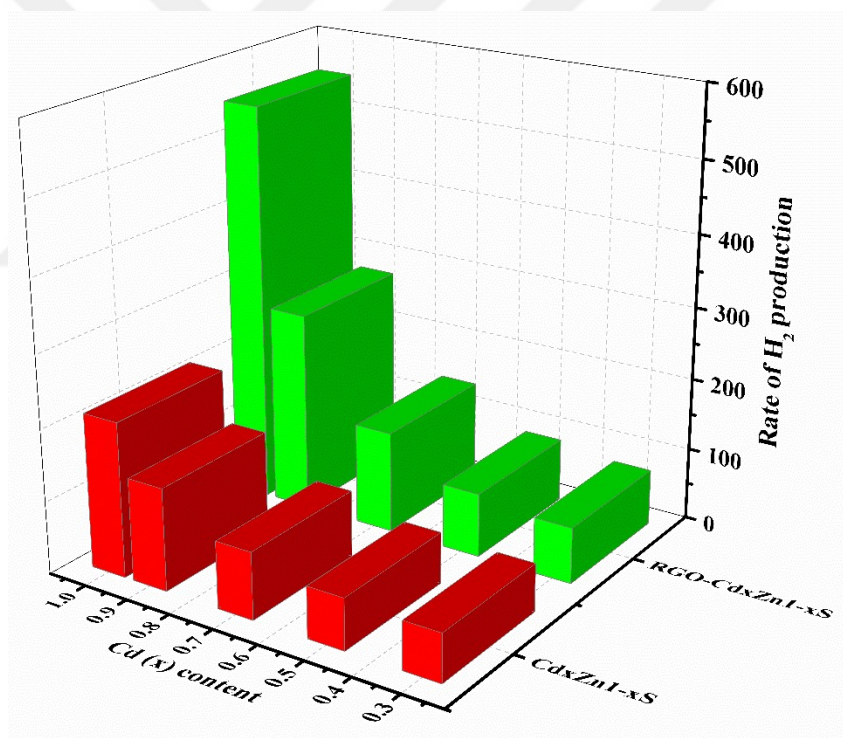


**Figure 3.20:** The comparison of rate of hydrogen production for all employed photocatalysts

## Brief comparison of this work with related previous literature

| Photoelectrocatalyst                      | Method                                  | Sacrificial reagents                                                                          | Light source                                                             | Band gap (eV) | Efficiency (ABPE%) | Current Density (mA/cm <sup>2</sup> ) | Ref.  |
|-------------------------------------------|-----------------------------------------|-----------------------------------------------------------------------------------------------|--------------------------------------------------------------------------|---------------|--------------------|---------------------------------------|-------|
| 3D TiO <sub>2</sub> /RGO/CdS              | SILAR approach                          | Na <sub>2</sub> S                                                                             | AM 1.5 Illumination<br>90 mW cm <sup>-2</sup>                            | -             | 0.36               | 3.00                                  | [132] |
| Zn <sub>0.5</sub> Cd <sub>0.5</sub> S/RGO | Cation-exchange                         | Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>                                             | >400 nm, cutoff filter, 300 W Xe arc Lamp                                | —             | —                  | 0.1                                   | [137] |
| RGO-Cd <sub>0.5</sub> Zn <sub>0.5</sub> S | One-pot single step hydrothermal method | —                                                                                             | Simulated solar light (160 mW/cm <sup>2</sup> )                          | 3.1           |                    | 0.058                                 | [138] |
| CdS-Nanorod                               | Solvothermal                            | Na <sub>2</sub> SO <sub>3</sub> and Na <sub>2</sub> S, Na <sub>2</sub> SO <sub>3</sub> for PC | >420 nm, UV cutoff filter<br>300 W Xe arc Lamp (100 mW/cm <sup>2</sup> ) | 2.42          | 2.63               | 2.63                                  | [131] |
| Cd <sub>0.3</sub> Zn <sub>0.7</sub> S     | Thermal sulfurization                   | Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>                                             | >420 nm, UV cutoff filter<br>300 W Xe arc Lamp (100 mW/cm <sup>2</sup> ) | 3.14          | 0.76               | 0.79                                  | TW    |
| Cd <sub>0.5</sub> Zn <sub>0.5</sub> S     |                                         |                                                                                               |                                                                          | 2.90          | 0.99               | 1.04                                  |       |
| Cd <sub>0.7</sub> Zn <sub>0.3</sub> S     |                                         |                                                                                               |                                                                          | 2.79          | 1.05               | 1.33                                  |       |
| Cd <sub>0.9</sub> Zn <sub>0.1</sub> S     |                                         |                                                                                               |                                                                          | 2.42          | 1.96               | 2.0                                   |       |
| CdS                                       |                                         |                                                                                               |                                                                          | 2.37          | 0.66               | 3.5                                   |       |
| RGO-Cd <sub>0.3</sub> Zn <sub>0.7</sub> S |                                         |                                                                                               |                                                                          | 3.32          | 1.50               | 1.12                                  |       |
| RGO-Cd <sub>0.5</sub> Zn <sub>0.5</sub> S |                                         |                                                                                               |                                                                          | 2.98          | 1.19               | 1.61                                  |       |
| RGO-Cd <sub>0.7</sub> Zn <sub>0.3</sub> S |                                         |                                                                                               |                                                                          | 2.86          | 1.45               | 2.1                                   |       |
| RGO-Cd <sub>0.9</sub> Zn <sub>0.1</sub> S |                                         |                                                                                               |                                                                          | 2.58          | 2.65               | 4.42                                  |       |
| RGO-CdS                                   |                                         |                                                                                               |                                                                          | 2.41          | 2.67               | 6.5                                   |       |

#### 4. Conclusion

In the work, a novel method, thermal sulfurization has been utilized for the synthesis of photocatalysts and spin coating technique has been adopted for the preparation of photoanodes (ITO/Cd<sub>0.3</sub>Zn<sub>0.7</sub>S, ITO/RGO-Cd<sub>0.3</sub>Zn<sub>0.7</sub>S, ITO/Cd<sub>0.5</sub>Zn<sub>0.5</sub>S, ITO/RGO-Cd<sub>0.5</sub>Zn<sub>0.5</sub>S, ITO/Cd<sub>0.7</sub>Zn<sub>0.3</sub>S, ITO/RGO-Cd<sub>0.7</sub>Zn<sub>0.3</sub>S, ITO/Cd<sub>0.9</sub>Zn<sub>0.1</sub>S, ITO/RGO-Cd<sub>0.9</sub>Zn<sub>0.1</sub>S, ITO/CdS, and ITO/RGO-CdS). Optimization was carried out for annealing temperature, coating layers and RGO-contents in sample. After optimization, all photoanodes were prepared with 20 coats, annealed at 550 C and decorated with 0.3 wt% of RGO. The physical and structural characterization techniques has approved not only the successful formation of Cd<sub>x</sub>Zn<sub>1-x</sub>S, RGO-Cd<sub>x</sub>Zn<sub>1-x</sub>S but also revealed the improved morphology of photocatalyst because of sulfurization method. XRD analysis approved the hexagonal structure system for synthesized photocatalyst and crystal size for each of the sample was determined. It was seen that with the increase in Cd-contents in photocatalyst, crystalline size decreases first and then increases.

Additionally, Raman spectroscopy also confirmed the formation of RGO decorated Cd<sub>x</sub>Zn<sub>1-x</sub>S by detecting its characteristic signal peaks. The shifts in the 1 LO and 2 LO peaks also confirmed the doping of RGO on the photocatalyst. SEM also confirmed the diameter of particle as 250 nm. Furthermore, with help of EDS, weight ratio and composition of sample was also confirmed.

Moreover, the role of RGO in improving the absorption capacity of photocatalyst was observed with UV-vis diffusive reflectance spectroscopy. All of the RGO decorated photocatalyst presented higher absorption as compared to normal Cd<sub>x</sub>Zn<sub>1-x</sub>S. With Kubelka-Munk function, the band gaps of photocatalysts were measured and it was found that with the increase in Cd-contents, the band gap decreases while on the other hand, RGO decorated photocatalysts band gaps are greater than their respective counter-parts.

Furthermore, all prepared photocatalytic sample exhibit excellent photo-activity with incredible stability. The addition of RGO not only improved light absorption capacity of photocatalyst but also increased the life-span of photogenerated charge carriers by transporting, storing and shuttling. OCP proved the dominant effect of RGO over the inhibition of recombination of electron-hole pair. I-V curves exhibited the excellent photocurrent generation by the photocatalyst over the applied window of voltage. RGO-CdS

appeared to give  $7.1 \text{ mAcm}^{-2}$  photocurrent density at the applied voltage of 0.542 V (vs.RHE) which was highest obtained photocurrent density among all synthesized photocatalysts.

Additionally, it was also seen that photocurrent production capacity of photocatalyst was also increased with increasing Cd-contents. However, with the decoration of RGO, the photocurrent density of each photocatalyst raised to almost two folds. RGO played an important role in improving the light absorption and by suppressing the electron-hole recombination enhances photocatalytic activity. Moreover, Mott-Schottky analysis explained the band structure of RGO-CdS photocatalyst as the CB was found to be located at -0.4 eV while valance band was at 2.01 eV. Similarly, the density of space charges or donor density  $N_D$  was also estimated with the same analysis and it appeared that RGO-CdS has greater  $N_D$  () as compared to CdS () and this difference takes its roots from doping effect of RGO.

The photo-activity of photocatalysts were checked with the help of EIS analysis, which revealed that RGO-CdS has higher conductivity in the light as well as under dark conditions of experimentation as compared to CdS alone. Furthermore, in order to verify the behavior that we have found in I-V curves, chronoamperometry was performed and the results were same. RGO-CdS topped the list with  $6.5 \text{ mAcm}^{-2}$  photocurrent density value which is almost the 89% of its theoretical value  $7.3 \text{ mAcm}^{-2}$  estimated from its band gap (2.41 eV). Again the same behavior was observed that with the increase in Cd-contents, from ITO/Cd<sub>0.3</sub>Zn<sub>0.7</sub>S to ITO/CdS the photocurrent density increased from amount 0.79 to  $6.5 \text{ mAcm}^{-2}$ . Similarly, the decoration of RGO almost enhanced produced photocurrent density of each sample of photocatalyst to almost 2 times. At the end of the work, rate of hydrogen production for each sample of photocatalyst was estimated in which RGO-CdS gave the highest rate of hydrogen production of  $551.1 \mu\text{molhr}^{-1}$  as compared to rest of photocatalysts and here as well the effect of RGO was very dominant.

At the end, it can be said that in this work Cd<sub>x</sub>Zn<sub>1-x</sub>S and RGO-Cd<sub>x</sub>Zn<sub>1-x</sub>S was analyzed (x=0.3, 0.5, 0.7, 0.9, and 1.0) and it was realized that the role of Zn was not enough dominant and had no or negligible effect on the stability of photocatalyst. On the other hand, RGO-CdS appeared to be the most efficient and photo-stable photocatalyst having the highest photocurrent density as compared to previous literature and possesses very good value of ABPE. So on the whole, we suggest RGO-CdS as the very efficient photocatalyst and it has a huge potential for the further research and applications.

## 5. References

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## **ARTICALS**

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