Development of organic CdS/Spinacia Oleracea based photocatalyst for bioconversion and remarkable production of Hydrogen

Thesis Submitted by

Ayantan Biswas

Master of Bioprocess Engineering

Class Roll Number: **002110303008**

Registration Number: **140024** of **2017-2018**

Examination Roll No.: **M4BPE23002**

Under the Guidance of

Prof. Kajari Kargupta

Nanoengineering and Sustainable Energy Laboratory

Chemical Engineering Department

Jadavpur university

Kolkata – 700032

September 2023

Faculty of Engineering and Technology
Jadavpur University

Certificate

This is to certify that **Mr. Ayantan Biswas**, Final year Masters of Bioprocess Engineering (MBPE) student of **Department of Chemical Engineering, Jadavpur University**, Class Roll No. **002110303008**, Registration No. **140024 of 2017- 2018** has completed the Project work titled, "Development of organic CdS/Spinacia Oleracea based photocatalyst for bioconversion and remarkable production of Hydrogen" under the guidance of **Prof. Kajari Kargupta** during his Master's Curriculum. This work has not been reported earlier anywhere and can be approved for submission in partial fulfilment of the course work.

……………………………….	…………………………..
Prof. Rajat Chakrabarty	**Prof. Kajari Kargupta**
Head of the Department	Project Supervisor
Chemical Engineering Department	Chemical Engineering Department
Jadavpur University	Jadavpur University

………………………………….

Signature of the Dean
Faculty of Engineering and Technology
Jadavpur University
Kolkata – 700032

Place – Kolkata

Date – 13 September 2023

Declaration

I hereby declare that the contents of this thesis is composed of original research work and literature review by the undersigned as a part of Master of Bioprocess Engineering (Department of Chemical Engineering) studies. The information in this document is in accordance with the ethical conduct and the academic rules.

I also declare that I have cited all the references for the material that are not original to this work.

Place – Kolkata

Date – 13 September 2023

…………………………………

Ayantan Biswas
Roll No.- 002110303008
Exam Roll No.- M4BPE23002
Master of Bioprocess Engineering
Chemical Engineering Department
Jadavpur University

This thesis is dedicated to my beloved parents

For their constant love, support and encouragement

Acknowledgement

I would like to express my sincere gratitude to my guide, **Prof. Kajari Kargupta**, for her unwavering support and guidance throughout the course of this research project. Her expertise, encouragement, and patience have been invaluable to me, and I could not have completed this work without her assistance.

I am incredibly grateful to Prof. **Rajat Chakraborty**, Head of the Chemical Engineering Department, for all the necessary help I got during my project work.

I would also like to thank my lab mates of NSEL, **Mr. Sayantanu Mandal**, **Ms. Arundhati Sarkar, Mr. Arindam Mandal** and **Ms. Swagata Das** for their collaboration, feedback, and support. Their insights and contributions were crucial to the success of this project, and I am grateful for their willingness to share their time and knowledge with me.

In addition, I would like to extend my thanks to our lab assistant of NSEL, **Mr. Ajay Kr. Pradhan**, for his assistance with the practical aspects of this project. His help with laboratory experiments and equipment maintenance made a significant difference in the quality and accuracy of our results.

I am also indebted to **Jadavpur University, Dept. of Chemical Engineering**, for supporting me and giving me the opportunity to use the equipment to do my research.

Finally, I would like to acknowledge the support of my mother **Mrs. Latika Biswas** and father **Mr. Bipul Kumar Biswas** and also my friends who have encouraged me throughout my academic journey and provided me with the emotional and logistical support necessary to complete this project.

Thank you all for your contributions to this work.

Place – Kolkata

Date – 13 September 2023

……………………………….

Ayantan Biswas

Chemical Engineering Department

Jadavpur University

Table of Contents

****

Table of Figures

****

List of Tables

****

Abstract

Photocatalytic Hydrogen generation from Biomass is an emerging approach to produce renewable Hydrogen. The objective of this study is to produce green hydrogen from biomass with the help of full band solar irradiation which can be used as fuel and can substitute the fossil fuels in the coming days. Here, a biomass based photocatalyst has been synthesised, characterized and evaluated for the Hydrogen generation using a full band solar spectrum. The Hybrid photocatalyst CdS/Spinacia Oleracea has been tested for hydrogen generation via photocatalytic water splitting under full band solar irradiation. The Spinacia Oleracea is known for its high amount of chlorophyll, which act as photosensitizer in the hybrid photocatalyst. The synthesised photocatalyst were characterised using different morphological and optical tools like FE-SEM, EDX, XRD, TEM, UV-Vis and PL spectroscopy. The synthesised photocatalyst (CdS/Spinacia Oleracea) has been shown higher hydrogen generation than the pristine CdS photocatalyst. It has been shown that the activity of synthesised photocatalyst has been increased nearly six times than the pristine photocatalyst. The solar full band irradiation activity of the CdS/Spinacia Oleracea photocatalyst is measured to be 29.80 mmol g^{-1} h^{-1}, which is higher than the activity of pristine CdS, which is 4.59 mmol g^{-1} h^{-1}. The Apparent quantum efficiency of CdS/Spinacia Oleracea is 18.21% at 420 nm and 15.63% at 350 nm of Band Pass Filter using solar simulator. A proposed mechanism has been also forwarded showing improved electron-hole separation and low charge recombination. These type of low cost photocatalyst having high green Hydrogen generation performance result to industrial and scale up applications.

***Keywords**: Photocatalytic Hydrogen generation, photocatalyst, biomass, Spinacia Oleracea.*

****

“CHAPTER-I”

Introduction

&

Literature Survey

Introduction

One of the renewable resources with the highest availability is biomass. Fossil fuels, produced from ancient biomass, power our economy today. Finding a sustainable source of energy is essential due to the gradual depletion of these non-renewable resources and the problems of CO_2 emissions. H_2 can be useful to generate electricity [1], but current production of H_2 is unsustainable as it depends on fossil fuel reforming. Economical use of renewable energy without interfering with food production may be possible by producing H_2 fuel directly from waste biomass without the need for fossils.

However, we must consider the fact that, at the moment, about 95% of the hydrogen that the world uses are produced from fossil fuels such as coal, natural gas and petroleum, primarily through high-temperature thermocatalytic and gasification processes. Fossil fuels are not practical hydrogen sources because they cannot be renewed in our lifetime, and further carbon dioxide emissions from them will exceed the atmosphere's capacity and contribute to global warming. Consequently, hydrogen produced in this manner cannot be considered an environmentally friendly fuel. [2]

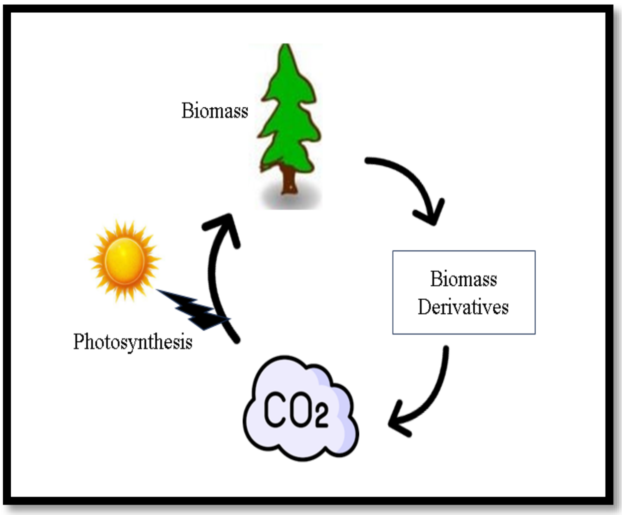


Fig. 1.1: *Carbon Neutral Cycle of Biomass.*

Biological substrates such as plant, starch, oil and lipids are sources of biomass derivatives such as ethanol, glycerol, sugars and methane. They are considered a part of the current carbon cycle (Fig. 1.1) as renewable resources. The biomass and derivatives are used to generate Hydrogen along with carbon dioxide generate during the conversion of biomass through plant photosynthesis. During the Hydrogen generation, CO_2 is also generated and absorb by plants resulting no greenhouse gas emission in the environment.

1.1 Introduction of Biomass

Biomass [3] refers to organic matter, such as plants and animals, that can be used as a source of renewable energy. Biomass conversion is one of the most effective ways to meet the world's energy needs to reduce carbon emissions and climate change impacts. Biomass is essential when it comes to recycling and reuse of materials and in generating electricity. [4]

Biomass can be classified into different types (Fig. 1.2) based on the source of organic matter [5], as follows:

- Agricultural biomass: Organic matter that is produced from crops, such as corn, wheat and sugarcane.
- Forest biomass: Organic matter found in forests, such as trees, branches and leaves.
- Urban Biomass: Organic matter produced from urban areas, such as parks, gardens and lawns.
- Industrial biomass: Organic matter that is produced from industrial processes, such as paper, food and textile production.
- Animal Biomass: Organic material that originates from animals, such as manure and other waste products.

Overall, biomass has the potential to be a significant source of renewable energy and the type of biomass used will depend on the specific application and availability in the local area.

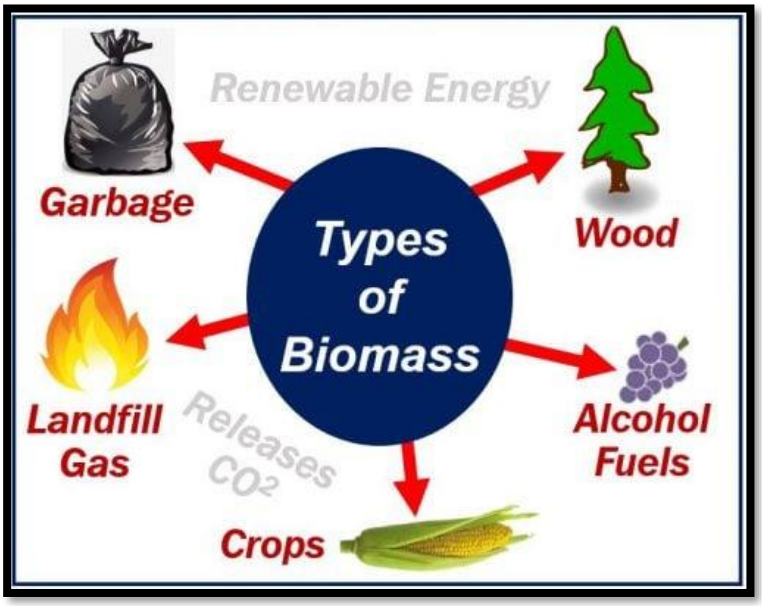


Fig. 1.2: *Different types of Biomass.*

(Max (2023) What is biomass energy: Pro and cons, working and practical uses - industrial manufacturing blog, linquip. Available at: https://www.linquip.com/blog/what-is-biomass-energy/)

1.2 Biomass as a substrate of Photocatalyst

It is an innovative approach to use biomass as a substrate for photocatalytic hydrogen production due to its availability, high organic content, and potential to contribute to sustainable energy production. Sugars, lignin and cellulose are examples of some biomass which are used as substrates. But it’s highly desirable to use raw biomass derived from plants as a substrate for hydrogen generation to lower the hydrogen production cost.[6] There are so many examples of raw biomass are used for hydrogen production such as wooden branch, sawdust, rice husk, grass, cherry wood, bagasse and fescue grass which have been used as substrates.

1.3 Fuel of the Future: Hydrogen

Although hydrogen (H_2) is the most abundant element on earth, it rarely exists in its simplest form. It is a flexible energy source with a wide range of forms, each with unique properties and applications. Most of the differences between the different types of hydrogen can be found in their production methods.

- **Grey Hydrogen:** Grey hydrogen production is now the most popular and least expensive method. It doesn't emit greenhouse gases on its own, but the production process does. Grey hydrogen is produced from natural gas by steam reforming, which separates the hydrogen from the natural gas. The carbon emissions produced during the process are discharged into the atmosphere.

- **Blue Hydrogen:** The steam reforming method is also used to extract blue hydrogen, but it varies from grey hydrogen in that the emitted carbon emissions are captured and stored. This method reduces the carbon emissions but not completely eliminates them.

- **Green Hydrogen:** Green hydrogen is a true source of clean energy because it is produced from renewable resources, which results in zero emissions throughout its entire life cycle. It is produced by electrolyzing water with clean electricity produced from redundant sustainable wind and solar energy. The process causes a reaction that splits water into its components of hydrogen and oxygen. It's a fantastic replacement for the grey and blue techniques.

- **Black Hydrogen:** Black and brown hydrogen is created using either type of coal in the extraction process. The electrolysis of green hydrogen is one end of a spectrum, while this process, called gasification, is the other. The emissions are subsequently released into the atmosphere, where they cause pollution and turn into the most environmentally hazardous form of hydrogen.

- **Pink Hydrogen:** Nuclear energy is used for the electrolysis process that extracts pink hydrogen. Pink hydrogen is occasionally mentioned as purple hydrogen or red hydrogen.

- **Turquoise Hydrogen:** Methane pyrolysis, a procedure that includes heating methane (the main ingredient of natural gas) to high temperatures without oxygen, produces turquoise hydrogen. Hydrogen and solid carbon, which can be used as a useful byproduct, are produced by this method. Although turquoise hydrogen is still in its early stages, it has the potential to become a cheap and low-emissions source of hydrogen.

- **Yellow Hydrogen:** Another new entry is yellow hydrogen, which is produced through electrolysis specifically using solar energy, much like the method used to produce green hydrogen but with a sunnier nickname.

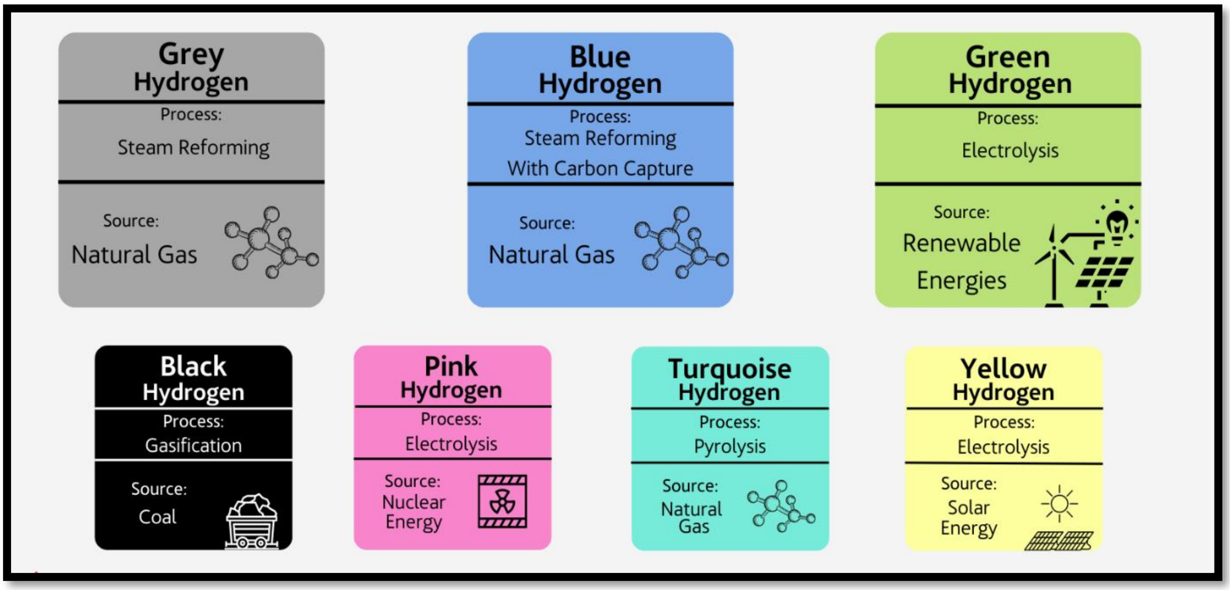


Fig 1.3: *The Hydrogen Colour Spectrum.*

(https://www.acciona.com.au/updates/stories/what-are-the-colours-of-hydrogen-and-what-do-they-mean/?_adin=02021864894)

Rather than being a fundamental energy source, hydrogen is considered an energy transporter. Only water, a reusable and environmentally friendly product, can be produced when hydrogen is burned in air. As a result, no pollution is emitted that could harm climate change, the ozone layer or global warming. Hydrogen is a viable alternative to fossil fuels. The physical and chemical properties of hydrogen are compared with those of several fossil fuels in the table (Table 1.1). The amount of heat produced when a fuel is completely burned can be used to represent the energy of each fuel.

Fuel	**Density (g/L)**	**Lower Heating Value (MJ/Kg)**	**Carbon Percentage (%)**
Natural Gas	0.77	47.1	75
Crude Oil	880	44.6	85
Petrol	730	43.7	85
Diesel	850	42.5	87
Hydrogen	0.90	120	0

Table 1.1: *Energy content of different fuels.* [7]

The steam engine, developed over 250 years ago, gave its name to that era of modern technology. However, with the extraction of fossil fuels and their application in all aspects of daily life, the world has entered the petroleum age. The world is now ready for a new era, the era of hydrogen [8], thanks to extensive research into the production and use of hydrogen fuel.

1.4 Advantages of Using Hydrogen as Energy

Hydrogen is a versatile, zero-emission, efficient energy career.[9] It has so many advantages if we use it as a replacement of fossil fuels such as :

- Clean energy : When burned or used in fuel cells, hydrogen remains a clean energy source that emits no harmful pollutants or greenhouse gases. This makes it a desirable alternative to fossil fuels, which have a major impact on climate change and air pollution.

- Abundant resource: One of the most abundant elements in the universe is hydrogen, which exists in various natural resources such as water, natural gas and biomass. Hence it can act as a constant supply of energy.

- Versatile: Hydrogen has a wide range of uses, including generating energy, heating buildings and powering cars. It can generate power using fuel cells or can be used directly as fuel.

- High energy density: Hydrogen has a high energy density, which makes it possible to produce a lot of energy from a very small amount of gas. As a result, it can be a useful source of energy.

- Long-term storage: Hydrogen is a reliable energy source as it can be kept in storage for long periods of time without losing energy potential.

Overall, hydrogen is a promising alternative energy source that offers several advantages over traditional fossil fuels. However, challenges such as the cost and infrastructure required for large-scale production and distribution of hydrogen must also be overcome.

Additionally, hydrogen can be produced from a variety of sources, including renewable sources such as wind, solar, and hydropower. This means that hydrogen has the potential to be a renewable and sustainable energy carrier, as long as the production process is powered by renewable energy. Although there is a lot of hydrogen in the universe, most of it is found in compounds rather than in its pure state. Therefore, in order to use it as a fuel, it must be separated from its compounds.

Fig. 1.4: *Advantages of using Hydrogen as fuel.*

(Jain, Vatsal & Kandasubramanian, Balasubramanian. (2020). Functionalized graphene materials for hydrogen storage. Journal of Materials Science. 55. 10.1007/s10853-019-04150-y).

1.5. Advantage of using Biomass over Water for Hydrogen Generation

Water is a very stable compound. Due to the challenging oxygen evolution reaction (OER, eqn. 1.2), H_2 generation from water splitting (eqn. 1.2, 1.3) faces a large thermodynamic barrier ($\Delta E^0 = -1.23V$). Additionally, a highly explosive mixture of H_2 and O_2 is also produced.

$$2H^+ + 2e^- \rightleftharpoons H_2 \qquad E^0 = 0\ V \qquad (1.1)$$

$$H_2O \rightleftharpoons \tfrac{1}{2} O_2 + 2H^+ + 2e^- \qquad E^0 = +1.23\ V \qquad (1.2)$$

$$H_2O \rightleftharpoons H_2 + \tfrac{1}{2} O_2 \qquad \Delta E^0 = -1.23\ V \qquad (1.3)$$

$$C_6H_{12}O_6 + 6H_2O \rightleftharpoons 12H_2 + 6CO_2 \qquad \Delta E^0 = +0.001V \qquad (1.4)$$

However, the whole reaction consisting biomass (eqn. 1.4) is almost energy neutral (ΔE^0 = +0.001V) which means that the energy is only needed to overcome activation barriers.[6] That's why it's more feasible to use biomass over water for hydrogen generation.

1.6. Photocatalysis Hydrogen Generation Method

An exciting hydrogen production strategy is photocatalytic hydrogen production from water and biomass derivatives. In this system, photoenergy and photocatalysts can convert water and biomass derivatives into hydrogen and carbon dioxide (Fig 1.5). Biomass can be broken down into small organic molecules (derivatives) such as ethanol and methane by fermentation after plant growth, or the carbon dioxide produced can be converted into carbohydrates by photosynthesis in plants. On the other hand, with just water generation, the produced hydrogen is used to generate electricity through fuel cells or to provide power through hydrogen-fuelled engines.

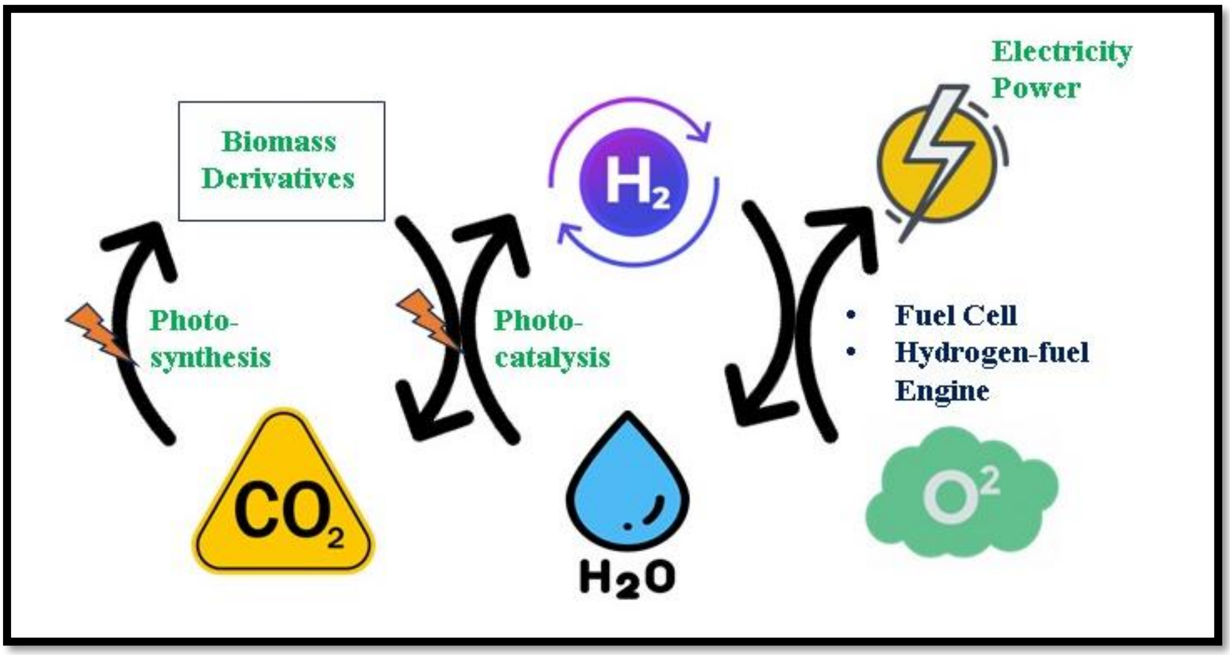


Fig. 1.5: *Carbon Neutral Cycle of Photocatalysis.* [2]

The production of photocatalytic hydrogen from water and biomass derivatives has gained study attention in the twenty-first century. It is proven that, as illustrated in eqn (1.5) and

Fig. 1.6, hydrogen and carbon dioxide were created at room temperature and atmospheric pressure.

$$C_xH_yO_z + (2x - z)H_2O \rightarrow (2x - z + y/2)H_2 + xCO_2 \qquad (1.5)$$

This technique conducts the reformation under ambient conditions by photoexciting a semiconductor. Electrons are excited from the valence band to the conduction band when a semiconductor material is exposed to light, creating electron-hole pairs. When these electron-hole pairs are involved in redox reactions, reactive oxygen species (ROS) are generated. ROS can break down organic pollutants or convert CO_2 into usable fuel. The performance of a semiconductor material in photocatalysis depends on its bandgap strength, surface area, and reactivity.

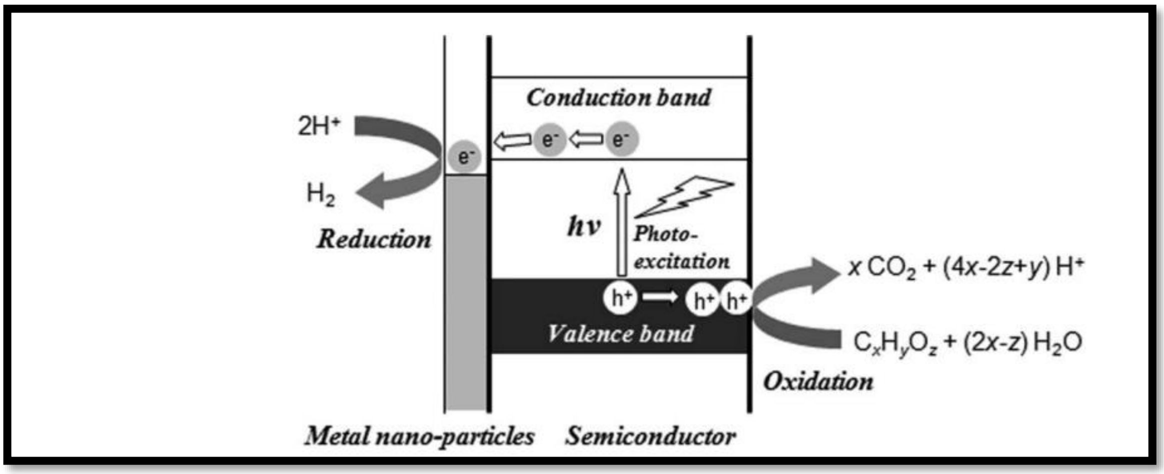


Fig. 1.6: *Photocatalytic hydrogen production from biomass*. [2]

1.7 Photocatalytic Hydrogen Generation from Biomass

1.7.1 Mechanism of Photocatalytic Hydrogen Generation

Using a photocatalyst and solar energy, biomass can be converted to hydrogen through photocatalytic hydrogen generation.[10] The mechanism of this process involves many processes taking place on the surface of the photocatalyst such as :

- Absorption of photons : As a result of photocatalyst absorption of photons from sunlight, electrons in the valence band are excited into the conduction band and form electron-hole pairs.

$$\text{Photon} + \text{Photocatalyst} \rightarrow \text{Electron} + \text{Hole}$$

- Formation of reactive species : Hydroxyl radicals (-OH) and hydrogen ions (H^+) are produced when excited electrons in the conduction band interact with water. The holes in the valence band interact with water to form oxygen and hydrogen ions.

$$\text{Electron} + H_2O \rightarrow H^+ + \text{-OH}$$

$$\text{Hole} + H_2O \rightarrow O_2 + H^+$$

- Formation of intermediates : Carbonaceous species in biomass such as glucose or cellulose combine with hydrogen ions to form intermediates such as alcohols, aldehydes and organic acids.
- Conversion of intermediates to hydrogen : Through a sequence of redox events involving electrons and holes on the surface of the photocatalyst, the intermediates are eventually converted to hydrogen and carbon dioxide.

$$\text{Intermediate} + \text{Electron} \rightarrow \text{Hydrogen} + CO_2$$

- Separation of hydrogen and oxygen : The hydrogen gas produced in the reaction diffuses out of the reaction mixture, while the oxygen produced reacts with the pores of the photocatalyst to form oxygen gas.

$$2H^+ \rightarrow H_2 \text{ (hydrogen gas)}$$

In general, solar energy is used to drive the conversion of biomass into hydrogen gas. The bandgap energy, surface area and reactivity of the photocatalyst used, as well as the properties of the biomass used, affect how efficient the process is. The method has the potential to produce hydrogen fuel from renewable resources in a sustainable manner.

1.7.2 Advantages and limitations of Photocatalytic Hydrogen Generation

Photocatalytic hydrogen generation is a very widely used method because it has so many advantages such as :

- **Renewable and sustainable:** A renewable and sustainable resource, biomass, is converted into hydrogen using solar energy. As a result, a clean and sustainable source of energy can be obtained.

- **High efficiency:** With conversion efficiencies of up to 10%, photocatalytic hydrogen generation has the potential to be very efficient.

- **Low-cost:** This method is economically viable as it uses abundant and cheap materials for photocatalyst and biomass feedstock.

- **Versatility:** The process is adaptable to different geographies and feedstock availability as it can employ several biomass feedstocks including wood chips, municipal solid waste and agricultural waste.

- **Minimal emissions:** The process results in reduced or non-existent emissions of hazardous gases such as CO_2 or NO_x.

Also this process has some limitations also which are:

- **Low production rates:** Photocatalyst efficiency and sunlight accessibility currently limit the speed of hydrogen synthesis.

- **Reactor Design:** Optimizing the reactor design is necessary to obtain high conversion rates as it may affect the process efficiency.

- **Scale-up challenges:** Scaling up the process from lab size to commercial scale can present significant difficulties in terms of cost, efficiency and reactor design.

Although photocatalytic hydrogen generation offers numerous advantages overall, there are also issues that need to be addressed if hydrogen is to be a competitive and efficient source of fuel.

1.8 Applications of Hydrogen Generation from Biomass

Due to its adaptability as a clean and effective energy carrier, hydrogen generation has a wide range of uses across numerous industries. The use of renewable feedstocks, the reduction of carbon emissions, and the possibility of a more sustainable hydrogen supply are all advantages of this strategy. Here are a few uses for photocatalytic hydrogen production:

- **Renewable Hydrogen Production:** It provides an environmentally friendly way to make hydrogen without using fossil fuels. This procedure can help to produce a more sustainable and clean energy system because it uses sunlight as its energy source.

- **Hydrogen Fuel Production for Fuel Cells:** Photocatalysis can generate hydrogen gas, which can be utilised as a fuel for fuel cells. With water as the only byproduct, hydrogen fuel cells provide a highly efficient way to convert hydrogen into electricity.

- **Water Purification:** Photocatalysts used for hydrogen generation can purify water by dissolving organic contaminants and disinfecting water sources while being exposed to light. When delivering clean water in distant or disaster-affected areas, this dual functionality can be especially helpful.

- **Waste Treatment and Bioremediation:** Processes for producing biohydrogen can be used to treat organic waste and wastewater. Microorganisms have the ability to decompose organic waste and generate hydrogen as a byproduct. This procedure can produce useful energy while also helping in waste management.

- **Transportation Fuel:** Hydrogen produced from biomass can be used to power hydrogen fuel cell cars. In comparison to battery electric vehicles, these vehicles release just water vapour and have larger driving ranges. Utilising biohydrogen for transportation can help the transportation sector produce fewer emissions and lessen its dependency on fossil fuels.

Although biomass-derived hydrogen has several advantages, there are still a number of obstacles to be overcome, including optimizing manufacturing procedures, resolving feedstock availability, ensuring environmental sustainability, and raising overall energy efficiency.

1.9 Effect of Semiconductors in Photocatalytic Hydrogen Generation

In the production of photocatalytic hydrogen from biomass, semiconductors are essential. In this method, hydrogen is produced using a photocatalytic process using biomass as a renewable fuel. Semiconductors are utilised to absorb light energy and transform it into chemical energy to speed up the reaction.

Semiconductors are useful for the photocatalytic process because of their special characteristics, including a broad bandgap, excellent stability, and an appropriate energy level. [11] The wavelength of light that semiconductors can absorb is determined by their bandgap energy, which is essential for effective photocatalysis. The semiconductor produces electron-hole pairs as it absorbs light, and these pairs can later take part in the redox reactions required to produce hydrogen. Hydrogen gas, which may be captured and used as a clean energy source, is generated when the electrons and holes interact with water and cellulose. However, several variables, such as the semiconductor type, the biomass feedstock and the reaction circumstances, affect how effectively photocatalytic hydrogen may be produced from biomass. Therefore, by creating new semiconductors and enhancing the reaction conditions, researchers are constantly attempting to increase the process's effectiveness.

Overall, semiconductors are crucial to produce photocatalytic hydrogen from biomass, and the advancement of this exciting clean energy technology depends on their development and optimisation.

Literature Survey

Title of the paper	Author	Year of Publication & Volume	Description	Reference
Heterogeneous photocatalytic hydrogen production from water and biomass derivatives	Katsuya Shimura and Hisao Yoshida	2011, 15	Presently, the major method for producing hydrogen is the high-temperature reforming of natural gas and petroleum, which requires a significant amount of energy. So, the creation of a different hydrogen generation technique is very necessary to address the energy and environmental problems. In this brief review, we remind everyone that systems for producing hydrogen through photocatalysis from water and biomass derivatives including ethanol, glycerol, sugars, and methane should be taken into consideration as potential candidates.	[2]

A critical review on Biohydrogen generation from biomass	B. Senthil Rathi, P. Senthil Kumar, Gayathri Rangasamy , Saravanan Rajendran	2022, 24	With a biological process that is sustainable, waste can be turned into energy. A future-proof method for creating biofuels, biohydrogen generation from lignocellulosic materials is clean and environmentally friendly. The synthesis of hydrogen from biomass and carbohydrate raw materials has always been done on a lab scale, despite the fact that it is advantageous and preferred. Reviewing various forms of biomass and biohydrogen derived from biomass was the article's primary goal. Also, it discussed the processes involved in each type of production, their benefits and drawbacks, as well as the factors that influence all types of production.	[4]
Solar Hydrogen Generation from Lignocellulose	Moritz F.Kuehnel and Erwin Reisner	2018, 7	The production of renewable H_2 using lignocellulosic biomass and photocatalytic reforming is a new strategy. At room temperature and pressure, this process combines photooxidation of aqueous biomass with photocatalytic	[6]

			hydrogen evolution. Water splitting requires more energy than biomass conversion, which produces high-purity H_2 without the need for O_2 creation. Direct photo reforming of unprocessed, raw biomass offers the ability to produce cheap, clean energy from trash and resources found nearby. The thermodynamic barrier for producing H_2 from water splitting is high ($\Delta E^0 = -1.23$ V), whereas the thermodynamic barrier for biomass reformation is practically energy neutral ($E^0 = +0.001$ V), implying that energy is only required to overcome activation barriers.	
Photocatalytic hydrogen evolution from biomass conversion	Kayla Davis, Sunghoon Yoo, Eric W. Shuler, Benjamin D. Sherman, Seunghyun Lee	2021, 19	A summary of recent developments in the synthesis and fundamental physical/mechanistic studies of novel photocatalysts for the conversion of biomass to hydrogen is provided in this paper. Recent developments in hydrogen evolution efficiency with relation to biomass and substrates obtained from biomass are also summarised. Methods that use synthetic	[10]

			photocatalysts or unprocessed biomass as a substrate are given particular attention since their development will result in greater benefits for a sustainable path for the evolution of hydrogen and generation of chemical feedstocks.	
A review on biomass based hydrogen production technologies	Dan Bahadur Pal, Arvind Singh, Ashish Bhatnagar	2022, 20	This article looked at the development of bio-hydrogen technology as a new sustainable and environmentally friendly energy technology. It is essential to keep up the research and development needed to improve H_2 synthesis rates and final yields. Solar integration along with biomass gasification could be a workable substitute. This article highlighted the potential of biohydrogen as a healthy substitute as well as the areas in which further research is necessary to bring about the hydrogen economy.	[12]

Photocatalytic hydrogen generation coupled to pollutant utilisation using carbon dots produced from biomass	Demetra S. Achilleos, Hatice Kasap and Erwin Reisner	2020, 9	Here, we demonstrate the creation of highly reproducible and inexpensive carbon nanodots from lignocellulosic waste that, when paired with photocatalyst produce hydrogen gas when exposed to light.	[13]
Hydrogen generation by photocatalytic reforming of glucose with heterostructured CdS/MoS2 composites under visible light irradiation	Chunhe Li , Hongmei Wang, Julan Ming, Min Liu, Pengfei Fang	2017, 11	In this paper In a straightforward one-pot hydrothermal process, a binary heterostructured CdS/MoS_2 flower-like composite photocatalyst was created. Compared to pure MoS_2, this photocatalyst produced more hydrogen through photocatalysis. The combination of CdS and MoS_2 can greatly increase the photocatalytic H_2 production by effectively accelerating the separation of the photogenerated holes and electrons. According to this study, it may be possible to reform abundant and inexpensive biomass feedstocks for water splitting to produce hydrogen.	[14]

A current perspective for photocatalysis towards the hydrogen production from biomass-derived organic substances and water	Chao-Wei Huang , Ba-Son Nguyen, Jeffrey C.-S. Wu , Van-Huy Nguyen	2020, 16	This article provides a brief explanation of photocatalysis, which uses two methods to make hydrogen as solar fuel: splitting water, and reforming organic compounds produced from biomass. Oxygenated substrates obtained from biomass might be subject to selective photocatalytic reformation in the presence of renewable solar radiation. Important obstacles, opportunities, and the necessity of paying closer attention to photocatalysis in order to produce H_2 are also addressed.	[15]
Cadmium sulfide-based nanomaterials for photocatalytic hydrogen production	Yong-Jun Yuan, Daqin Chen, Zhen-Tao Yu and Zhi-Gang Zou	2018, 25	This review focuses on current developments in CdS-based photocatalyst material design and technological issues for applications in photocatalytic H_2 production. This article also discusses a road map for potential future research in the area of CdS-based photocatalysts for solar H_2 production.	[16]

Photocatalytic reforming of biomass: A systematic study of hydrogen evolution from glucose solution	Xianliang Fua, Jinlin Longa, Xuxu Wanga, Dennis Y.C. Leung, Zhengxin Ding, Ling Wua, Zizhong Zhang, Zhaohui Lia, Xianzhi Fu	2008, 8	The current study reveals the anaerobic photocatalytic reforming of glucose, a molecule that can be produced from biomass, to produce sustainable hydrogen. The Langmuir-Hinshelwood kinetics model may accurately depict the impact of initial glucose concentration on the hydrogen evolution rate. We analysed and offered a potential mechanism for the photocatalytic reforming procedure.	[17]
Photocatalytic hydrogen evolution from biomass (glucose solution) on Au/CdS nanorods with Au3+ self-reduction	Xulin Wang, Xiuzhen Zheng, Huijuan Han, You Fan, Sujuan Zhang, Sugang Meng, Shifu Chen	2020, 26	This study describes the photocatalytic synthesis of renewable hydrogen from glucose using Au/CdS-nanorods (Au/CdS-NRs). Under visible light irradiation, the Au/CdS-NRs catalyst exhibits a better H_2 evolution rate of 90.0 mol g^{-1} h^{-1}. According to this research, self-reduction of Au^{3+} to Au may significantly boost the photocatalytic efficiency of H_2 evolution from biomass, which facilitates the separation and conveyance of photogenerated charge carriers.	[18]

Biomass gasification for hydrogen production	Alex C.C. Chang, Hsin-Fu Chang, Fon-Jou Lin, Kuo -Hsin Lin, Chi-Hung Chen	2011, 9	This study examines the setup of the biomass gasifier to create syngas and biohydrogen. Syngas and hydrogen can be produced with efficiency by gasifying agricultural waste or biomass. In the future, a catalyst could be added to the gasifier to increase the hydrogen production and decrease tar formation. For gasification, air has frequently been employed as the oxygen source. Several studies have examined the effectiveness of the biomass gasification process with and without air and steam.	[19]
Hydrogen Production from Biomass Gasification	Sotiris Karellas	2015, 21	This chapter introduced a wide range of technological techniques that enable the gasification of biomass and subsequent upgrading of the syngas produced to yield a stream of pure hydrogen as an output. Because the biomass-to-hydrogen conversion pathway ideally results in no net carbon emissions, it has no impact on the greenhouse effect.	[20]

Table 1.2: *Literature Survey.*

"CHAPTER-II"

Aim & Objective

Research Gaps

This field of research is constantly growing with the objective of making photocatalytic hydrogen generation a practical and sustainable method for production the of hydrogen. Despite significant progress there is still room for improvement in the rate of hydrogen production. Some of the significant research gaps are :

- Designing Narrow band-gap materials for higher hydrogen generation rates.
- Development of more active as well as stable photocatalysts driven in the visible light.
- Photocatalytic Hydrogen Generation has shown encouraging results at the laboratory scale but further research is needed to determine the process's scalability and economic sustainability.

Objectives

The main objectives of this work are following :

- Selection of Biomass for hydrogen generation by photocatalytic water splitting.
- Selection of Semiconductor for synthesizing photocatalyst for hydrogen generation by photocatalytic water splitting.
- Synthesis of hybrid photocatalyst CdS/Spinacia Oleracea for the production of hydrogen by the process of photocatalytic water splitting.
- Characterization of synthesized photocatalyst CdS/Spinacia Oleracea.

a) **Morphological Characterization**
  i. FE-SEM
  ii. EDX
  iii. TEM
  iv. XRD

b) **Optical Characterization**
  i. UV-VIS
  ii. PL

- Batch Study of hydrogen evolution reaction by using CdS/Spinacia Oleracea photocatalyst at full band solar spectrum by using a solar simulator.

- Batch Study of hydrogen evolution reaction by using CdS/Spinacia Oleracea photocatalyst at 350 nm and 420 nm wavelengths of solar spectrum for the calculation of Apparent Quantum Efficiency.

- Cost analysis of the whole process of hydrogen generation for the hydrogen evolution reaction.

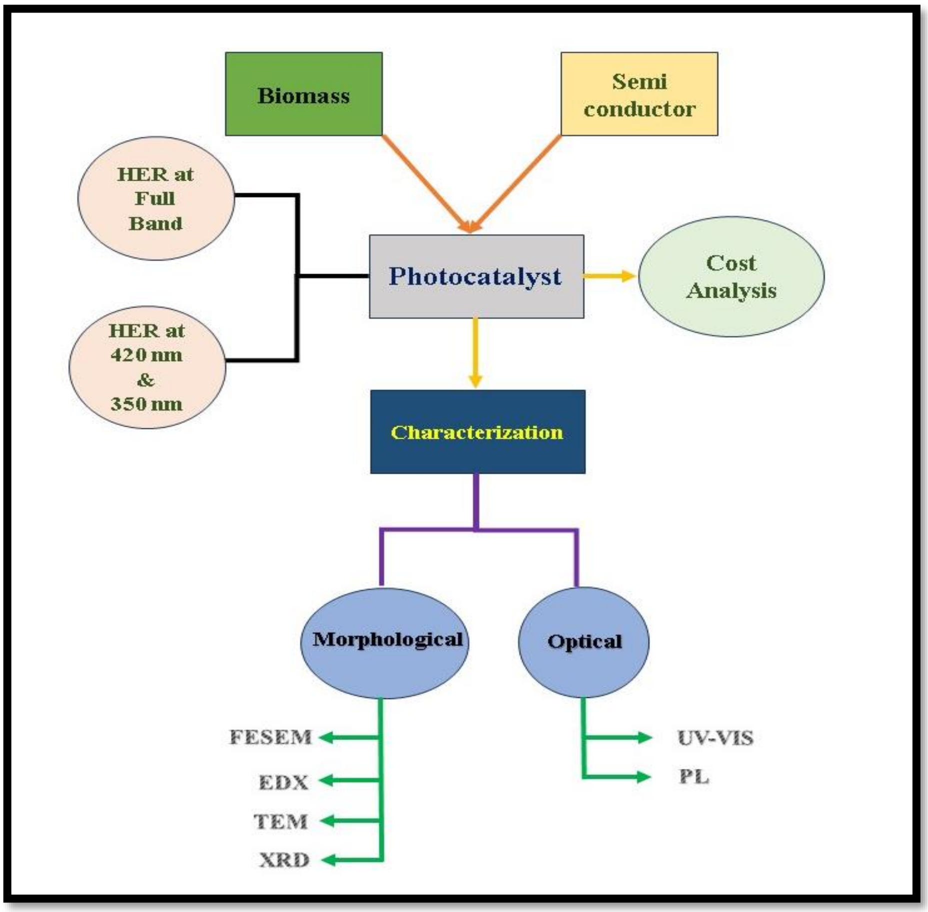


Fig 2.1: *Scheme and overview of the objectives of this study.*

“CHAPTER-III”

Experimental

Experimental

3.1 Selection of Spinacia oleracea

Spinacia Oleracea is a leafy green vegetable that can be grown in various climates and soil types. It contains a high percentage of chlorophyll [21], a natural pigment that absorbs light and starts photosynthesis, making it a suitable biomass source for the photocatalytic process of producing hydrogen. Since it can be grown in abundance, making biomass from it is an environmentally friendly option. Hydrogen may be produced from biomass feedstocks via photocatalysis, a technique that uses light energy to drive chemical processes.

Source of Biomass	Chlorophyll Content (% of leaf's dry wt.)
Cabbage	0.1 – 0.4
Grass	0.1 – 0.6
Lettuce	0.1 – 0.5
Sunflower	0.3 – 1.0
Spinacia Oleracea	0.6 – 1.5

Table 3.1: *Chlorophyll Percentages in different source of biomass.*

In photocatalysis, light energy is transferred to the biomass feedstock using a catalyst material, which subsequently undergoes a chemical reaction to make hydrogen. Because Spinacia Oleracea has a lot of chlorophyll, it can serve as a photosensitive agent and absorb light energy, which can be utilised to start the photocatalytic reaction that produces hydrogen.

High hydrogen yields could also be achieved by using Spinacia Oleracea as a biomass feedstock for photocatalysis that produces hydrogen. Spinacia Oleracea can offer a consistent source of biomass, and its high chlorophyll content can boost the effectiveness of the photocatalytic reaction and result in larger hydrogen outputs.

3.2 Selection of CdS as Semiconductor

Cadmium Sulphide (CdS) is a semiconductor material with a maximum absorption peak of 514 nm and a bandgap of around 2.42 eV. As a result, CdS is more effective for visible light photocatalysis [22], [23] because it can absorb visible light or UV light with a wavelength of less than 514 nm. More significantly, the CdS conduction band edge is located lower than the positions of other common semiconductors (such as TiO_2, $SrTiO_3$, and ZnO) [24] , which indicates that CdS photoelectrons have a stronger reducing power in the photocatalytic reaction. As a result, CdS has been considered as a suitable photocatalyst for this process. The amount of recovered photocatalyst is severely limited by the CdS material's mild susceptibility to corrosion. Although there are a few ways to increase the use ratio of CdS in order to address this fundamental issue. The most popular technique is to create CdS composite materials by doping them with ions or using various components. In order to fully utilise the visible spectrum of natural light, the CdS composite also improves the absorption of long wavelength light. Furthermore, co-catalysts like platinum (Pt), nickel (Ni) or cobalt (Co) can simply be added to CdS to boost its photocatalytic activity for hydrogen production. Higher hydrogen yields can be achieved by using these co-catalysts, which can increase the separation of electron-hole pairs and enhance the reaction kinetics.

Semi Conductor	**Band Gap Structure (pH = 7)**			**Reference**
	Cb	Vb	Eg/eV	
ZnS	1.04	2.56	3.60	[23]
TiO_2	0.50	2.70	3.20	[25]
ZnO	0.31	2.89	3.20	[26]
CuO	1.16	0.85	2.00	[27]
CdS	0.90	1.50	2.40	[28]

Table 3.2: *Band Gaps of previously reported photocatalysts.*

3.3 Materials and Methods

- **Chemical Reagents:**
  - I. Cadmium Acetate Dihydrate (Sigma-Aldrich)
  - II. Thiourea (Sigma-Aldrich)
  - III. Ethanol (Jiangsu Huaxi International)
  - IV. Deionized Water
  - V. Petroleum Ether (Sigma-Aldrich)

- **Equipment and Instruments:**
  - I. Solar Simulator (Newport LCS-100)
  - II. Magnetic Stirrer (Tarsons Products Limited)
  - III. Muffle Furnace (S. C. Dey & Co.)
  - IV. Hot Air Oven
  - V. Petri dish
  - VI. Mortar and Pestle
  - VII. Beaker
  - VIII. Laboratory balance
  - IX. Filter Paper
  - X. Plastic Vial
  - XI. Teflon Hydrothermal Container

3.3.1 Extraction of Chlorophyll from Plant Residue

Our main target is to extract chlorophyll from Spinacia Oleracea leaves. Chlorophyll can be removed from plant extract in many ways [29] but our aim is to remove chlorophyll from plant extract without losing other secondary metabolites. The method of removal chlorophyll as follows:

At first the Spinacia Oleracea leaves are bought from the local market of Jadavpur, Kolkata. Then the Spinacia Oleracea leaves are cut in short pieces and a mortar & pestle is used to grind the leaves into fine powder. After that a small amount (around 4gm) of powdered leaf material was taken in a beaker. 20 gm petroleum ether was added to the beaker to cover the powdered leaf material. Then the mixture was stirred on a magnetic stirrer at 600 rpm for one hour under room temperature. Then the mixture was filtered with the help of a filter paper to separate the liquid (petroleum ether) from solid leaf material. After that the petroleum ether was evaporated when the mixture was put into a hot air oven at 80°C for 1 hour. At last the chlorophyll residue which were left behind were collected and stored in a labelled container and was put in a desiccator.

3.3.2 Synthesis of Cadmium Sulphide (CdS) :

5.56 gm Cadmium acetate [30] was taken in a beaker with 50 ml. of DI water and was stirred on a magnetic stirrer at 800 rpm for 1 hour . Then 3.806 g of Thiourea was also taken with 50 ml of DI water in another beaker and stirred at 800 rpm for 1 hour. After that these two solutions were taken in a comparatively large beaker and mixed at 600 rpm using a magnetic stirrer at 80°C for 10 hours. Finally, we got the CdS solution which is of yellow colour. The colour change was the indication of the formation of CdS solution. After that the solution was taken in a petri dish and put into a hot air oven at 80°C for 2 hours. Then we got the CdS solution in powder form which was stored in a labelled vial and was put in a desiccator.

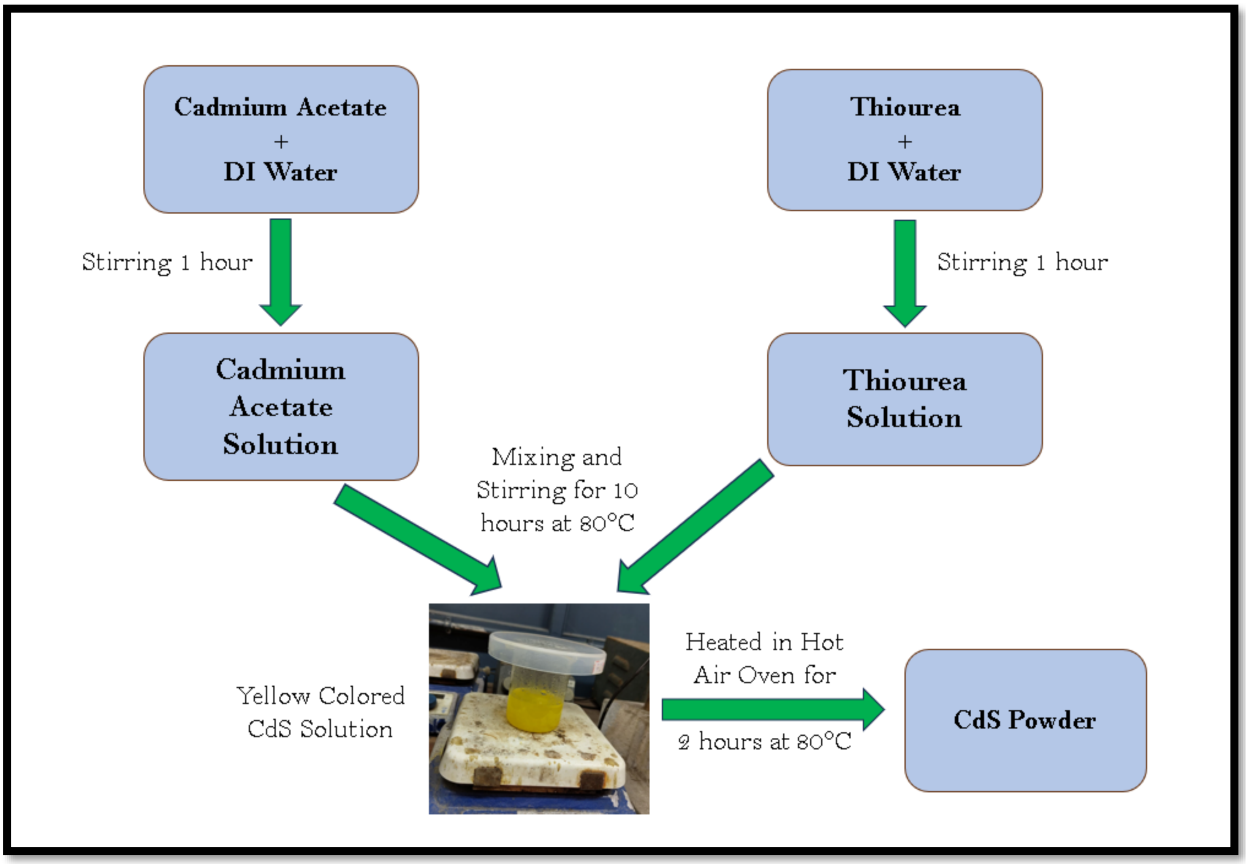


Fig 3.1: *Scheme of synthesis of CdS Powder.*

3.3.3 Synthesis of CdS/Spinacia Oleracea Photocatalyst :

The biomass powder which was stored was taken in a small beaker and 50 ml. of Ethanol was added to it. Then the mixture was stirred at 600 rpm using a magnetic stirrer for one hour at 40°C. Again the CdS was taken in another beaker and 50 ml. Ethanol was added to it. This mixture was also stirred at 600 rpm and 40°C for one hour with the help of a magnetic stirrer. After that both the mixture was mixed in a large beaker and was stirred at 800 rpm and 60°C for an hour. Then the mixture was poured into a set of Teflon hydrothermal containers and then hydrothermally treated at 180°C for 10 hours in a muffle furnace. After that the prepared mixture was washed with Ethanol and taken in a petri dish and was put into a hot air oven for further 2 hours for heating at 80°C. At last we will get the synthesized photocatalyst in powder form. The powder was put into a labelled vial and stored in a desiccator.

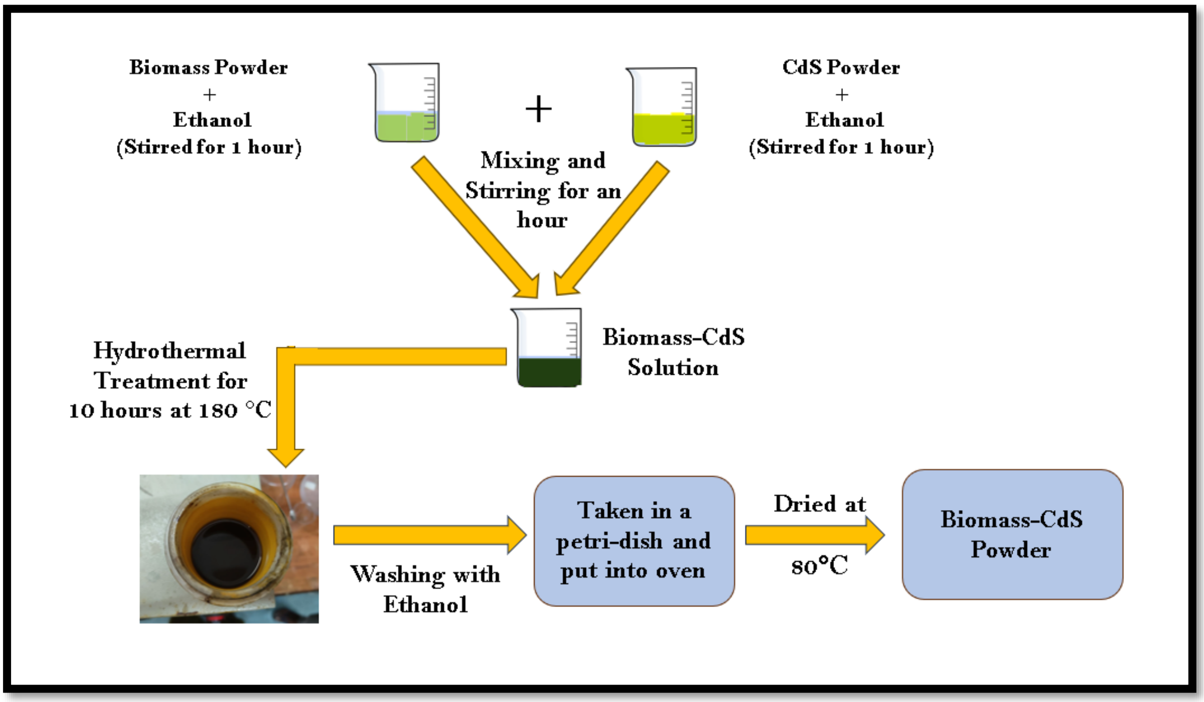


Fig 3.2: *Scheme of synthesis of CdS/Spinacia Oleracea Powder.*

3.4 Characterization of photocatalyst

3.4.1 Morphological Characterization

3.4.1.1 Scanning Electron Microscope (SEM)

A concentrated electron beam is used to scan a sample's surface in a scanning electron microscope (SEM), which creates images of the sample. The sample's surface topography and chemical composition are revealed by the signals that are created as a result of the electrons' interactions with the sample's atoms. An image is created by combining the position of the electron beam with the strength of the signal being detected while it is being scanned in a raster scan pattern.

Principle of SEM

High voltage is supplied between the heated filament and the sample, which causes electrons to be created from the filament and accelerated in the direction of the sample.[31] When the electrons hit the sample's surface, they interact with the atoms and molecules, leading to a variety of interactions like secondary electron emission, inelastic scattering, and elastic scattering. A detector picks up the signal created by the resulting interactions, which

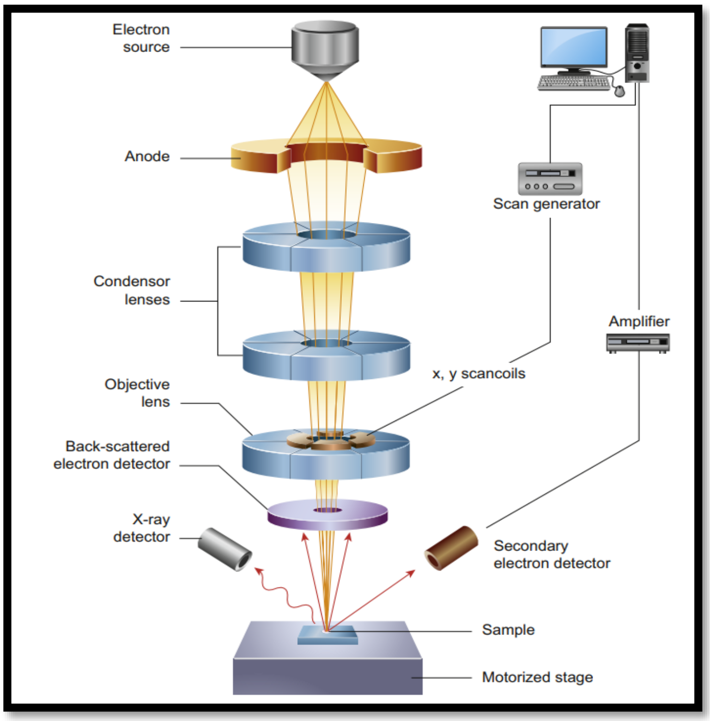


Fig 3.3: *Schematic Diagram of different parts of a SEM.* [32]

is then utilised to build an image of the sample's surface. The surface of the sample is traversed by the electron beam in a raster pattern, and the signals that are produced are then processed to produce a picture. The SEM is furnished with several detectors to pick up various signals, including secondary electrons, backscattered electrons, and X-rays, which can be utilised to learn more about the composition, structure, and topography of the sample.

In general, the SEM works by using a focussed electron beam to scan a sample's surface and then detecting the resultant signals to provide an image with high resolution and magnification.

3.4.1.2 Energy dispersive X-ray analysis (EDX)

EDX analysis is a typical analytical method for examining chemical compositions. The EDX method examines the X-rays that a substance emits in response to electromagnetic radiation. [33] A high-energy beam is focused on the sample under investigation in an EDX device. In principle, secondary electrons from an inner shell are ejected when an electron beam impacts a material, and the resulting void is filled by higher shell electrons. X-rays, which are both distinctive of the element and dependent on the shell from which electrons travel into the holes, are produced as a result of the surplus energy. A material's composition may be determined using the EDX data.

3.4.1.3 Transmission electron microscopy (TEM)

The TEM works with a high voltage electron beam to create the image, where the electron gun is placed at the top which produces the electron that travels through the vacuum tube. The ultra-fine electron beam that passes through the thin material is focused using the electromagnetic lens. The fluorescent screen located at the bottom of the microscope receives the transmitted electrons. Based on the specimen's density, an image of the specimen and all of its many sections shows on the screen. The resultant image can be photographed or studied immediately.

TEM can be used to characterize the morphology and size of a nanoparticle. In addition, sample purity can easily be checked using TEM by differentiating between EVs and non-EV particles of similar size.

3.4.1.4 X-Ray Diffraction (XRD)

The experimental science of X-ray diffraction (XRD), in which the crystal structure causes a beam of incident X-rays to diffract into numerous distinct directions, is used to identify the atomic and molecular structure of crystals. An image of the density of electrons within the crystal can be created in three dimensions by measuring the angles and intensities of these diffracted beams. The mean locations of the atoms in the crystal, their chemical bonds, their crystallographic disorder, and several other details can all be inferred from this electron density.[34]

Principle of XRD

The foundation of XRD is a crystalline sample and constructive interference of monochromatic x-rays. These x-rays are produced by a cathode ray tube and are monochromatically focused radiation that is directed towards the sample. The well-known Bragg's law ($n\lambda = 2d \sin\theta$) provides the foundation for the powder XRD method.

Bragg’s Law states that the X-ray's angle of incidence, and angle of scattering, are the same when it strikes a crystal surface. Additionally, constructive interference will happen when the path difference, d, is equal to n wavelengths, where n is a whole number.

According to Bragg’s Equation : $n\lambda = 2d \sin\theta$ where d is path difference and θ is incident angle.

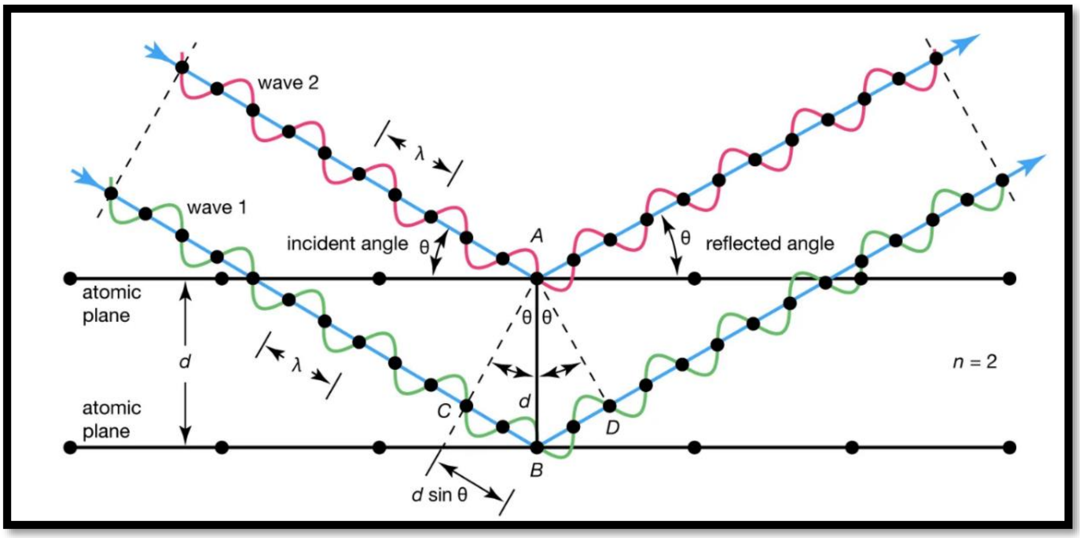


Fig 3.4: *Visualisation of Bragg’s law.*

(Britannica, T. Editors of Encyclopaedia (2022, March 15). Bragg law. Encyclopedia Britannica. https://www.britannica.com/science/Bragg-la)

3.4.2 Optical Characterization

3.4.2.1 Ultraviolet Visible Spectroscopy (UV-VIS)

A method for measuring light absorbance across the ultraviolet and visible regions of the electromagnetic spectrum is known as ultraviolet-visible (UV-Vis) spectroscopy. For a fixed path length, UV-Vis spectroscopy can be used to determine the concentration of the absorbing species. This method is remarkably simple, flexible, rapid, exact, and affordable. A UV-Visible/NIR spectrophotometer (Lambda 365) is a tool which is used for UV-VIS Spectroscopy. This can be used to explore liquids, gases, and solids by utilising radioactive radiation related to the far and near ultraviolet (UV), visible (Vis) sections of the electromagnetic spectrum. Thus, for these regions, the following preset wavelengths have been established: UV: 300–400 nm; visible light: 400–765 nm.

Principle of UV Vis

In UV spectrophotometers, the Beer-Lambert Law is applied.[35] According to this law, whenever a beam of monochromatic light passes through a solution containing an absorbing substance, the concentration of the solution and the incident radiation are proportional to the rate at which the radiation intensity decreases and the thickness of the absorbing solution. This law is expressed through this equation:

$$A = \log (I_0/I_t) = ECL \tag{3.1}$$

where A denotes absorbance, I_0 denotes light intensity falling on a sample cell, I_t denote light intensity leaving the sample cell, C denotes solute concentration, L denotes sample cell length, and E denotes molar absorptivity.

Based on the Beer-Lambert law, it has been determined that the extent of light absorption increases with the number of molecules capable of absorbing light at a particular wavelength.

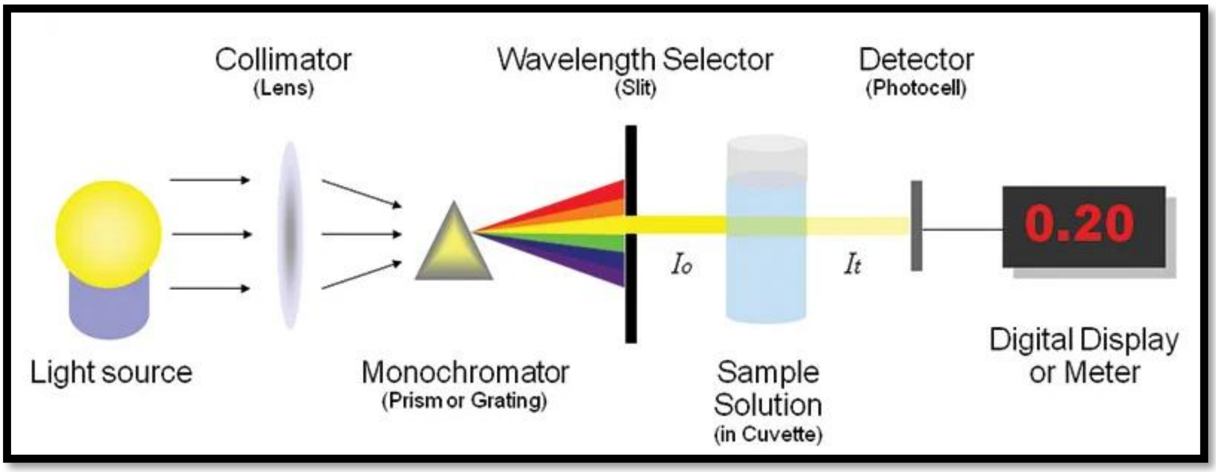


Fig 3.5: *Principle of UV-VIS Spectroscopy.*

(Aryal, S. et al. (2023) Spectrophotometer- principle, instrumentation, applications, Microbe Notes)

Tauc Method :

The optical bandgap of disordered or amorphous semiconductors is determined using a Tauc plot. The equation of this method is

$$(\alpha.h.\lambda)^2 = B(h.\lambda - E_g) \qquad (3.2)$$

Where, α is absorbance, h is planck constant, λ is photon’s frequency, B is a constant and E_g denotes Band Gap Energy.

3.4.2.2 Photoluminescence Spectroscopy (PL):

Photoluminescence (PL) is a process in which a substance absorbs photons (electromagnetic radiation) and then radiates photons again. According to quantum mechanics, this can be explained as an excitation to a state with a greater energy followed by a return to a state with a lower energy and the emission of a photon. An electron can be moved from the valence band up to the conduction band across the forbidden energy gap if a light particle (photon) with an energy greater than the band gap energy is absorbed. The electron typically has excess energy throughout this photoexcitation process, which it loses before coming to rest at the lowest energy in the conduction band. The electron energy eventually moves back to the valence band at this point. As a result, the material loses energy, which is then transformed back into a luminous photon and emitted. Thus the process of photon excitation followed by photon emission is called photoluminescence.

The quantity of PL emitted from a material is directly related to the relative amount of recombination rates. The photoexcitation of electrons from the valence band to the conduction band happens when samples are exposed to photons. The electrons then lose extra energy through non-radiative relaxation and fall to the lowest energy in the conduction band. If the sample is fully free of contaminants, or pure, the electrons may radioactively recombine with the valence band holes, and a very small binding energy exciton is formed between these two carriers. If the sample is impure or doped, radiative recombination also may occur via shallow donor or acceptor levels. As a result, analysing the photoluminescence pattern can reveal details on the material's impurity, energy transfer, and band gap.

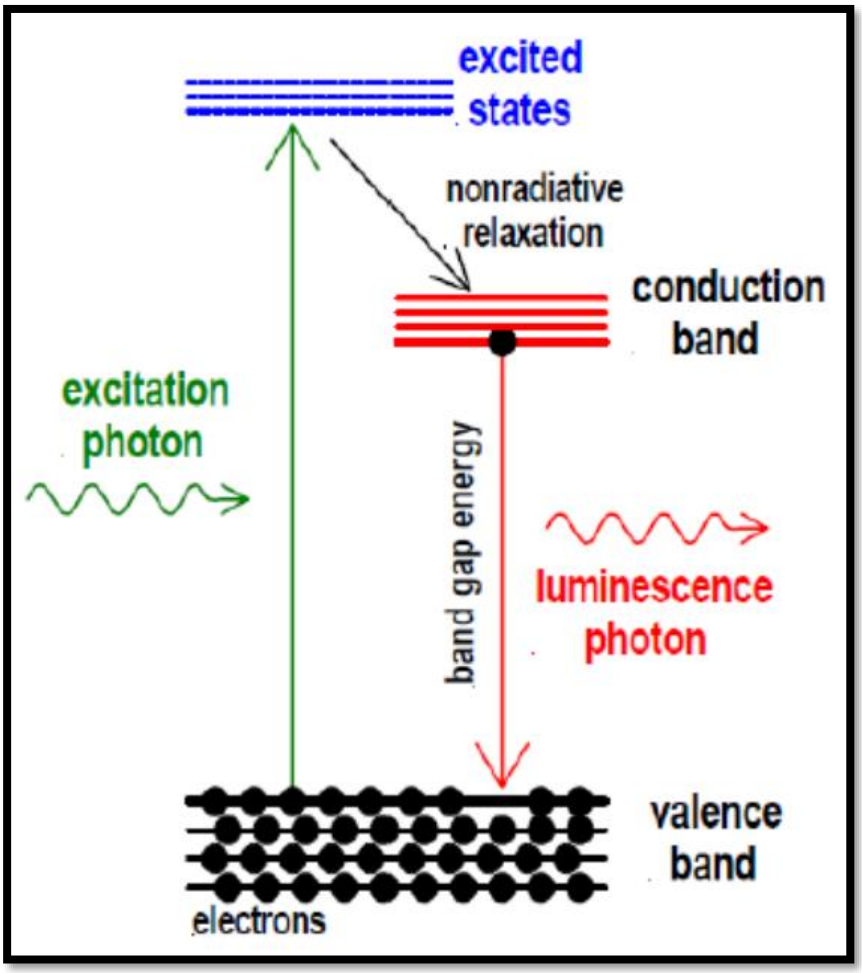


Fig 3.6: *Principle of photoluminescence spectroscopy (PL).*

(Mahalingam, Vallikkodi. (2018). SYNTHESIS, GROWTH AND CHARACTERIZATION OF PIPERAZINIUM p-AMINOBENZOATE AND PIPERAZINIUM p-CHLOROBENZOATE NONLINEAR OPTICAL SINGLE CRYSTALS. 10.13140/RG.2.2.16046.8224).

3.5 Solar Simulator

A Solar Simulator is an electronics device which can be used as a source of artificial sunlight for controlled laboratory experimental purpose. It offers similar intensity and spectral composition to natural sunlight. In our work we have used ORIEL LCS – 100 ^{TM} small area Sol.1A series solar simulator. The surface area of the solar simulator's irradiation is 4 cm^2. Xenon lamps are used in this solar simulator and lamp wattage is 100 W.

Fig 3.7: *Newport LCS - 100 Solar Simulator.*

Oriel Instruments, A.N.Corp.B. (2014) LCS-100 solar simulators, Photonics Media.

Principle of working of solar simulator

- A Xenon short arc lamp is housed inside an oval reflector, which captures a large portion of its output. It is powered by a power source. The output of the lamp is redirected close to an optical homogenizer assembly.

- The condenser lens, ellipse, and homogenizer lens combine to provide homogeneous light. The optical path is folded using mirrors as necessary for the task.

- To provide repeatable spectrum shaping throughout the whole work plane, the filter is placed right before the homogenizer assembly.

- The optical shutter is placed behind the spectrum filter and homogenizer so that after the first system warm-up, those optical elements and their mounts may reach thermal equilibrium and provide reliable performance.

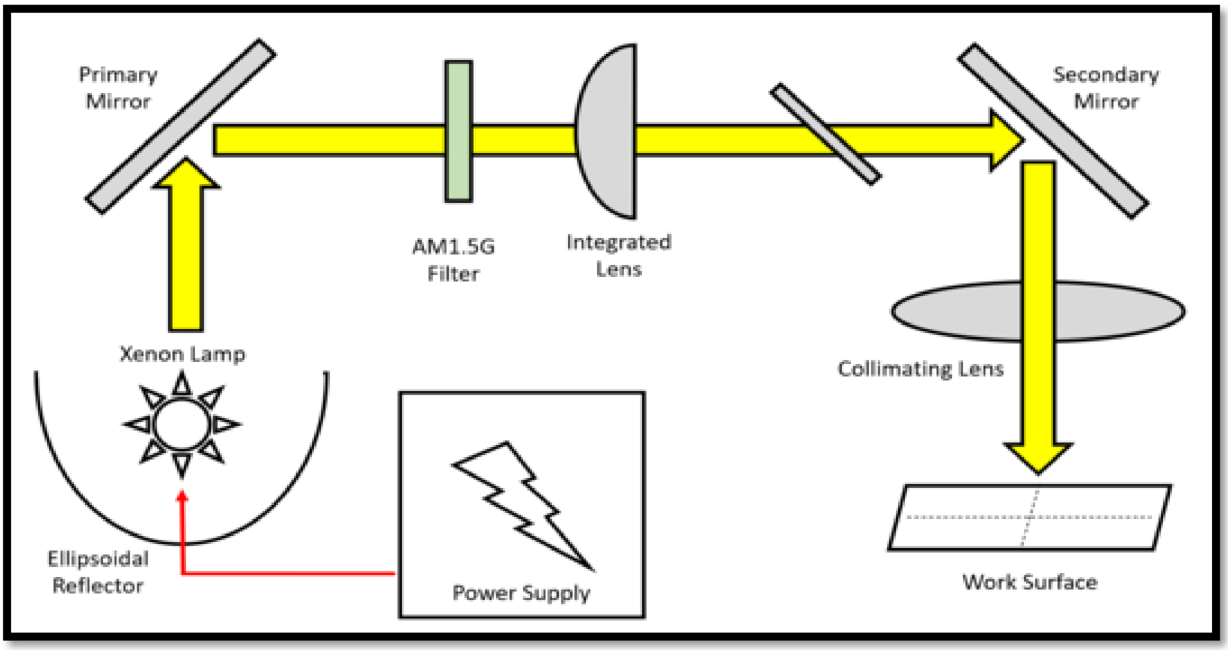


Fig 3.8: *Principle of working of a solar simulator.*

Solar simulator (2023) Wikipedia. Available at: https://en.wikipedia.org/wiki/Solar_simulator

Band Pass Filter

Optical band pass filters are those that block some wavelength bands while allowing some to pass. They essentially remove the necessary light spectrum. To determine the apparent quantum yield of various photocatalytic devices, band pass filters are utilised. We have used two filters which have wavelengths of 350 nm and 420 nm respectively.

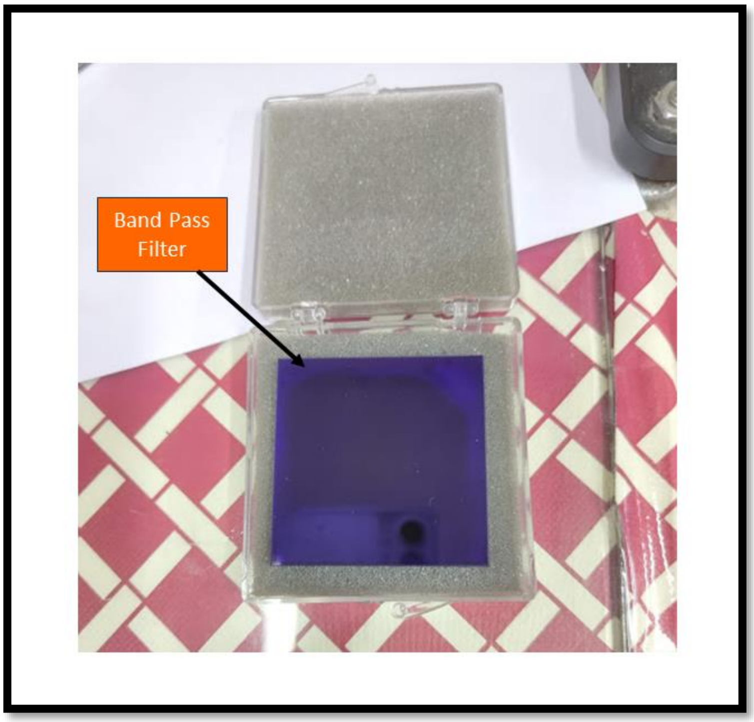


Fig 3.9: *Picture of Band Pass Filter of 350nm.*

3.6 Experimental Setup

The experimental setup consists of various parts such as :

1. Solar Simulator as a source of light.
2. Reaction Vessel.
3. Gas Outlet.
4. Water Displacement Unit.
5. Control Valve.

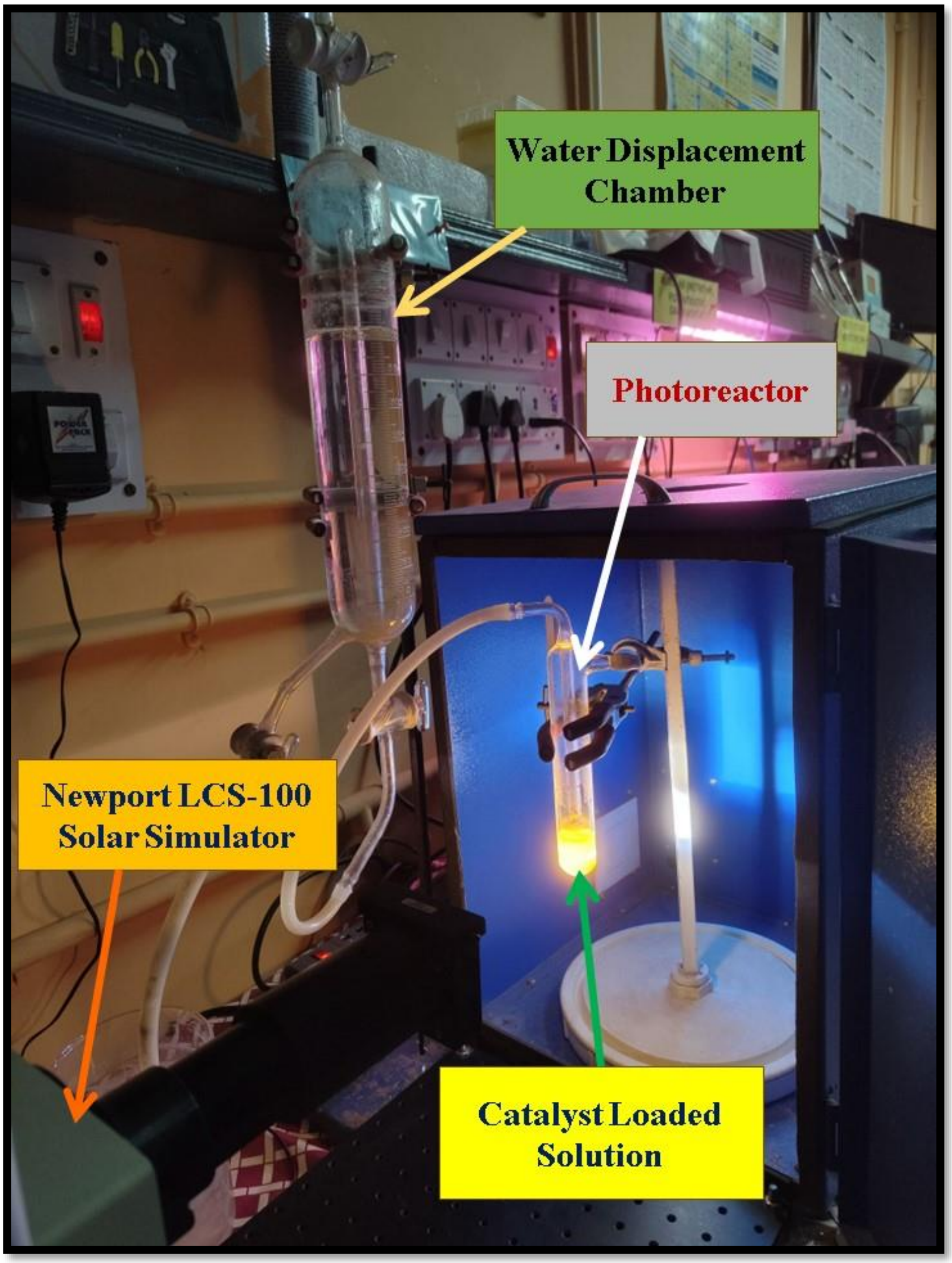


Fig 3.10: *Experimental Setup of Photocatalytic Hydrogen Generation.*

3.7 Batch Study of Hydrogen Generation

3.7.1 Performance Study

For this particular experimental study 0.05 gm. of synthesized CdS/Spinacia Oleracea photocatalyst and 10 ml water is taken in a beaker and stirred for 1 hour. A Solar simulator (94011A, Manual shutter, Newport Oriel LCS-100) is utilized to simulate and the intensity was adjusted to 113 mW.cm^{-2} . The Solar Simulator includes an AM 1.5 G air mass filter which provides Class A spectral performance based on current applicable standards at 1 sun irradiance output. The mixture containing photocatalyst is taken in a photoreactor and is used for photocatalysis for 6 hours. Before starting the experiment, all the air is evacuated from the experimental setup with the help of a vacuum pump. When light irradiates from the solar simulator and on the reactor where the catalyst loaded solution is taken, a chemical reaction occurs and hydrogen gas is produced. The produced gas then passes through the pipe and goes to the water displacement chamber. The gas displaces the water from the chamber and accumulates in the chamber. We can measure the volume of hydrogen evolved from how much water is displaced from the chamber by reading the volume measurement from the scale on the side of the chamber.

3.7.2 Performance Analysis

The following performance metrics were assessed in order to measure the function of the photocatalyst:

- **Activity of photocatalyst**

The amount of water that is displaced in the system is used to calculate the moles of hydrogen that are produced. The volume which is in ml. is converted into millimole. Photocatalytic activity denotes the effectiveness of the photocatalyst. The amount of hydrogen generated from per gm. Catalyst in per unit time is known as photocatalytic activity.

$$Activity = \frac{moles\ of\ hydrogen\ generated\ (mmol)}{Irradiation\ time\ (hr)\ .\ photocatlyst(gm.)}$$

- **Apparent Quantum Yield (AQY)**

It is defined as the ratio of the number of emitted photons divided by the number of absorbed photons. To obtain high solar energy conversion efficiency, the quantum efficiency of photocatalytic reaction must be increased over a wide range of wavelengths. If a photon (E_{photon}) of wavelength of λ(nm) is incident during a photocatalytic water splitting reaction, the energy of this one photon calculated using the equation:

$$E_{photon} = \frac{hc}{\lambda}$$

Where, h = Plank's constant (J.s),

c = Speed of light ($m.s^{-1}$).

And the total energy of the incident monochromatic light (E_{total}) is calculated [36] using the following equation:

$$E_{total} = P.s.t$$

Where, P = power density of that incident monochromatic light (W/m^2),

s = area that is being irradiated (m^2),

t = duration of the exposure of the incident light (s).

The total number of incident photons can be determined from the given equation:

$$\text{No. of incident photons} = E_{total} / E_{photon}$$

$$= \frac{P.s.\lambda.t}{h.c}$$

So, the Apparent Quantum Yield = $(2.n_{H2}.N_A.h.c)/(P.s.\lambda.t) \times 100\ \%$

Where, nH_2 = number of molecules of Hydrogen evolved over the duration t of the incident light (mol)

N_A = Avogadro's constant (mol^{-1})

****

“CHAPTER-IV”

Result & Discussion

Result & Discussion

4.1 Characterization Result

4.1.1 Morphological Characterizations:

4.1.1.1 SEM Analysis:

SEM was used for microscopic study. SEM images showed the surface morphology of CdS and CdS/Spinacia Oleracea nanoparticles in the following fig.4.1. From the images fig. 4.1(a) we can see that more or less a mixture of unevenly distributed spheroid and rod-like structures cover the surface layer of CdS. And from the other two images fig. 4.1(b) which are of CdS/Spinacia Oleracea, we can clearly observe that there are few pores in some places.

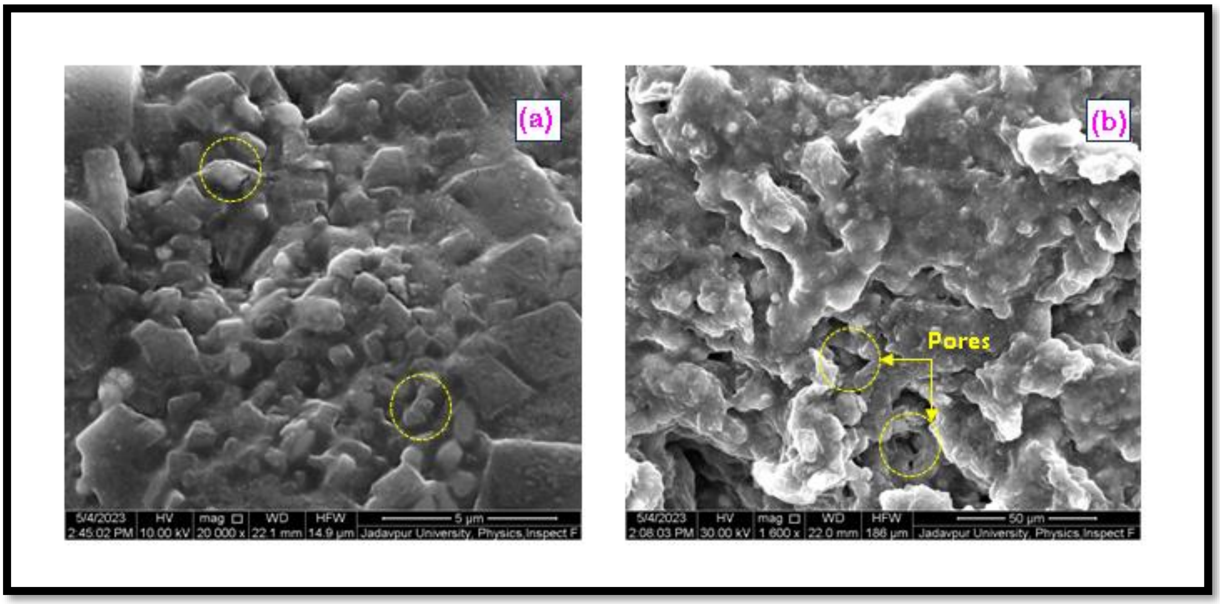
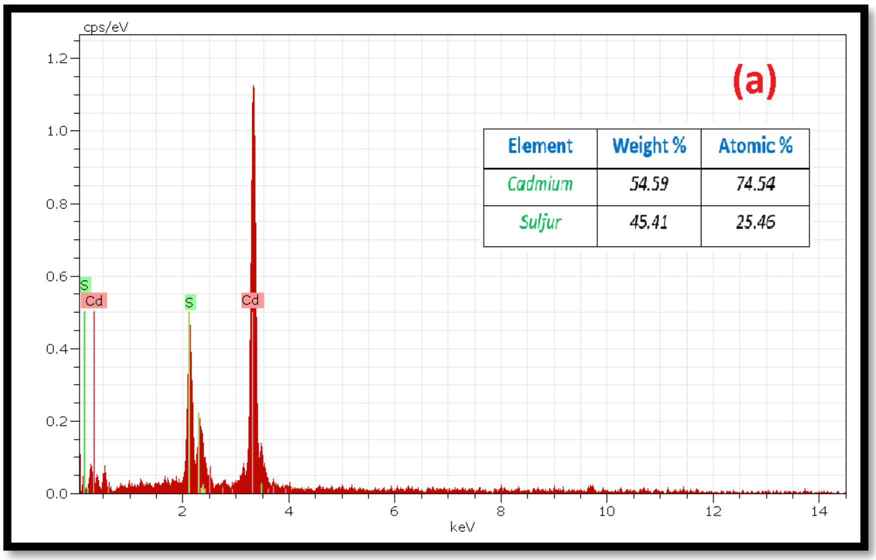


Fig. 4.1: *The SEM images of the synthesized (a) CdS nanoparticles and (b) CdS/Spinacia Oleracea nanoparticles*

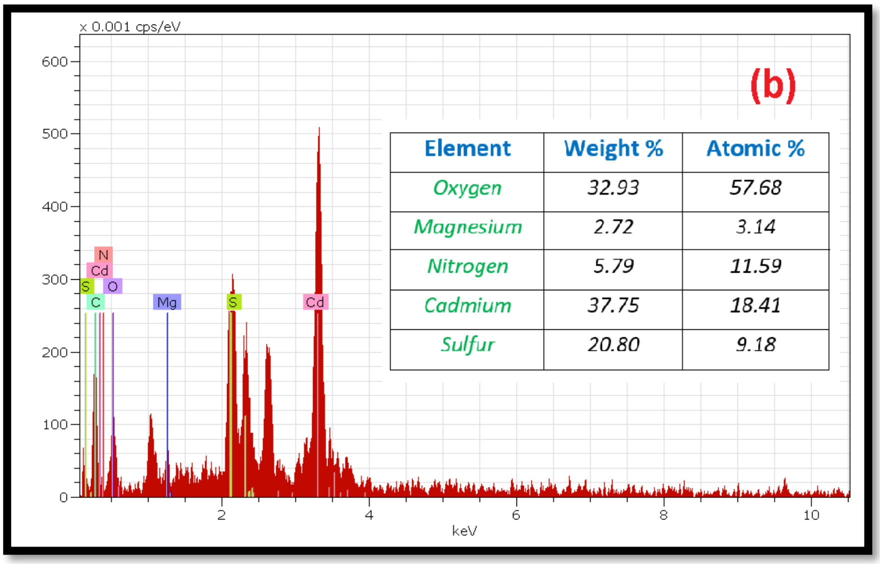
4.1.1.2 EDX Analysis:

The EDX analysis is done or both the catalysts. From the fig. 4.2 (a) and 4.2 (b) we can clearly see the presence of the elements which are used to synthesize the catalysts. Also the chemical composition and their concentration are obtained from the figures. There's a spike of Carbon (C) visible in the fig. 4.2 (b) but that's not recorded in the data as the sample was kept carbon coated during EDX analysis.



Element	Weight %	Atomic %
Cadmium	54.59	74.54
Sulfur	45.41	25.46

Fig. 4.2(a): *EDX image of the synthesized CdS nanoparticles.*



Element	Weight %	Atomic %
Oxygen	32.93	57.68
Magnesium	2.72	3.14
Nitrogen	5.79	11.59
Cadmium	37.75	18.41
Sulfur	20.80	9.18

Fig. 4.2(b): *EDX image of the synthesized CdS/Spinacia Oleracea photocatalyst.*

4.1.1.3 TEM Analysis:

TEM was also used for microscopic study. The TEM images suggest that the CdS nanoparticles fig. 4.3(a) are not uniform and those are attached to each other. From fig. 4.3(b) we can see the hexagonal structure of the CdS/Spinacia Oleracea nanoparticles. Also we can calculate the particle sizes which are of different length from 10 nm to 35 nm which confirm CdS/Spinacia Oleracea is present in nanocomposite form.

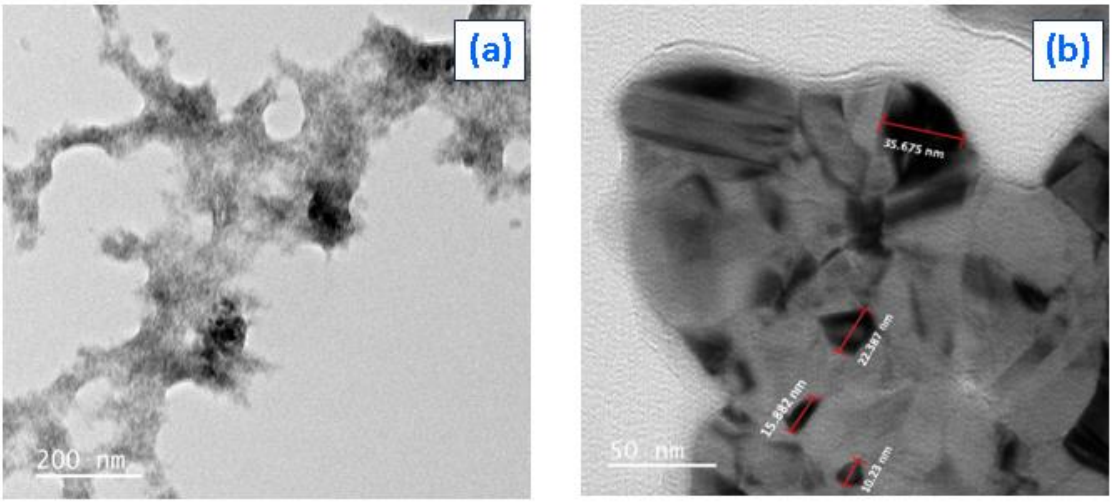


Fig. 4.3: *TEM images of the synthesized (a) CdS nanoparticles and (b) CdS/Spinacia Oleracea nanoparticles.*

4.1.1.4 XRD Analysis:

Figure 4.4(a) shows the XRD patterns of CdS nanoparticles. In this figure the peaks are observed at the 2θ values of 25.09°, 26.70°, 28.12°, 43.79°, 48.19° and 51.32°. These peaks closely match with the (100), (002), (101), (110), (103), (112) crystalline planes of the hexagonal structure of CdS. We get the XRD patterns and peaks of synthesized CdS/Spinacia Oleracea photocatalyst from the fig. 4.4(b). Here also we observe the peaks at the 2θ values of 15.19°, 20.05°, 22.49°, 25.02°, 33.24°, 46.34°, 52.19° and 62.12°. Some peaks also closely match with the (100), (103), (112) crystalline planes of the hexagonal structure of CdS. The other peaks comes from the other metal which is present in the Biomass.

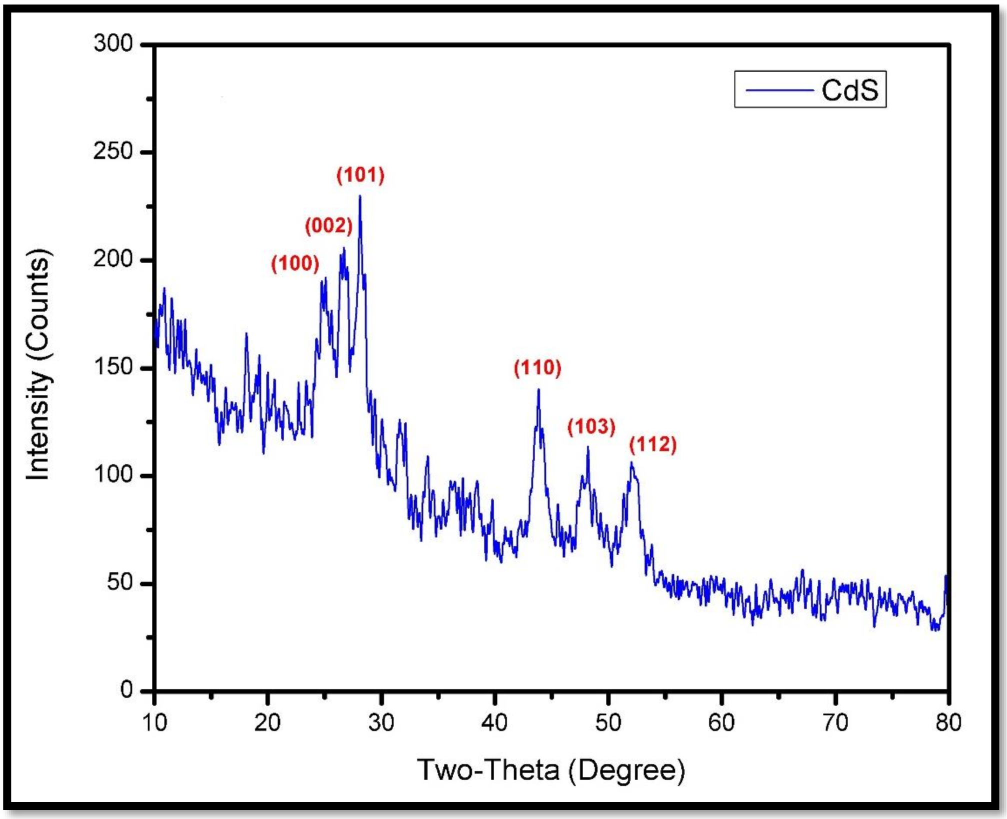


Fig. 4.4(a): *XRD peaks of CdS.*

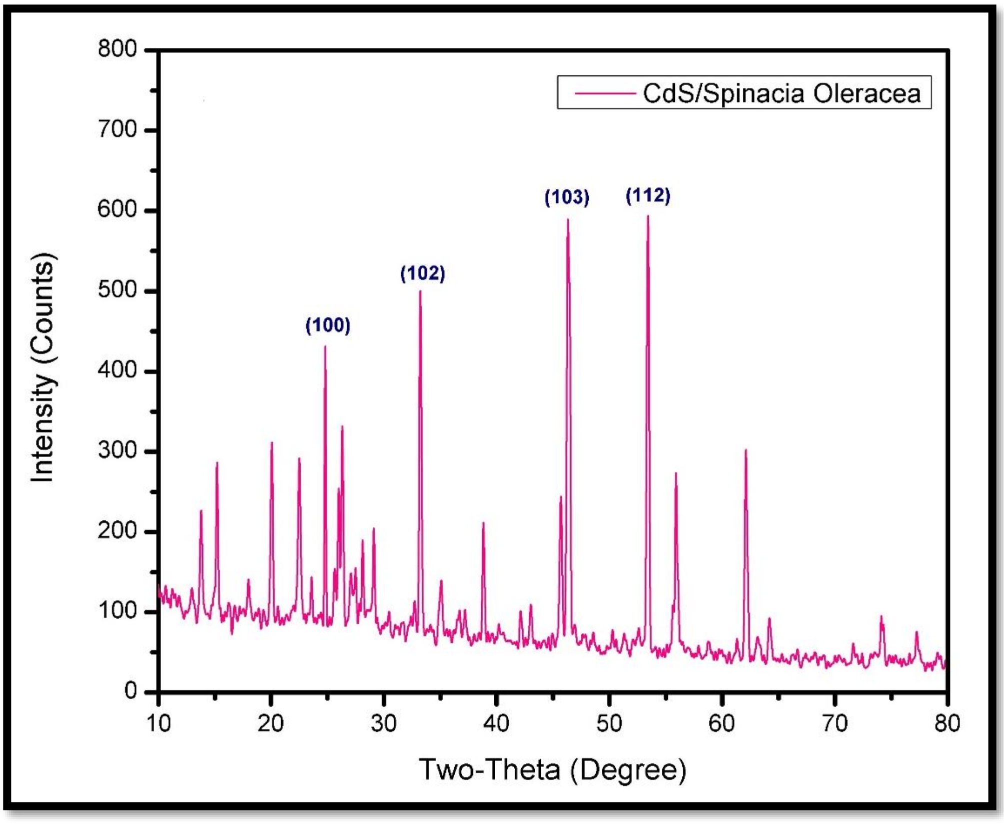


Fig. 4.4(b): *XRD peaks of CdS/Spinacia Oleracea.*

4.1.2 Optical Characterization:

4.1.2.1 UV-VIS Study:

By using Ultraviolet-Visible Spectroscopy, the optical absorption characteristics of CdS and CdS/Spinacia Oleracea were thoroughly examined (Fig.4.5). By using the Tauc plot method, the optical band gap energies were also estimated. The pristine CdS showed a strong absorption at around 460 nm which attributed to the narrow band gap. The CdS/Spinacia Oleracea showed very low absorbance in the visible light spectra. The peaks are obtained mainly in the UV Spectra, 350 nm for CdS and 400 nm for CdS/Spinacia Oleracea.

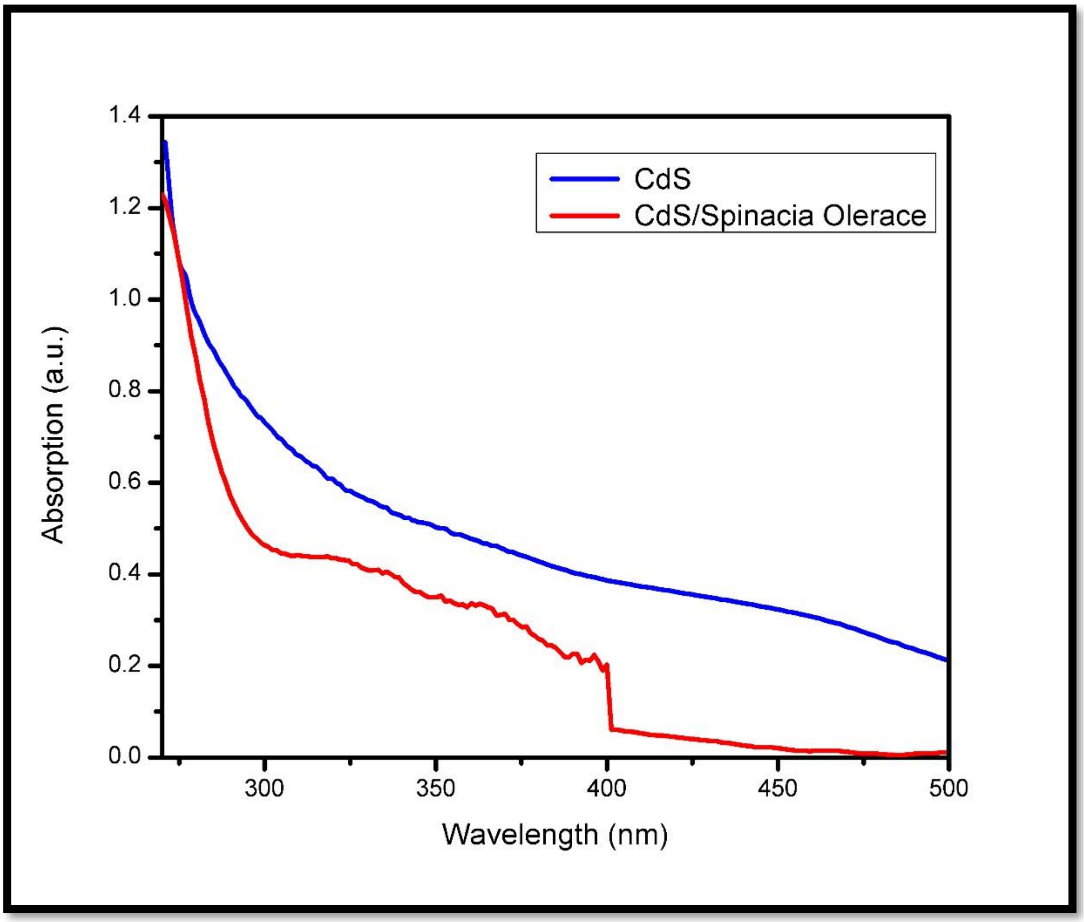


Fig. 4.5: *UV-VIS Spectroscopy of different photocatalyst.*

Tauc Plot

We have calculated the band gaps of the photocatalysts using the tauc plot method. For CdS it's 2.4 eV and 2.3eV for CdS/Spinacia Oleracea, as seen in fig.4.6. It's found that when we are adding the Spinacia Oleracea powder with CdS the Eg value is increasing. That's why the Band Gap is reduced for the CdS/Spinacia Oleracea composite.

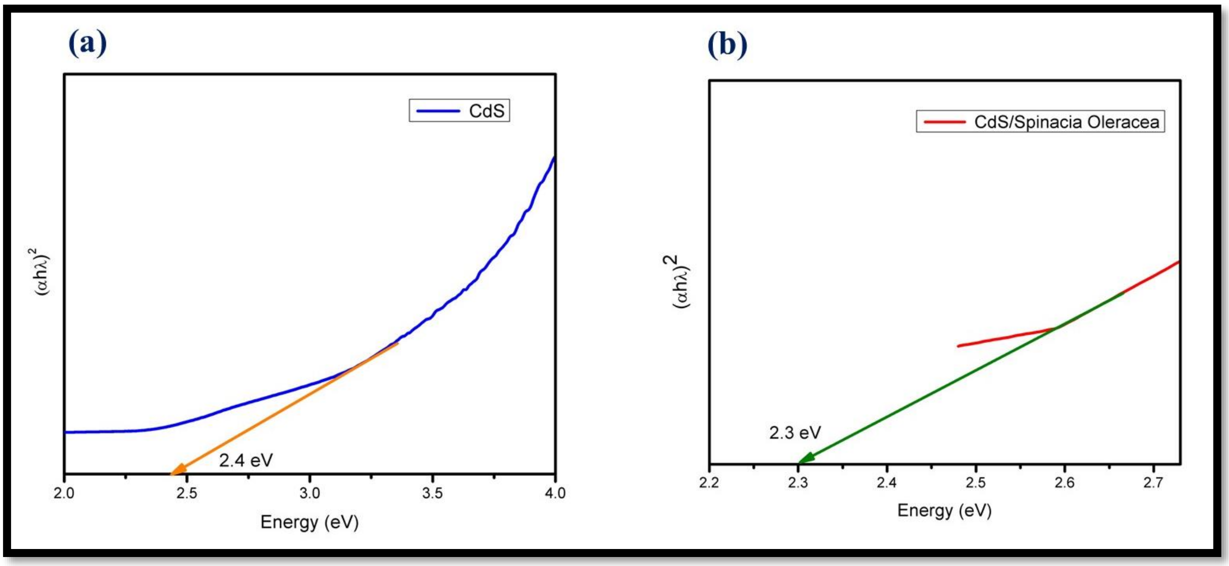


Fig. 4.6: *Band Gap Calculation using Tauc Plot for (a) CdS and (b) CdS/Spinacia Oleracea.*

4.1.2.2 <u>Photoluminescence (PL) Study</u>:

Photogenerated charge transfer and recombination were found out through photoluminescence analysis, and the results are shown in Fig. 4.7. CdS emission showed a significant peak at about 360 nm and the peak intensity was high due to high recombination rate of photogenerated electron hole pairs. In the case of CdS/Spinacia Oleracea composite, the peak intensity was low suggesting a low rate of recombination of electrons and holes. It enables a high rate of photoreaction. That's why it exhibited a better performance than pristine CdS.

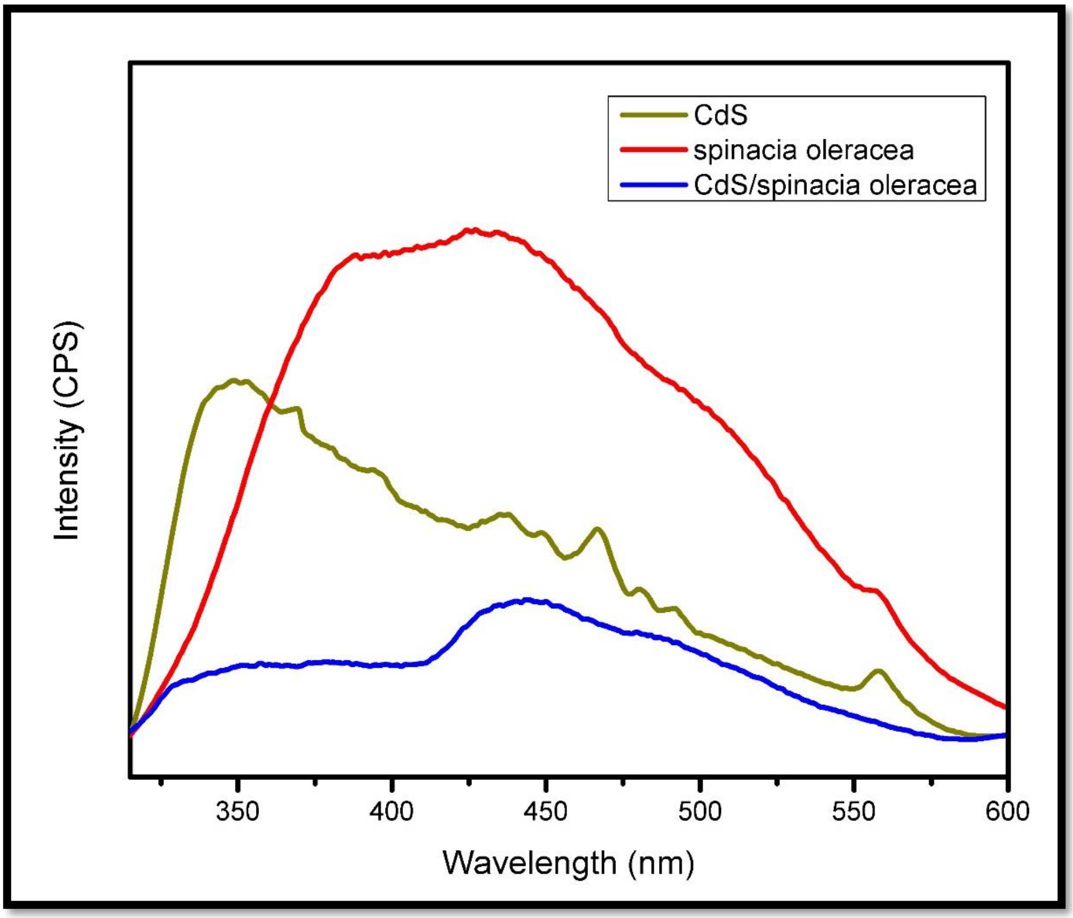


Fig. 4.7: *PL Spectra of the Photocatalysts*.

4.2 Batch Study of Hydrogen Generation

The synthesized photocatalysts are studied carefully and analysed how many moles of hydrogen are generated. Mainly two important parameters are calculated from the results which are :

- Activity of the photocatalysts.
- Apparent Quantum Yield of the process.

4.2.1 Hydrogen Generation rate using synthesized CdS/Spinacia Oleracea Photocatalyst under full band solar irradiation:

From the figure (Fig. 4.8) below we can see the amount of hydrogen evolved with respect to time when we are using very small amount (0.05 gm.) of CdS and CdS/Spinacia Oleracea photocatalyst under full band solar irradiation.

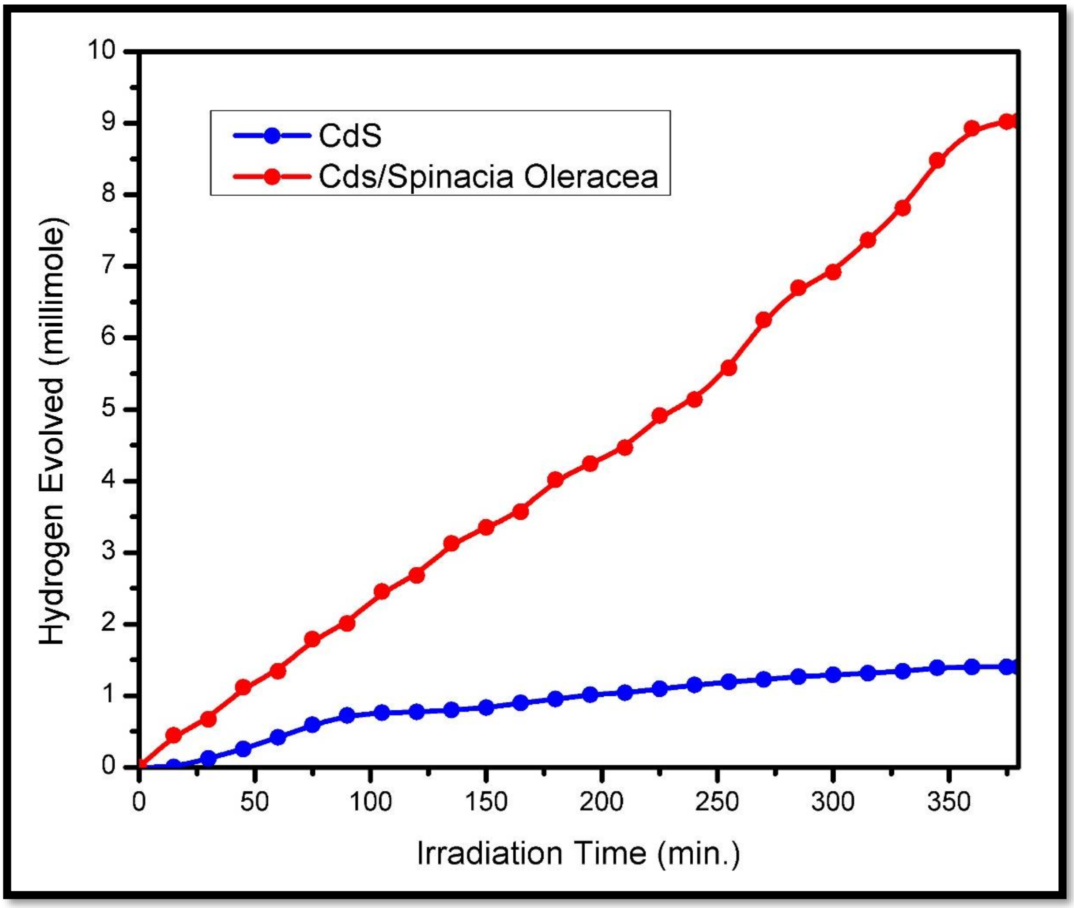


Fig. 4.8: *Amount of evolved Hydrogen in millimole using CdS and CdS/Spinacia Oleracea photocatalyst under full band solar irradiation.*

4.2.2 Hydrogen Generation using synthesized CdS/Spinacia Oleracea Photocatalyst in different wavelengths:

The following experiment is done in three different conditions:

- Full band of solar spectrum
- 420 nm of solar spectrum
- 350 nm of solar spectrum

We have conducted the experiment in three different wavelengths of solar spectrum and it's clear that the moles of H_2 Generation are greater in case of full and of solar spectrum and slowly decreasing when we move to 420 nm and 350 nm respectively. In each case we used 0.05 gm of photocatalyst.

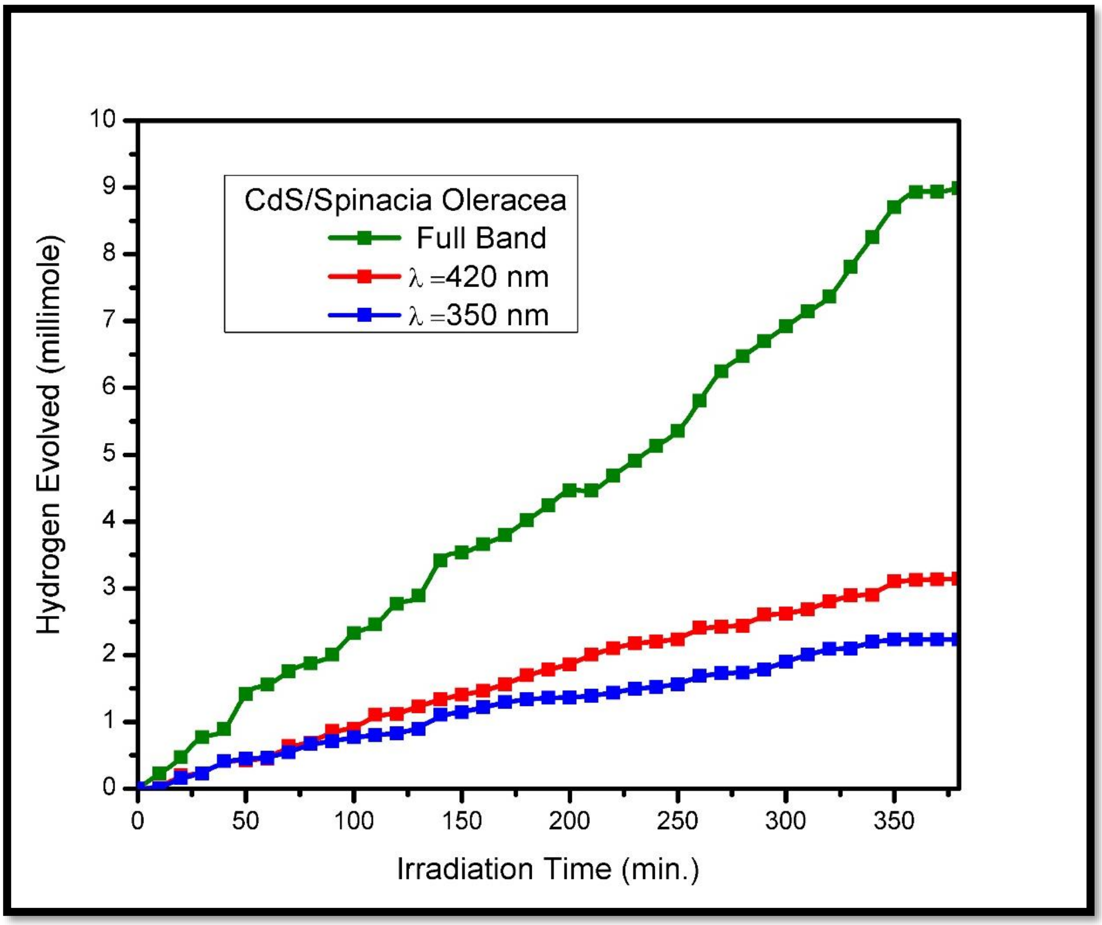


Fig. 4.9: *Amount of evolved Hydrogen in millimole using CdS and CdS/Spinacia Oleracea photocatalyst under fixed wavelength of solar spectrum using Band Pass Filter.*

Wavelength	Moles of Hydrogen Generated in 6 hrs. (mmol)
Full band	8.92
420 nm	3.12
350 nm	2.23

Table 4.1: *Amount of evolved Hydrogen in millimole using CdS/Spinacia Oleracea photocatalyst at different wavelength of solar spectrum.*

4.2.3 Comparative performance analysis of different photocatalyst:

From the following table 4.2 we can compare the moles hydrogen generated using the CdS and CdS/Spinacia Oleracea catalysts and also their photocatalytic activities. It's clear that using same amounts of photocatalyst and under full band solar spectrum, photocatalytic activity is more than six times greater in CdS/Spinacia Oleracea than in pristine CdS. It's also illustrated in the fig. 4.10.

Catalyst name	Moles of Hydrogen generated (mmol) in 6 hrs.	Photocatalytic activity ($mmol.g^{-1}.h^{-1}$)
Pristine CdS	1.40	4.59
CdS/Spinacia-Oleracea 350 nm	2.23	7.43
CdS/Spinacia-Oleracea 420 nm	3.12	10.40
CdS/Spinacia-Oleracea Full Band	8.92	29.80

Table 4.2: *Amount of evolved Hydrogen in millimole and photocatalytic activity of CdS and CdS/Spinacia Oleracea photocatalyst.*

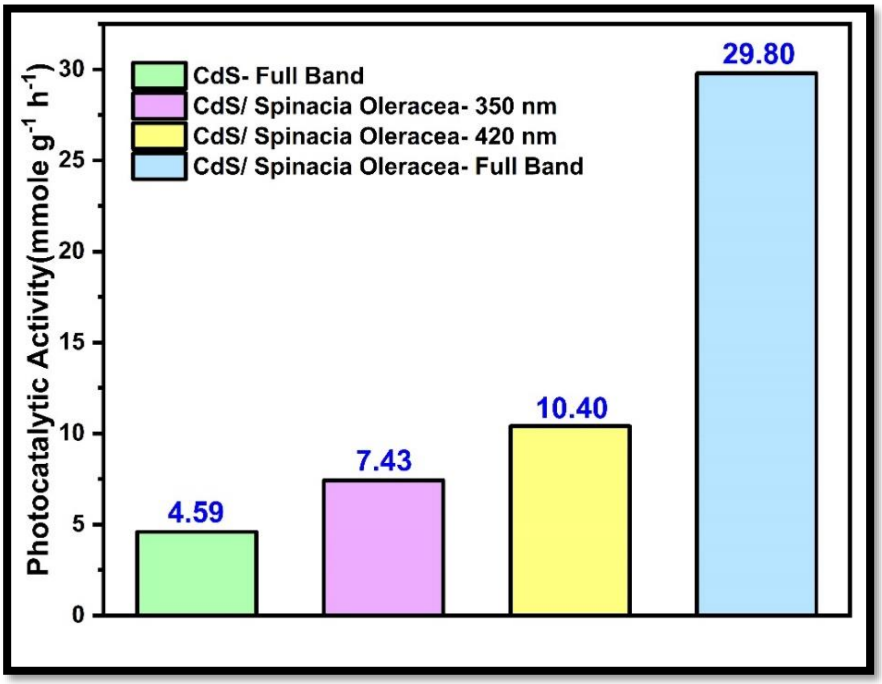


Fig 4.10: *Activity Comparison of Different Photocatalyst.*

Photocatalyst	**Substrate**	**Activity (mmol h^{-1} g.cat^{-1})**	**Reference**
5% Pt/TiO2	Turf	0.033	[37]
5% Pt/TiO2	Rice plant	0.058	
0.2% Pt/TiO2	Fescue grass	0.061	
5% Pt/TiO2	Chlorella algae	0.09	
0.5% Pt/TiO2	Rice husk	0.095	
0.5% Pt/TiO2	Alfalfa stems	0.10	
Co/CdS/CdOx	Bagasse	0.37	
Co/CdS/CdO$_x$	Sawdust	0.75	
Co/CdS/CdO$_x$	Grass	1.0	
Co/CdS/CdO$_x$	Wooden Branch	5.31	
CdS/Spinacia Oleracea	**Spinacia Oleracea**	**29.8**	This Work

Table 4.3: *Comparative table of Photocatalytic hydrogen production from raw biomass with synthesized photocatalyst.*

4.2.4 Apparent Quantum Yield study of different photocatalyst:

The ratio of the number of emitted photons divided by the number of absorbed photons is defined as quantum yield. The quantum efficiency of photocatalytic reactions needs to be enhanced throughout a broad range of wavelengths in order to achieve high solar energy conversion efficiency.

Apparent Quantum Yield analysis of CdS/Spinacia Oleracea photocatalyst at different band pass filter:

Catalyst Name	Filter	AQY (%)
CdS/Spinacia Oleracea	420	18.21
	350	15.63

Table 4.4: *Apparent quantum yield of synthesized CdS/Spinacia Oleracea photocatalyst.*

4.3 Cost Analysis:

Items		Amount Needed/ Hours Used	Price in Rs. (INR)	Price in $ (USD)
Chemical Used	Cadmium Acetate Dihydrate	5.56 g.	247.50	2.99
	Thiourea	3.806 g.	249.00	3.01
	Ethanol	150 ml.	36.00	0.44
	Petroleum Ether	20 ml.	98.50	1.19
Electricity Used	Magnetic Stirrer	17 hrs.	2.38	0.029
	Solar Simulator	6 hrs.	4.20	0.051
	Muffle Furnace	10 hrs.	140	1.69
	Hot Air Oven	5 hrs.	70	0.85
Total			848	10.25

Table 4.5: *Cost Analysis of Hydrogen Generation method using CdS/Spinacia Oleracea photocatalyst.*

From the above table we can estimate the total cost is $10.25 to produce 8.92 mmol of Hydrogen.

So, the estimated cost for producing 1 mole of Hydrogen by this method is $853.13 using CdS/Spinacia Oleracea photocatalyst.

****

“CHAPTER-V”

Conclusions

Conclusions

The production of hydrogen from biomass through photocatalytic method has attracted a lot of interest as it has the capacity to convert solar energy and other renewable resources into the chemical potential of storable hydrogen. Also the process for converting biomass to hydrogen ultimately results in zero net carbon emissions and therefore, it has no impact on the greenhouse effect. In this work a photocatalyst CdS/Spinacia Oleracea has been developed from biomass to generate hydrogen efficiently. The following is a list of some of the conclusions :

- The synthesized **CdS/Spinacia Oleracea** photocatalyst is highly active in UV region of solar spectrum as the absorption rate is high in this range.
- The photocatalytic activity of the **CdS/Spinacia Oleracea** catalyst is also recorded as **29.80 mmol g^{-1} h^{-1}** which is higher that the pristine CdS which is **4.59 mmol g^{-1} h^{-1}**.
- It’s also looked at how effectively the synthesized photocatalyst has produced hydrogen. According to the experimental findings, **CdS/Spinacia Oleracea**'s AQY at **420 nm** is **18.21 %** and at **350 nm** it’s **15.63 %**.
- Chlorophyll molecules can act as sensitizers by transferring their excited electrons to the CdS nanoparticles which improves the efficiency of charge separation. By reducing charge recombination and improving electron-hole separation, the photocatalytic activity is increased for CdS/Spinacia Oleracea photocatalyst.
- The estimated cost to produce 1 mole of Hydrogen by this method is $853.13 using CdS/Spinacia Oleracea photocatalyst.
- It is anticipated that hydrogen generation from biomass soon will be one of the most used method to produce hydrogen because it’s very effective and ecologically friendly too.

“CHAPTER-VI”

Bibliography

Bibliography:

[1] A. Sarker, K. Azad, M. Rasul, and A. Doppalapudi, “Prospect of Green Hydrogen Generation from Hybrid Renewable Energy Sources: A Review,” Energies (Basel), vol. 16, p. 1556, Feb. 2023, doi: 10.3390/en16031556.

[2] K. Shimura and H. Yoshida, “Heterogeneous photocatalytic hydrogen production from water and biomass derivatives,” Energy and Environmental Science, vol. 4, no. 7. pp. 2467–2481, Jul. 2011. doi: 10.1039/c1ee01120k.

[3] M. Antar, D. Lyu, M. Nazari, A. Shah, X. Zhou, and D. L. Smith, “Biomass for a sustainable bioeconomy: An overview of world biomass production and utilization,” Renewable and Sustainable Energy Reviews, vol. 139, p. 110691, 2021, doi: https://doi.org/10.1016/j.rser.2020.110691.

[4] B. Senthil Rathi, P. Senthil Kumar, G. Rangasamy, and S. Rajendran, “A critical review on Biohydrogen generation from biomass,” Int J Hydrogen Energy, 2022, doi: 10.1016/j.ijhydene.2022.10.182.

[5] “RESOURCE CLASSIFICATION OF BIOMASS ENERGY.” https://polarpedia.eu/en/biomass-energy-2/ (accessed Jun. 19, 2023).

[6] M. F. Kuehnel and E. Reisner, “Sonnengetriebene Wasserstofferzeugung aus Lignocellulose,” Angewandte Chemie, vol. 130, no. 13, pp. 3346–3353, Mar. 2018, doi: 10.1002/ange.201710133.

[7] “The Engineering Toolbox.” https://www.engineeringtoolbox.com/fuels-higher-calorific-values-d_169.htmlhttps://www.engineeringtoolbox.com/fuels-higher-calorific-values-d_169.html (accessed Jun. 28, 2023).

[8] P. Purayil and S. Chandran, Fossil Fuels to Green Hydrogen: A Paradigm Shift? An Examination of Capital Project Management Perspectives in the Post-Pandemic Era. 2022. doi: 10.2523/IPTC-22359-MS.

[9] M. H. McCay and S. Shafiee, “Hydrogen: An Energy Carrier,” in Future Energy (Third Edition), T. M. Letcher, Ed., Elsevier, 2020, pp. 475–493. doi: https://doi.org/10.1016/B978-0-08-102886-5.00022-0.

[10] K. A. Davis, S. Yoo, E. W. Shuler, B. D. Sherman, S. Lee, and G. Leem, “Photocatalytic hydrogen evolution from biomass conversion,” Nano Convergence, vol. 8, no. 1. Korea Nano Technology Research Society, Dec. 01, 2021. doi: 10.1186/s40580-021-00256-9.

[11] F. Zhang et al., “Recent advances and applications of semiconductor photocatalytic technology,” Applied Sciences (Switzerland), vol. 9, no. 12. MDPI AG, Jun. 01, 2019. doi: 10.3390/app9122489.

[12] D. B. Pal, A. Singh, and A. Bhatnagar, “A review on biomass based hydrogen production technologies,” International Journal of Hydrogen Energy, vol. 47, no. 3. Elsevier Ltd, pp. 1461–1480, Jan. 08, 2022. doi: 10.1016/j.ijhydene.2021.10.124.

[13] D. S. Achilleos, H. Kasap, and E. Reisner, “Photocatalytic hydrogen generation coupled to pollutant utilisation using carbon dots produced from biomass,” Green Chemistry, vol. 22, no. 9, pp. 2831–2839, May 2020, doi: 10.1039/d0gc00318b.

[14] C. Li, H. Wang, J. Ming, M. Liu, and P. Fang, “Hydrogen generation by photocatalytic reforming of glucose with heterostructured CdS/MoS2 composites under visible light irradiation,” Int J Hydrogen Energy, vol. 42, no. 27, pp. 16968–16978, Jul. 2017, doi: 10.1016/j.ijhydene.2017.05.137.

[15] C. W. Huang, B. S. Nguyen, J. C. S. Wu, and V. H. Nguyen, “A current perspective for photocatalysis towards the hydrogen production from biomass-derived organic substances and water,” Int J Hydrogen Energy, vol. 45, no. 36, pp. 18144–18159, Jul. 2020, doi: 10.1016/j.ijhydene.2019.08.121.

[16] Y. J. Yuan, D. Chen, Z. T. Yu, and Z. G. Zou, “Cadmium sulfide-based nanomaterials for photocatalytic hydrogen production,” Journal of Materials Chemistry A, vol. 6, no. 25. Royal Society of Chemistry, pp. 11606–11630, 2018. doi: 10.1039/c8ta00671g.

[17] X. Fu et al., “Photocatalytic reforming of biomass: A systematic study of hydrogen evolution from glucose solution,” Int J Hydrogen Energy, vol. 33, no. 22, pp. 6484–6491, 2008, doi: 10.1016/j.ijhydene.2008.07.068.

[18] X. Wang et al., “Photocatalytic hydrogen evolution from biomass (glucose solution) on Au/CdS nanorods with Au3+ self-reduction,” J Solid State Chem, vol. 289, Sep. 2020, doi: 10.1016/j.jssc.2020.121495.

[19] A. C. C. Chang, H. F. Chang, F. J. Lin, K. H. Lin, and C. H. Chen, “Biomass gasification for hydrogen production,” in International Journal of Hydrogen Energy, Oct. 2011, pp. 14252–14260. doi: 10.1016/j.ijhydene.2011.05.105.

[20] S. Karellas, “Hydrogen Production from Biomass Gasification,” 2015, pp. 97–117. doi: 10.1007/978-94-017-7330-0_4.

[21] A. Agarwal and S. Dutta Gupta, “Assessment of spinach seedling health status and chlorophyll content by multivariate data analysis and multiple linear regression of leaf image features,” Comput Electron Agric, vol. 152, pp. 281–289, Sep. 2018, doi: 10.1016/j.compag.2018.06.048.

[22] A. Kudo and Y. Miseki, “Heterogeneous photocatalyst materials for water splitting,” Chem Soc Rev, vol. 38, no. 1, pp. 253–278, 2009, doi: 10.1039/B800489G.

[23] N. C. Zheng, T. Ouyang, Y. Chen, Z. Wang, D. Y. Chen, and Z. Q. Liu, “Ultrathin CdS shell-sensitized hollow S-doped CeO2 spheres for efficient visible-light photocatalysis,” Catal Sci Technol, vol. 9, no. 6, pp. 1357–1364, 2019, doi: 10.1039/c8cy02206b.

[24] YONG XU and MARTIN A.A. SCHOONEN, “The absolute energy positions of conduction and valence bands of selected semiconducting minerals,” 2000.

[25] M. D. Ward, J. R. White, and A. J. Bard, “Electrochemical Investigation of the Energetics of Particulate Titanium Dioxide Photocatalysts. The Methyl Viologen-Acet ate System,” 1983.

[26] by Srikanth Gunti et al., “Enhanced Visible Light Photocatalytic Remediation of Organics in Water Using Zinc Oxide and Titanium Oxide Nanostructures,” 2017.

[27] P. E. De Jongh, D. Vanmaekelbergh, and J. J. Kelly, “Cu 2 O: a catalyst for the photochemical decomposition of water?,” 1999.

[28] Malcolm F. Finlayson et al., “Determination of Flat-Band Position of CdS Crystals, Films, and Powders by Photocurrent and Impedance Techniques. Photoredox Reaction Mediated by Intragap States,” 1985.

[29] J. D. Hiscox and G. F. Israelstam, “A method for the extraction of chlorophyll from leaf tissue without maceration,” Canadian Journal of Botany, vol. 57, no. 12, pp. 1332–1334, Jun. 1979, doi: 10.1139/b79-163.

[30] M. Pattabi and J. Uchil, “Synthesis of Cadmium Sulphide nanoparticles,” Solar Energy Materials and Solar Cells, vol. 63, no. 4, pp. 309–314, 2000, doi: https://doi.org/10.1016/S0927-0248(00)00050-7.

[31] D. Titus, E. James Jebaseelan Samuel, and S. M. Roopan, “Chapter 12 - Nanoparticle characterization techniques,” in Green Synthesis, Characterization and Applications of Nanoparticles, A. K. Shukla and S. Iravani, Eds., Elsevier, 2019, pp. 303–319. doi: https://doi.org/10.1016/B978-0-08-102579-6.00012-5.

[32] “A Brief Introduction to SEM (Scanning Electron Microscopy).” https://www.scimed.co.uk/education/sem-scanning-electron-microscopy/ (accessed Jun. 28, 2023).

[33] T. Mudalige, H. Qu, D. Van Haute, S. M. Ansar, A. Paredes, and T. Ingle, “Chapter 11 - Characterization of Nanomaterials: Tools and Challenges,” in Nanomaterials for Food Applications, A. López Rubio, M. J. Fabra Rovira, M. martínez Sanz, and L. G. Gómez-Mascaraque, Eds., Elsevier, 2019, pp. 313–353. doi: https://doi.org/10.1016/B978-0-12-814130-4.00011-7.

[34] P. B. Raja, K. R. Munusamy, V. Perumal, and M. N. M. Ibrahim, “5 - Characterization of nanomaterial used in nanobioremediation,” in Nano-Bioremediation : Fundamentals and Applications, H. M. N. Iqbal, M. Bilal, and T. A. Nguyen, Eds., Elsevier, 2022, pp. 57–83. doi: https://doi.org/10.1016/B978-0-12-823962-9.00037-4.

[35] “UV-Vis Spectroscopy: Principle, Strengths and Limitations and Applications.”

[36] Y.-G. Yu et al., “Doping La into the depletion layer of the Cd0.6Zn0.4S photocatalyst for efficient H2 evolution,” Chemical Communications, vol. 49, no. 86, pp. 10142–10144, 2013, doi: 10.1039/C3CC45568H.

[37] D. W. Wakerley, M. F. Kuehnel, K. L. Orchard, K. H. Ly, T. E. Rosser, and E. Reisner, “Solar-driven reforming of lignocellulose to H2 with a CdS/CdOx photocatalyst,” Nat Energy, vol. 2, no. 4, p. 17021, 2017, doi: 10.1038/nenergy.2017.21.

****