Synthesis of Binary Metal Ferrite Nanoparticles ($Co0.5Zn0.5Fe_2O_3$) and their Application in Piezo-Photo Catalytic Studies

By

Saima Jabeen

(Registration No: 00000327207)

Department of Materials Engineering

School of Chemical and Materials Engineering

National University of Sciences & Technology (NUST)

Islamabad, Pakistan

(2024)

Synthesis of Binary Metal Ferrite Nanoparticles ($Co0.5Zn0.5Fe_2O_3$) and their Application in Piezo-Photo Catalytic Studies

By

Saima Jabeen

(Registration No: 00000327207)

A thesis submitted to the National University of Sciences and Technology, Islamabad,

in partial fulfillment of the requirements for the degree of

Master of Science in
Nanoscience and Engineering

Supervisor: Dr. Sofia Javed

Co Supervisor: Dr. Aftab Akram

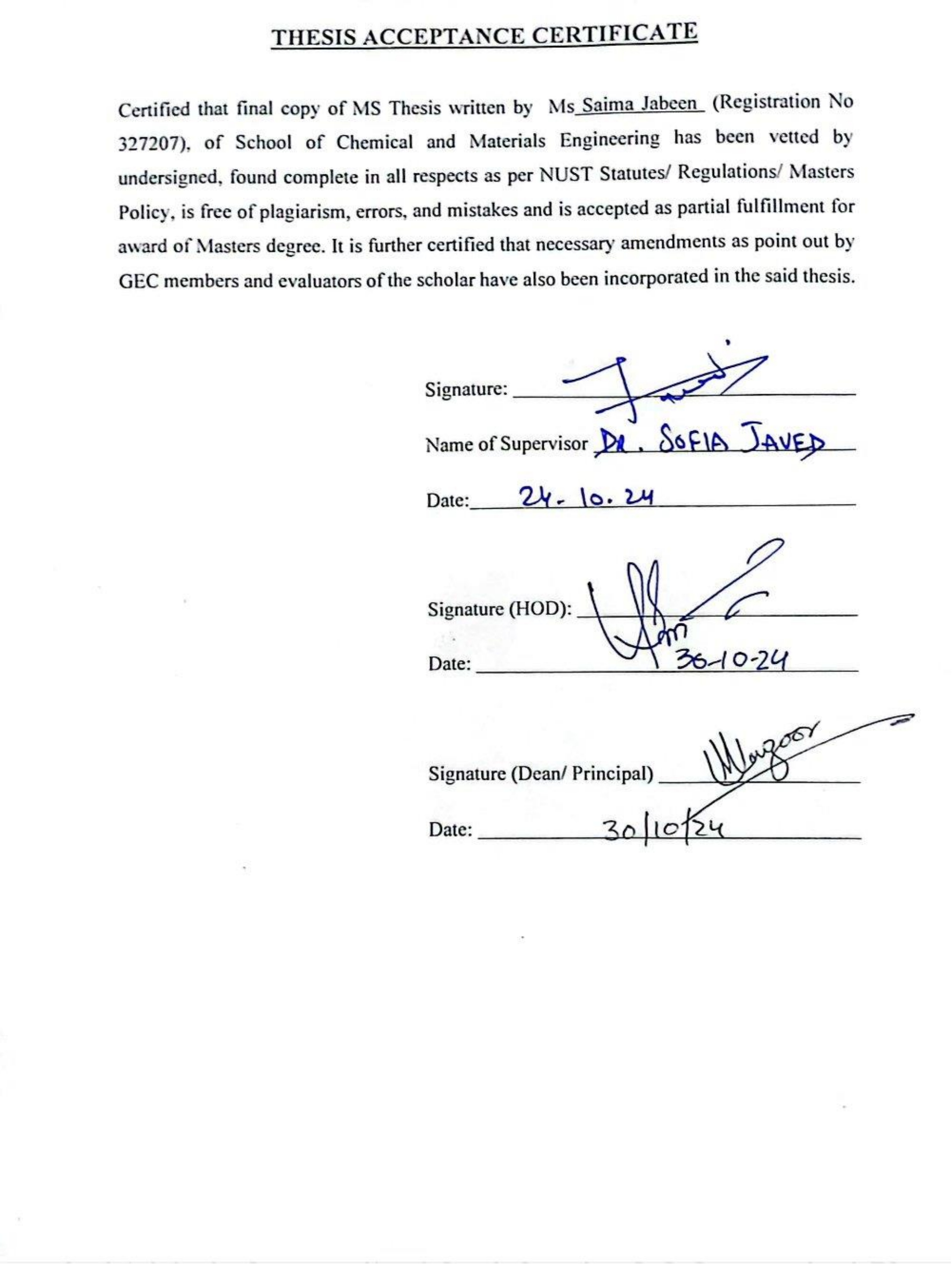
School of Chemical and Materials Engineering

National University of Sciences & Technology (NUST)

Islamabad, Pakistan

(2024)

THESIS ACCEPTANCE CERTIFICATE



THESIS ACCEPTANCE CERTIFICATE

Certified that final copy of MS Thesis written by Ms Saima Jabeen (Registration No 327207), of School of Chemical and Materials Engineering has been vetted by undersigned, found complete in all respects as per NUST Statutes/ Regulations/ Masters Policy, is free of plagiarism, errors, and mistakes and is accepted as partial fulfillment for award of Masters degree. It is further certified that necessary amendments as point out by GEC members and evaluators of the scholar have also been incorporated in the said thesis.

Signature:

Name of Supervisor DR. SOFIA JAVED

Date: 24. 10. 24

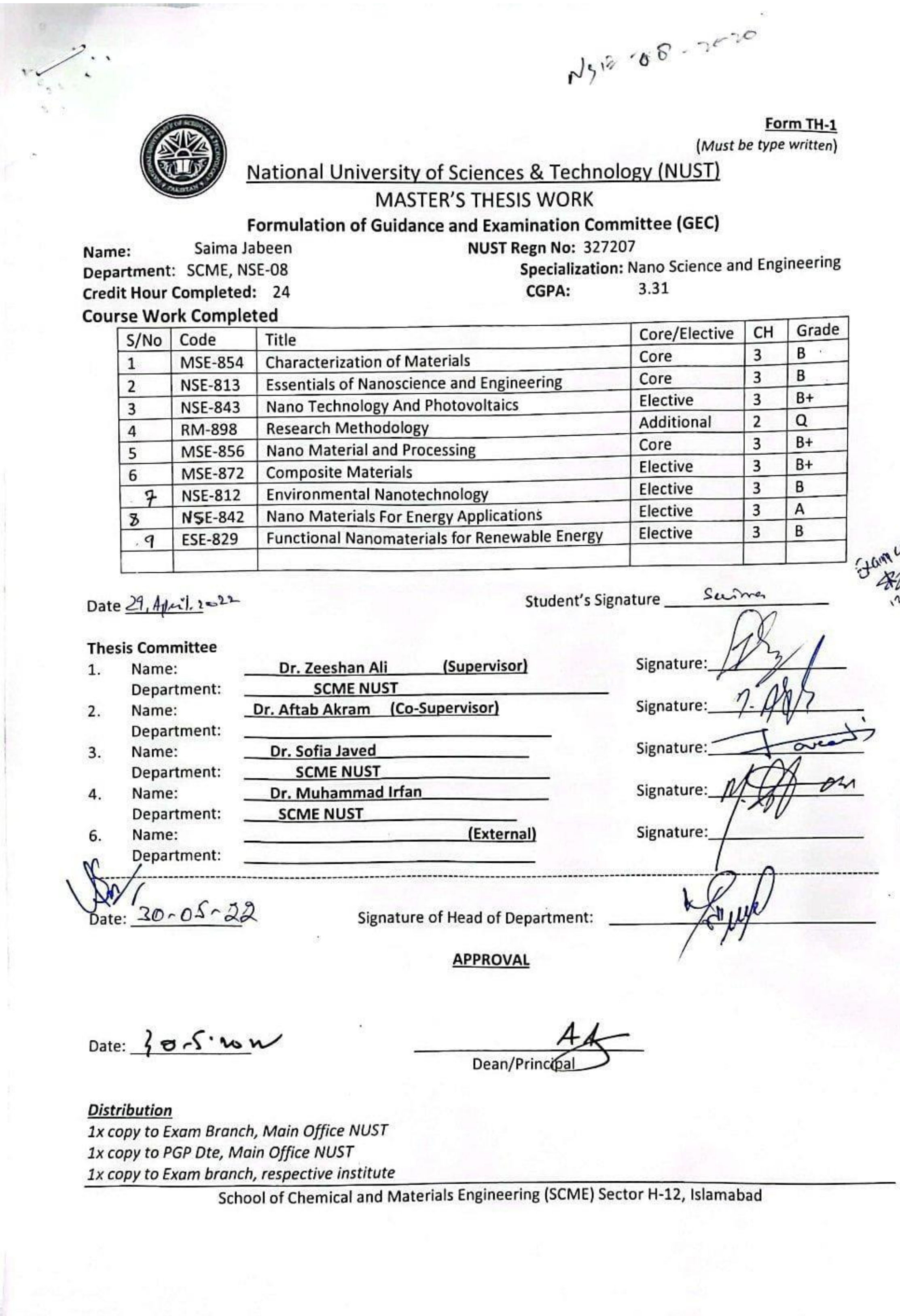
Signature (HOD):

Date: 30-10-24

Signature (Dean/ Principal) Manzoor

Date: 30/10/24

TH - 1



NSE 08 - 2020

Form TH-1
(*Must be type written*)

National University of Sciences & Technology (NUST)
MASTER'S THESIS WORK
Formulation of Guidance and Examination Committee (GEC)

Name: Saima Jabeen
NUST Regn No: 327207
Department: SCME, NSE-08
Specialization: Nano Science and Engineering
Credit Hour Completed: 24
CGPA: 3.31

Course Work Completed

S/No	Code	Title	Core/Elective	CH	Grade
1	MSE-854	Characterization of Materials	Core	3	B
2	NSE-813	Essentials of Nanoscience and Engineering	Core	3	B
3	NSE-843	Nano Technology And Photovoltaics	Elective	3	B+
4	RM-898	Research Methodology	Additional	2	Q
5	MSE-856	Nano Material and Processing	Core	3	B+
6	MSE-872	Composite Materials	Elective	3	B+
7	NSE-812	Environmental Nanotechnology	Elective	3	B
8	NSE-842	Nano Materials For Energy Applications	Elective	3	A
9	ESE-829	Functional Nanomaterials for Renewable Energy	Elective	3	B

Exam cell
12/5/22

Date 29, April, 2022

Student's Signature Saima

Thesis Committee

1. Name: **Dr. Zeeshan Ali (Supervisor)** Signature:
   Department: **SCME NUST**
2. Name: **Dr. Aftab Akram (Co-Supervisor)** Signature:
   Department:
3. Name: **Dr. Sofia Javed** Signature:
   Department: **SCME NUST**
4. Name: **Dr. Muhammad Irfan** Signature:
   Department: **SCME NUST**
6. Name: **(External)** Signature:
   Department:

Date: 30-05-22

Signature of Head of Department:

APPROVAL

Date: 30-5-2022

Dean/Principal

Distribution

1x copy to Exam Branch, Main Office NUST
1x copy to PGP Dte, Main Office NUST
1x copy to Exam branch, respective institute

School of Chemical and Materials Engineering (SCME) Sector H-12, Islamabad

TH – 4

National University of Sciences &Technology (NUST)

FORM TH-4

MASTER'S THESIS WORK

We hereby recommend that the dissertation prepared under our supervision by

Regn No & Name: **00000327207 Saima Jabeen**

Title*:* **Synthesis of Binary Metal Ferrite Nanoparticles and their Application in Piezo-Photo Catalytic Studies.**

Presented on: **03 Oct 2024** at: **1500 hrs in SCME Seminar Hall**

Be accepted in partial fulfillment of the requirements for the award of Masters of Science degree in **Nano Science & Engineering.**

Guidance & Examination Committee Members

Name: **Dr Ghulam Ali** Signature: Ghulam A

Name: **Dr Mohsin Saleem** Signature: Mohsin

Name: **Dr Muhammad Aftab Akram** (Co-Supervisor) Signature:

Supervisor's Name: **Dr Sofia Javed** Signature:

Dated: 28-10-24

Head of Department
Date 28-10-24

Manzoor
Dean/Principal
Date 29/10/24

School of Chemical &Materials Engineering (SCME)

AUTHOR'S DECLARATION

I Saima Jabeen hereby state that my MS thesis titled "Synthesis of binary metal ferrite nanoparticles (Co0.5Zn0.5Fe2O3) and their application in piezo-photo catalytic" is my own work and has not been submitted previously by me for taking any degree from National University of Sciences and Technology, Islamabad or anywhere else in the country/ world.

At any time if my statement is found to be incorrect even after I graduate, the university has the right to withdraw my MS degree.

Name of Student: Saima Jabeen

Date: 03 Oct, 2024

PLAGIARISM UNDERTAKING

I solemnly declare that research work presented in the thesis titled "Synthesis of binary metal ferrite nanoparticles ($Co0.5Zn0.5Fe_2O_3$) and their application in piezo-photo catalytic studies" is solely my research work with no significant contribution from any other person. Small contribution/ help wherever taken has been duly acknowledged and that complete thesis has been written by me.

I understand the zero-tolerance policy of the HEC and National University of Sciences and Technology (NUST), Islamabad towards plagiarism. Therefore, I as an author of the above titled thesis declare that no portion of my thesis has been plagiarized and any material used as reference is properly referred/cited.

I undertake that if I am found guilty of any formal plagiarism in the above titled thesis even after award of MS degree, the University reserves the rights to withdraw/revoke my MS degree and that HEC and NUST, Islamabad has the right to publish my name on the HEC/University website on which names of students are placed who submitted plagiarized thesis.

Student Signature: Saima Jabeen

Name: Saima Jabeen

DEDICATION

"With immeasurable love and gratitude, I dedicate this thesis to my cherished parents and beloved brother and sisters. Your unwavering support, encouragement, and sacrifices have been my guiding light throughout this journey. This accomplishment reflects the values and strength you've instilled in me."

ACKNOWLEDGEMENTS

In the name of Allah, the Most Gracious, the Most Merciful.I am profoundly grateful to Allah Almighty, the source of all wisdom and strength, for guiding me through the intricate journey of knowledge and for granting me the perseverance to complete this thesis. His boundless blessings have illuminated my path and enriched my understanding, enabling me to overcome challenges and reach this significant milestone.

I extend my heartfelt gratitude to my esteemed supervisor, Dr. Sofia Javed, whose unwavering guidance, insightful feedback, and continuous encouragement have been pivotal in shaping the course of this research. I also extend my acknowledgement to my co-supervisor Dr. Aftab Iqbal for his mentorship and invaluable guidance which significantly contributed to the depth and quality of my thesis. I specifically would like to express my appreciation for my GEC members i.e. Dr. Mohsin Saleem, Dr. Zeeshan Ali and Dr. Ghulam Ali for their constructive feedback and expertise. Their scholarly input during design phase significantly contributed to my work.

To my cherished friends, lab fellows, and seniors, you have been the pillars of support throughout this academic expedition.

My gratitude also extends to my parents and siblings, whose unending love, sacrifices, and unwavering belief in my potential have been the cornerstone of my achievements. Your constant encouragement, understanding, and sacrifices have shaped me into the person I am today, and I am forever indebted for your boundless support.

In conclusion, this thesis stands as a testament to the collective efforts and contributions of many individuals, and I am humbled by the generosity and kindness I have received along the way. To all those who have played a part, whether big or small, in my academic pursuit, I offer my sincere appreciation. May this work contribute positively to the realm of knowledge, and may Allah bless us all in our endeavors.

With profound gratitude,
Saima Jabeen

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS, ABBREVIATIONS AND ACRONYMS

Fe_2O_4	Magnetite
Spinel ferrite nanomaterials	SFNs
Spinel ferrites	SFs
Metal Organic Frameworks	MOF’s

ABSTRACT

Utilizing strain induced polarization to amplify the performance of photocatalytic water splitting systems has garnered significant attention. However, achieving efficient charge separation, high underwater suspension efficiency and sustained cyclic stability remains a persistent challenge. In this study we employed co-precipitation technique to synthesize nanoparticles of ZnFe2O4, CoFe2O4, and their binary composite Zn0.5Co0.5Fe2O4. We report 22% increase in H_2 evolution with our synthesized composite. After introduction of simultaneous photo and piezoelectric potential by using ultrasonicator H_2 evolution is much enhanced 494 μmol/g-h surpassing individual piezo catalysis 232 μmol/g-h and photo catalysis 298 μmol/g-h. Additionally, catalyst demonstrates remarkable performance without any sacrificial agent further highlighting its exceptional potential. Moreover, we also uncover Zn0.5Co0.5Fe2O4 role in demonstrating promising efficiency for the generation of hydrogen (H_2) and oxygen (O_2) as well owing to its huge potential for electrocatalytic water splitting. This work was supported by performing electrochemical testings in which Zn0.5Co0.5Fe2O4 retained 94% in chronoamperometry test proving itself a a bifunctional water-splitting electrolyzer that can act efficiently as both OER and HER electrodes. Promising results were revealed by these electrochemical studies, confirming the presence of a spinel crystal structure within the nanoparticles, indicative of excellent electrochemical performance. This work provides an insight into harnessing and designing ingenuous composites for efficient and stable piezo photo catalysts and HER/OER electrode for efficient and stable water splitting systems.

KEYWORDS: binary metal ferrites, bi-catalysts, water splitting, piezoelectric, HER/OER

CHAPTER 1: INTRODUCTION

1.1 Advances in Nanotechnology

Technology advances as a result of ongoing study, invention, and development. Around the world, scientists, engineers, and researchers are continually exploring new ideas, refining old technology, and developing novel solutions to varied difficulties[1]. Furthermore, the growing need for more efficient, convenient, and sustainable solutions in domains such as energy has been a major driving force behind technical breakthroughs. This gives rise to the enormous demand for research in energy generation and energy storage devices. Previously energy storage devices were composed of materials in their bulk form, which tended to reduce the device's overall performance.

By moving from millimeter to nanomaterial size the overall efficiency and the performance of devices were improved by many folds. Nanoscience involves the study and application of structures within the size range of one to one hundred nanometers. The objective is to create materials and technologies that possess at least one dimension at the nanoscale[2].

Nanomaterials are classified depending on the number of dimensions that are restricted to the nano level i.e. 1-dimensional, 2-dimensional and 3-dimensional[3]. Figures 1[4] and 2[5] show the dimensional classification of Nanomaterial.

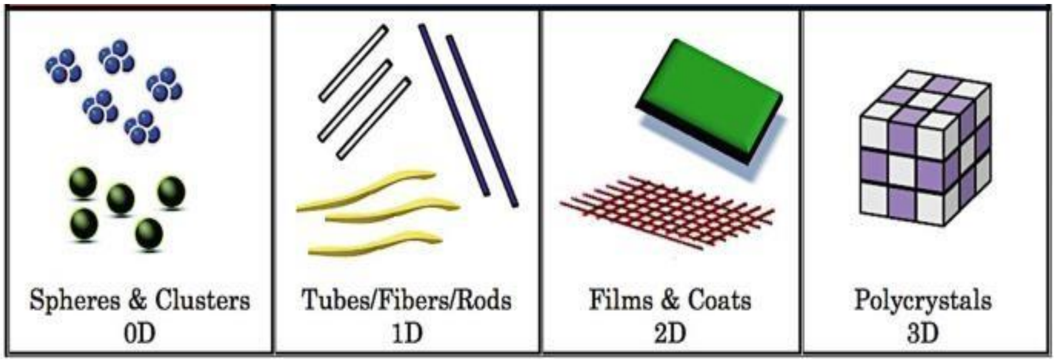


Figure 1.1: Dimensional classification of Nanomaterial[4]

Quantum dots, nanomaterials and other nanostructures that have all their physical dimensions lie within the range of 0-100nm and are classified as 0D nanomaterials. Nanorods, wires, ribbons, nanofilaments etc. are the nanomaterials that have one dimension outside the nanometer range greater than 100nm range and nanoclusters, old classical-shaped materials that have their dimensions outside the 100 nm nanometer range are 2D and 3D nanomaterials respectively.

The evolution of fuel from firewood to modern renewable fuels is a testimony of human creativity and ambition. It underpins ethical, environmental and geopolitical challenges for humanity as their quest for fuel is coined with their survival. In today's world waste water and energy shortage has posed serious challenge for the scientific researchers in their pursuits of cleaner environment. [1, 2]

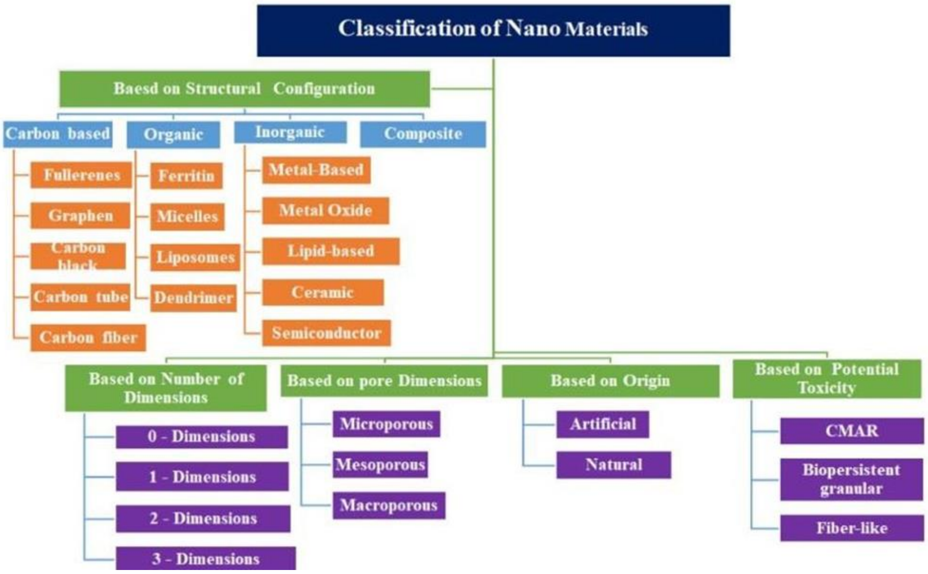


Figure 1.2: Classification of Nanomaterials[5]

Environmental contamination has overall disrupted natural ecosystem that affects safety of life on earth. Recent surge in energy demands, excessive use of fossil fuels, and their high environmental foot print have posed a serious obstacle towards green environment. [3] In the past few decades catalysis emerged as an encouraging approach towards clean water, soil and green fuels, that includes photo catalysis, piezo catalysis, piezo-photo catalysis and pyro-electric catalysis. New and sophisticated catalysts are used to harness abundant and natural primary energy sources like solar e.g. photons, mechanical e.g. piezo and triboelectrics and thermal e.g. pyro electrics. Photo catalysis is the most common and widely investigated whereas piezo and pyro electric catalysis are more recent approaches.[4, 5]

Although variety of renewable alternatives are available the key challenge still remains to efficiently convert either this renewable energy directly into electricity or in production of fuel with desired energy density as offered by existing fuel setup. Furthermore energy density considerations outnumber other renewable contenders in energy arena where its energy density is three times more than that of gasoline.[6]

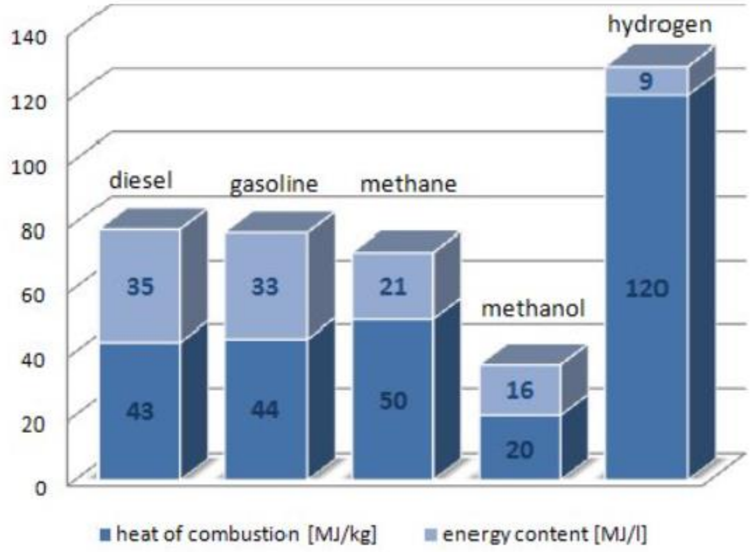


Figure 1.3: Shows a comparison between energy density of hydrogen versus other fossil fuels[6]

Water splitting technology plays a crucial role in the development of green fuels particularly in the hydrogen production that is believed to be a clean and sustainable energy source. Photo catalysis is most widely used process where electronic transitions from valance to conduction band takes place in photo active materials.

In the streak of photo catalysts specifically for water splitting reactions semiconductors as oxides, sulfides and selenides have been tried and tested over years for waste water dye degradation and hydrogen production. [7-9] However their optimization in terms of band gaps, suitable energy positions for desired reactions, low charge recombination, high photo and water stability, low toxicity and cost still remains a challenge. [10]

High band gaps of common semiconductors limits their direct use as they make catalyst more uv active and reduces its overall solar energy utilization. Extensive structural and band gap engineering is required to generate hydrogen under direct light irradiation. [11] Electron hole pairs generated through photo excitations triggers desired reactions. However, high band gap and charge recombination hampers the performance of a photo catalyst. It demands to devise new and more efficient mechanisms for water splitting reactions to increase yield.[12, 13]

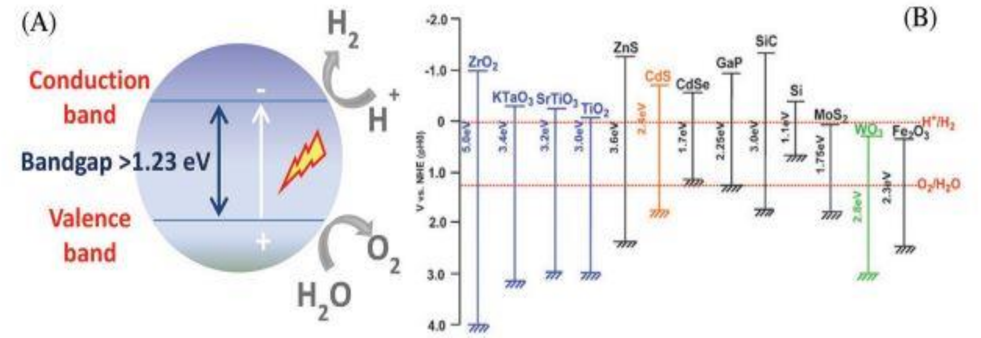


Figure 1.4: Schematics (A) water splitting over photo active material and (B) band structures of semiconductor materials vs redox potential for water splitting [14]

At the same time mechanical energy is another abundant form of green energy available in nature as wind, tide, vibration, sonication and atmospheric pressure. Certain materials can harness this energy in to an electrical energy and are termed as piezo materials. Charge separation in piezo materials takes places by mechanical stress triggering water splitting reactions. [5]

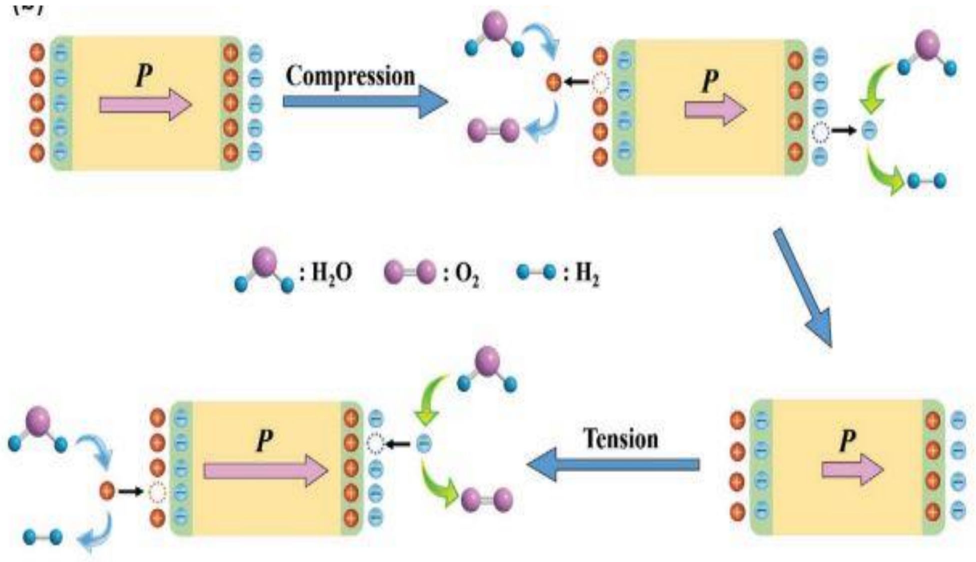


Figure 1.5:Schematics of piezo catalysis for water splitting[15]

Piezo-photo catalysis is an innovative concept that combines two fundamental concepts piezo-electricity and photo-catalysis. piezo active materials generate electrical charges when subjected to mechanical stress, whereas photo-catalysts utilize light energy to create electron hole pair that drive chemical reactions leading to water splitting.[16-18]

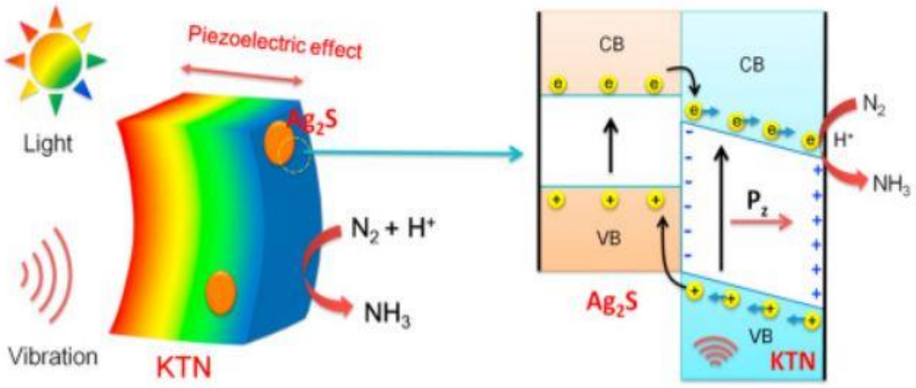


Figure 1.6: Schematics of piezo-photo catalysis for water splitting over KTN and AG_2S nano particles [19]

Internal polarization caused by mechanical stress induces strain in the photo catalyst thus altering its electronic configuration and facilitating charge carriers separation. This strain induced effect not only enhances charge separation but also its mobility. Convergences of these two concepts have synergistic affect that can improve efficiency and yield of water splitting reaction. [20]Although certain materials perform well as an either piezo or photo catalyst however same material provide better H_2 yield due to synergic effect of piezo-photo catalysis. [21, 22]

In the recent years perovskite materials have garnered substantial attention in the field of photo voltaics due to their photo electronic properties including high light absorption and charge mobility. The same properties made them suitable candidate for photo catalysis. [23, 24]Researchers have been working to enhance their light absorption in the visible region and devising new strategies to improve their stability in aqueous mediums. [25]

Perovskite being both photo and piezo active are excellent candidates for piezo-photo catalysis and variety of materials like titanates, niobates and ferrates have been investigated with or without use of metal loading. Few of the commonly investigated perovskite materials in their hybrids and composites are Bi0.5 Na0.5 TiO3, BaTiO3, CaTiO3-Bi2Ti2O7, NaNbO3, Bi2O6, BiVO4, AgNbO3, SrBaNb2O7 and BiFeO3 etc. [26-29]

Research also suggests photo active materials in their 2D nano configuration also depict piezo nature and are excellent contender for piezo-photo catalysis like RGO, carbon nitride and cadmium sulfide etc. These layered 2d piezo-photo materials provides an alternative material range for water splitting reactions. Carbon nitride seems to be the most potent one although high cost of material and slow reaction kinetics needs to be optimized. [27, 30]

However performance of piezo-photo catalysis depends upon variety of parameters including curie temperature, piezoelectric coefficient, conductivity, band gaps and band alignment to the redox potential of reactions. [31] Reaction kinetics is directly proportional to material conductivity, whereas stronger piezo electric coefficient tends to have poor conductivity. It makes material selection and design quiet a strategic balance of the two. [32]

Metal organic frameworks MOFs are more recent material in piezo-photo catalysis where longer polymeric chains of MOFs give more stability to metals from under water oxidation and enhance longevity of metal nano particles that are embedded in their polymeric structure. [33] Recently perovskite halides have been reinforced with non-metal as co-catalysts however very less established literature is available in domains of co-catalyst and promoters for piezo-phto catalysis. [34]

Moreover not only hybrid materials are a new stride but certain hybrid techniques pose new fad in water splitting arena such as combining tribo/piezo electric nano-generator TENG/PENG and photovoltaic prior photo electrochemical cell. [35, 36] They eliminate inherent limitation of external bais required for photo electrochemical cells. Integration of such different techniques offers room for coherence with other similar techniques like photo electrochemical cells, photo catalysis, piezo catalysis and piezo-photo catalysis. [37]

1.2 Electrochemical Water Splitting

Worldwide growing populations and living expenses contribute to a depletion of natural resources. Fossil fuels provide the vast majority of the world's energy requirements. Green energy technologies are being explored by the scientific community to reduce dependence on fossil fuels[8,9]. The hydrogen economy system is one possible approach to prevent such fluctuation[9]. A significant portion of the value of hydrogen is derived from its electrochemical capabilities; the significance of high energy density, long term storage potential of chemical bonds as an approach to storing and moving energy or creating products[10]. Water electrolysis is an alternate method of generating hydrogen[11]. It uses electric power to break the hydrogen H_2 and oxygen O_2 bonds within a water molecule[12,13]. Electrochemical water splitting, which is a greener way to produce hydrogen, is based on two half-reactions that take place within an electrochemical cell[14].

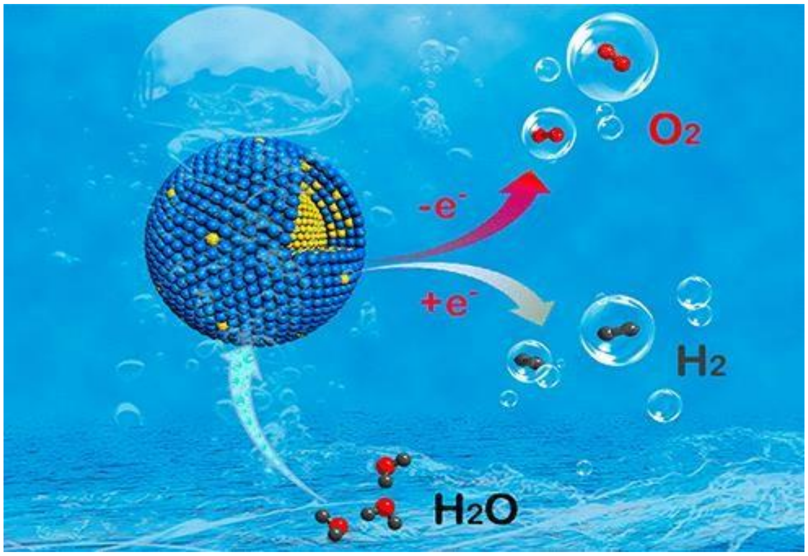


Figure 1.7:Water splitting mechanism[15]

Resulting in the generation of hydrogen at the cathode referred to as the hydrogen evolution reaction (HER) and the generation of oxygen at the anode referred to as the oxygen evolution reaction (OER)[15,16]. The choice of electrocatalyst material has a considerable impact on the efficiency of this process. Noble metals (Pt, Ru, Ir, Pd) and their oxides considered as finest electrocatalysts[17] due to their enhanced catalytic activity, corrosion resistance and surface reactivity[18,19] but due to scarcity and high cost limit their use in modern technologies where researchers are moving towards exploring more abundant and cost-effective[20]. Systems such as hydrogen generation from electrolysis of water, and fuel cells for converting hydrogen to electricity. Electrochemical water splitting is a novel method for producing hydrogen, a clean, sustainable, and environmentally beneficial energy source. Water-splitting half-reactions are the cathodic hydrogen evolution reaction (HER) and the anodic oxygen evolution reaction (OER)[21] as shown in Figure [22]

According to the Nernst equation, acidic circumstances encourage HER, whereas an alkaline medium facilitates OER. As a result, the majority of efforts in producing HER and OER electrocatalysts are focused on acidic and alkaline electrolytes, respectively[23]. To achieve water electrolysis, however, both HER and OER electrocatalysts are desired to act in the same electrolyte. Electrocatalysts, like traditional catalysts, serve an important role in enabling chemical reactions by decreasing the activation energy through the formation of appropriate intermediates, hence speeding up the reaction process. Overpotential, Tafel slope, and Faraday efficiency (FE), among other characteristics, are used to assess an electrocatalyst's performance. The difference between the actual voltage required to drive the reaction and the theoretical voltage imposed by thermodynamics is referred to as overpotential. The Tafel slope indicates the response rate by reflecting the additional voltage necessary to raise the current density tenfold.

1.2.1 HER (Hydrogen evolution reaction) @ cathode.

In water splitting, the Hydrogen Evolution Reaction is a process where an electrocatalyst is employed to aid in the generation of hydrogen gas from water. The electrocatalyst facilitates the separation of water into its elemental components, hydrogen, and oxygen, through electrochemical reactions. Selecting an appropriate electrocatalyst, frequently utilizing materials such as noble metals or their oxides, is vital for optimizing the efficiency of the HER and the overall water- splitting process.

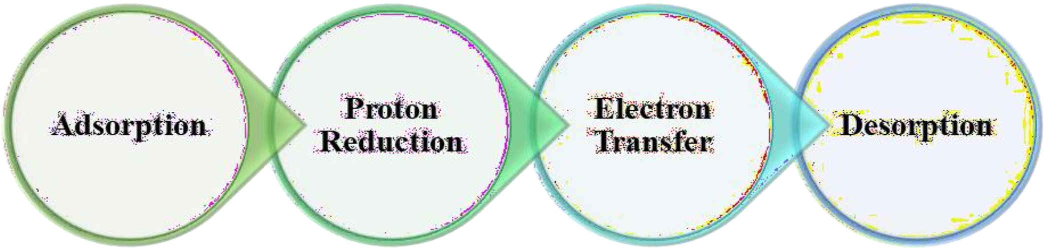


Figure 1.8: The Hydrogen Evolution Reaction (HER) mechanism involves several stages in the context of water splitting.

Here is a simplified breakdown:

Adsorption: Water molecules attach to the surface of the electrocatalyst.

Proton Reduction: In the HER, protons (H^+ ions) from water undergo reduction to produce hydrogen gas (H_2). This reduction process usually involves gaining electrons.

Electron Transfer: Electrons are provided to the electrocatalyst, facilitating the reduction of protons. These electrons can come from an external power source during electrolysis or from another half-reaction in a redox process.

Desorption: The generated hydrogen gas separates from the surface of the electrocatalyst. The overall reaction can be expressed as:

$2H_2O+2e^- \longrightarrow H_2+2OH^-$

This equation signifies the reduction of water to form hydrogen gas and hydroxide ions. The electrocatalyst, often a material with excellent conductivity and catalytic activity, expedites and enhances this reaction. The efficiency of the HER process in water splitting is significantly influenced by the choice of electrocatalyst and the reaction conditions.

1.2.2 OER /Oxygen evolution reaction @ anode

The The Oxygen Evolution Reaction (OER) involves the use of electrocatalysts to facilitate the generation of oxygen gas. The OER is an essential step in water electrolysis, where water undergoes separation into hydrogen and oxygen through the application of electrical energy. Here's a simplified overview of the process:

Adsorption: Water molecules adhere to the surface of the electrocatalyst.

Oxygen Evolution: Oxygen gas (O_2) is produced by oxidizing water, a process that typically entails the release of oxygen and the loss of electrons.

Electron Transfer: Electrons are transferred to the electrocatalyst during the oxygen evolution process. These electrons are often supplied by an external power source in electrolysis.

Desorption: The generated oxygen gas detaches from the electrocatalyst's surface. The overall reaction can be expressed as:

$$4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$$

This equation illustrates the oxygen evolution in the OER during water splitting. The electrocatalyst, typically composed of transition metal oxides or other materials with suitable catalytic properties, plays a pivotal role in enhancing the efficiency of the OER process. The selection of the electrocatalyst and the conditions of the reaction are critical factors influencing the overall performance of water electrolysis for hydrogen and oxygen production.

1.3 Introduction to Ferrites

Iron oxide is a key element in the crystal structure of ferrite, a magnetic oxide. Fe2O4 (magnetite), commonly known as a load stone, was the first magnetic substance ever found. Ferrites are the most significant type of magnetic minerals and have a wide range of uses.

They can be utilized in inductors, antenna rods, memory chips, transformers, and more. They have recently been utilized in medicine delivery, green anode material, and sensors. High electrical resistivity, low eddy current, and low dielectric losses are ferrite's three most crucial characteristics. Microwaves, computers, high frequencies, and magnetic freezers all make extensive use of ferrites.[38]

1.4 Background history of Ferrites

The discovery of stones that could draw iron many years ago is when the history of (magnetic) oxides began. These stones were most often discovered in the Magnesia area, which is where the mineral magnetite (Fe_2O_4) earned its name. Du-Bois (1890) performed the first-ever analysis of the magnetism of magnetite. The first ferrites were created by Hilpert in 1909, and they have the general formula (MOFe203). In this equation, M stands for a divalent metal ion, while O stands for oxygen atoms. Barth and Posnjak conducted the first-ever X-ray investigation of magnetic particles and found an inverted spinel structure. Early navigators utilised magnetite to determine magnetic north with practically the first usable contemporary ferrite that was developed in 1946. Lodestones were the first purpose that magnetite had for the ancients. Verwey demonstrated that the primary mechanism behind the electrical conductivity of ferrites is the hopping of electrons between Fe &Fe" ions. It has been demonstrated that ferrite with an inverted spinel structure is ferrimagnetic whereas ferrite with a normal spinel structure is nonmagnetic. Ferrites are used in a variety of biomedical applications, such as biosensing, drug delivery etc. Wet chemical techniques are frequently employed in more recent research to create nanoparticles of various ferrites. Numerous research have examined the relationship between high ferrites conductivity and high dielectric constant.[39]

1.5. Classification of Ferrites

Due to their diverse applications and unique features, ferrites may be divided into two primary groups, both softer and harder ferrites.

1.5.1. Soft ferrites

The application and removal of applied field makes it simple to magnetize and demagnetize soft ferrites. Only when a magnetic field is present will they continue to be magnetized. Hysteresis loop and coercivity are very low for soft ferrites, which implies that the material's magnetization may quickly change direction without expending a lot of energy.[40]

Soft ferrites have a higher intrinsic resistivity than other materials, which results in lower eddy current losses. They are therefore more suited for other magnetic materials.

A perfect ferrite ought to have:

- Low coercivity, high saturation magnetization, no hysteresis loss value, and high permeability [41]

1.5.2. Hard ferrites

They are magnetic materials with stability. They go by the name "Ceramic Magnets." When the applied field is withdrawn from hard ferrites, the magnetization or material is kept. Both their coercivity and hysteresis loop levels are high. Iron oxides, barium oxides, and strontium oxides behave like hard ferrites. Iron and oxides of barium or strontium make up hard ferrites. Due to their great magnetic permeability, they have the capacity to hold magnetic fields that are stronger than those of iron. Ferrites are utilised extensively as permanent magnets due to their incredibly low cost and inexpensive raw material. [42]

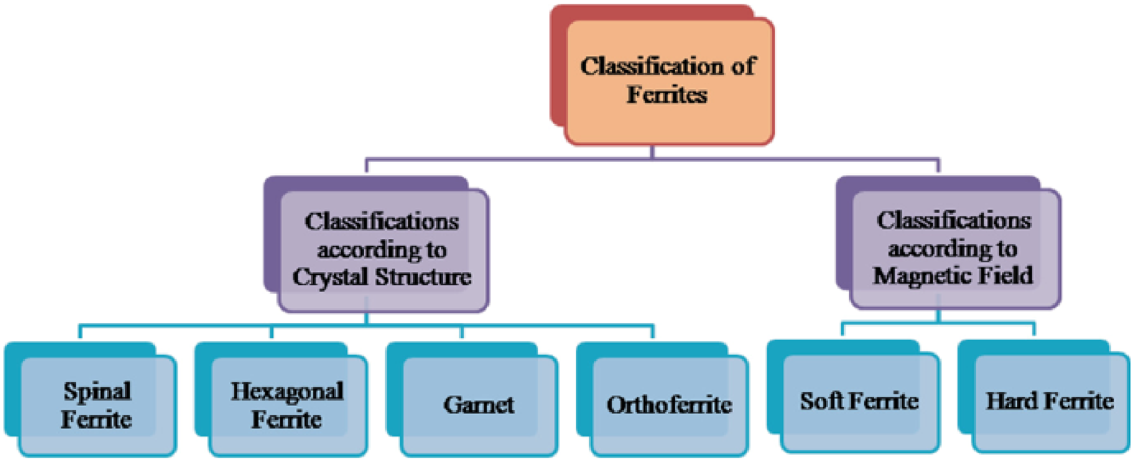


Figure 1.9: Classification of Ferrites

1.6 Types of Ferrites

There are two different categories for ferrites. Hexagonal and cube-shaped ferrites

1.6.1 Cubic Ferrites

Cubic ferrites are further classified into two types.

- Spinel Ferrites
- Garnet Ferrites

Spinel ferrites have the chemical formula M=divalent metal ion with tetrahedral sites [A] and octahedral sites [B]. The presence of cations causes modifications in their characteristics on both the octahedral B site and the tetrahedral A sites. There will be a great deal of spinal ferrites if divalent M is substituted by other metal ions. Iron ions (Fe*) are substituted with other trivalent ions as Al3+, Cr3+, Ga3+, etc., or with a mix of divalent and tetravalent ions. These ferrites are supple. Spinel ferrites have a high electrical resistivity and a low magnetic loss.[43]

1.6.1.1 Spinel Ferrites

Spinel ferrite nanomaterials (SFNs) offer special qualities and a variety of uses:

High-density for gas sensors, catalysts, and data storage, batteries that can be recharged, such as lithium batteries medical diagnostics and therapy; magnetic bulk cores; magnetic fluids; microwave absorbers; information storage systems; etc.

The typical molecular formula of spinel ferrites (SFs) is MFe2O4 (where M is Co, Fe, Mn, Ni, Cu, and Zn). The cubic symmetry of these ferrties is the same as that of the mineral spinel. [19] With a diameter of less than or equal to 20 nm, SFs exhibit super paramagnetic (SPM) characteristics on the nano scale.The metal cations at both sites are always chosen based on their propensity to occupy spaces where factors such as the energy of stabilization, ionic radii, size of the interstitial site, and their synthesis reaction conditions can have a substantial impact.[44]

1.6.1.2 Crystal structure and properties of spinel ferrites

The generic formula MFe_2Z_{04} may be used to describe the structural arrangement of spinel ferrites, which is derived from ($MgAl_20_4$). In this formula, Fe or a mixture of Fe and other trivalent ions replaces trivalent Al whereas M stands for a divalent metal ion. A potential alteration would be to replace the divalent Mg^{2+} ions in spinel ferrites with ions of Mn^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Zn^{2+}, or a mixture of these ions. Unpaired electron spins are produced using iron (Fe), iron in a high-spin state (Fe''), nickel in a high-spin state (Ni''), cobalt (Co), and manganese (Mn). The cubic close-packed (FCC) oxide structure (O), present in spinel ferrites, is characterized by the occupancy of the tetrahedral holes by A cations in a ratio of one eighth and the octahedral holes by B cations in a ratio of fifty percent.[45]

It is referred to as the inverse spinel structure if B cation occupies one eighth of the tetrahedral holes, one fourth of the octahedral sites, and the remaining one fourth.

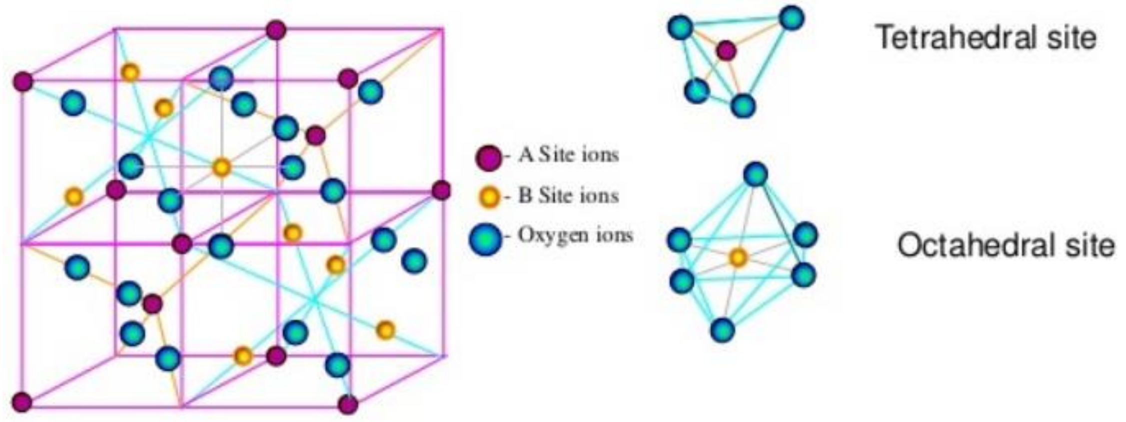


Figure 1.10: Unit cell of spinal ferrites showing tetrahedral and octahedral sites

Eight molecules make up each unit cell of the complicated structure of spinel ferrites. The FCC lattice of the 32 bigger oxygen ions has two different sorts of sites. The interstitial gaps, which are of two sorts, are filled by the smaller ions (metals). Tetrahedral [A]sites is one. Four oxygen ions surround 64 tetrahedral sites. The second site is known as an octahedral [B] site because the oxygen ions are positioned around its corners. There are 32 octahedral sites in all.

Types of spinel ferrites

Spinel structure has following types:

- Normal spinel
- Inverse spinel
- Random spinel

Basic Spinel Ferrites

If just one type of cation is present at the octahedral (B) site, the spinel is normal. The A-sites are occupied by eight divalent metal ions, while sixteen trivalent iron ions enter the B site.

2) Reversible Spinel Ferrites

In an inverse spinel ferrite crystal lattice, the trivalent ions are present on sites A and B whereas the divalent ions are only found on site B.

3) Unexpected Ferrites

Divalent metal ions are found on site A of a crystal lattice while trivalent metal ions are found on site B in typical ferrites. The ions in the A and B sites are distributed randomly in random spinels.[46]

1.6.1.3 Garnet ferrites

Geller and Gilleo made the discovery of garnet in 1957. In the unit cell of a pure iron garnet, there are eight formula units of M3Fe5O15, where M is a trivalent rare earth ion, such as Y, Gd, or Dy. Ferrites are distinct magnetic ceramics that are also transparent to light. They have uses in magneto optical technology. There are three sub-lattices in garnet ferrites. A cubic unit cell has eight formula units, or 160 atoms. The cubic cell has edges that are about 12.5A long. In an array of 96 oxygen ions, metal cations occupy three interstices. [47]

1.6.2 Ortho ferrites

These ferrites, which have high domain wall motion velocities, are used in mechanical quantities, optical networks, electrical circuits, communication methods, and magnetic field sensors.

1.6.3 Hexagonal Ferrites

They have strong coercive characteristics that were first identified in 1952 and are frequently utilized as permanent magnets. They have strong coercive forces and are frequently employed as permanent magnets. At the Philips laboratory in the Netherlands, progress was made on hexagonal ferrites. Due to its strong uniaxial magneto crystalline anisotropy, hexagonal ferrites are used in permanent (hard) magnets. Four different forms of hexagonal ferrites with the general formula $MO_6Fe_2O_3$ are denoted by the letters M, W, Y, and Z. M may be Ba, Sr, or Pb. Due to the difficulty of simply changing the direction of magnetization, they are hard ferrites.[48]

1.6.4 Advantages of ferrites

The following are benefits of ferrites.

a) Because ferrites are simple to shape, they are used in low-cost, high-loss applications like relays and miniature motors.

b) Ferrites have a moderately high permeability.

c) They suffer little loss.

d) They are resistant to wear well.

e) Mass production may be simply adapted to them.

1.6.5 Ferrites and their uses in water splitting:

Electrocatalysis is an effective way of production of hydrogen. However, the use of platinum as an electrode does not make it cost-effective, and therefore, there is a need of exploring a new material that shows catalytic performance equivalent to the platinum. Studies have been reflected that the ferrite is a promising material for electrocatalysis.

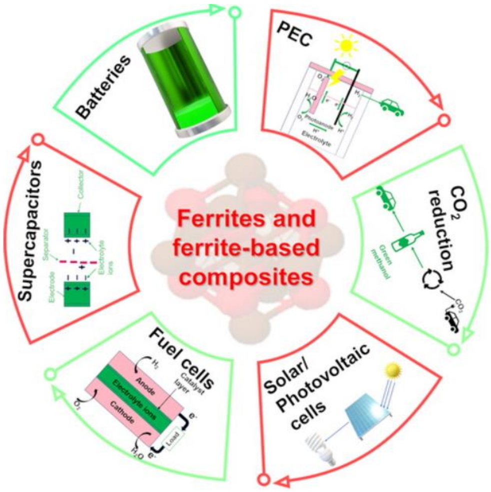


Figure 1.11: Different applications of ferrites and ferrite-based composites[49]

Ferrites have traditionally been employed mostly in magnetic applications, including inductors and transformers. Ferrite materials, a type of ceramic compound made of iron oxides and other metals, have gained popularity as water splitting catalysts due to their distinct magnetic and electrical properties. Ferrites have traditionally been employed mostly in magnetic applications, including inductors and transformers. The late 20th century saw the emergence of their potential in catalytic processes, nevertheless, as scientists looked for more economical and efficient ways to produce hydrogen.

Ferrites, such as spinels (e.g., Fe_3O_4) and magnetites, are used in water splitting because they provide a good blend of stability, conductivity, and catalyst activity. They use their electrical structure to improve performance by facilitating the electrochemical reactions required to break down water into hydrogen and oxygen. They work well for this purpose because of their large surface area and good electron absorption and transmission capabilities.Recently, ferrites have undergone structural and doping optimizations to increase their durability and efficiency. Their application offers a viable path toward the generation of sustainable hydrogen, meeting the world's energy needs while utilizing resources with well-established industrial uses

1.7 Objective of my research

The primary objective of this research is to conduct a comprehensive comparative study of Zinc (Zn) and cobalt (Co) substituted ferrite (Fe2O4) , Zinc ferrite and Cobalt ferrite for their potential application in electrocatalytic and photo-piezo water splitting.. This study aims to investigate and compare the electrochemical properties, H_2 evolution, O_2 evolution and overall performance of Co-substituted zinc ferrite based electrodes in water splitting. The research will encompass a multifaceted approach, including the synthesis, characterization, and evaluation of these materials, with the goal of advancing the field of hydrogen production and energy storage through the exploration of novel ferrite based material.

By gaining a deeper understanding of the electrochemical behavior and water splitting capabilities of Zn and Co substituted ZnCo-Fe2O4 ferrites, this research seeks to contribute valuable insights to the field of water splitting technology. Subsequent chapters will delve into the methodology, experimental procedures, and results, providing a comprehensive analysis of the research findings and their implications for the future of water splitting systems.

CHAPTER 2: LITERATURE REVIEW

2.1 Fuel history

Fuels and human history go hand in hand in shaping societies and economies over centuries. From firewood to the rise of fossil fuel and consistent quest for sustainable alternatives history of fuel is no less than an evolutionary journey filled with technical innovations, resource exploitation, environmental changes and one of the most controversial reason backing wars and effecting international alliances. [50]

One of the most crucial milestones in human evolution was the discovery of firewood and it laid solid foundation to inhabit new geographical regions and develop complex societies. Firewood as an early fuel till 18th century served as society's life line as it not only provide warmth but also was a sole source to cook food and provide protection from predators. [51] Growing societies and their ever increasing need for fuel increases the scope of biomass from firewood to crop residues and animal dung. However, this reliance has its own limitations and creates environmental and pollution issues in the form of deforestation and some type of air and soil pollution. [52, 53]

A seismic shift in the fuel history emerged between 18th to 19th centuries with the discovery of coal. The advent of industrial revolution and the rise of coal as a new energy source not only transformed the existing industries and transportation but also laid the foundation of urban life style. However, coal led industries resulted into unprecedented economic growth and for the first time in history fuel got coined with national security. [54] The industrial revolution paid huge environmental cost in the form of excessive air pollution leading to wide spread respiratory problems and mining accidents plagued communities settled around coal mines and factories.[55] Even today, coal abundance or availability of other energy density fuel is considered as necessary for the swift expansion and sustenance of industrialized nations. However, no one can deny the high carbon foot print of coal powered industries and its impact even go beyond borders. Recent research advancements in coal power plants have shown to replace entire plant facility with biomass technology in order to utilize existing installed capacity in the best of industrial and environmental use. [6, 56]

In many applications, fossil oils are considered to have displaced coal and ever since are considered to dominate transport industry. The late 19th century escorted a new candidate into the fuel world. [57]Fossil fuel with higher energy density as compared to coal and its refining into various products like kerosene, gasoline, diesel and heavy density oils not only make it more efficient but also more versatile when it comes to its utility. Crude oil to its core led the wide spread adoption of automobiles, reshaping conventional transportation and instigating urban planning.[54]

The 20th century marked another pivotal shift in fuel history and revolutionized the transportation by making airplanes, automobiles, and trains and ships an integral part of modern urban life. Furthermore, it also played a crucial role in developing more technically advanced industries like petrochemical industry that stems foundation for plastics, new synthetic materials and fabrics, and countless consumer products.[58]

Geographical positioning of oil reserves and its global thirst led to several geopolitical conflicts over a century. The two world wars of early 20th century brought fuel to the limelight in global geopolitics and have profoundly affected and shaped international relations over decades till date. [59, 60]Crude oil to its core is critical to military logistics and has been a driving force for innovation and development in oil extraction and redefining techniques. These wars and conflicts catalyzed the development of technologies like jet engine and missiles that have changed the dynamics of aviation and warfare. However, OPEC (the organization of the petroleum exporting countries) in the oil market emerged as a powerful player with significant influence over oil price and its supply worldwide.[61]

Concurrently, late 19th and early 20th century also marked the rapid electrification of societies. The advent of electricity added a new dimension to the fuel arena and also stems the foundation of modern electric green technologies. The thriving petrochemical industry backed by fossil oil mainly dominates transportation and military dynamics. [62] However advances in electrical engineering, power generation and transmission brought light, heating and machinery to homes and industry. On the whole electricity emerged as more flexible and efficient energy source that led transformation in daily life and industrial processes.[63]

The 20th century was marked with the advent of variety of fuel alternatives leading to numerous new technologies that revolutionized the society in general. Crude oil and electricity foots can be back traced by early 20th century however, nuclear energy came into light by mid-twenties. [64] Initially nuclear power plants were built to generate electricity by harnessing massive power of nuclear reactions for its softer domestic and industrial use. Later on seemingly early promising, cleaner and abundant energy source emerged to be one the most challenging alternative with complex safety concerns and immense risk of nuclear proliferation. [65] Secondly, nuclear technology with an enormous potential to be used in nuclear warfare as in WW-2 also restricts its wide spread expansion thus limiting its overall potential to be used as cleaner and safer alternative. [66]

2.2 Environmental concerns and renewable fuels

Early 20th century till date fossil oil still remains the key contender in energy and fuel arena however its high environmental foot print started raising red flags. Later half of the 20th century experienced exacerbated consequences of fossil oil burning. Greenhouse gases began releasing at alarm bells rate subsequently increasing air pollution index in urban societies. [67]Serious smog problems contributing to respiratory and air navigation problems as well as acid rains contaminating soil and causing certain health concerns are not the only problems but it has also increased overall global warming that results into natural environmental catastrophes. [68, 69]

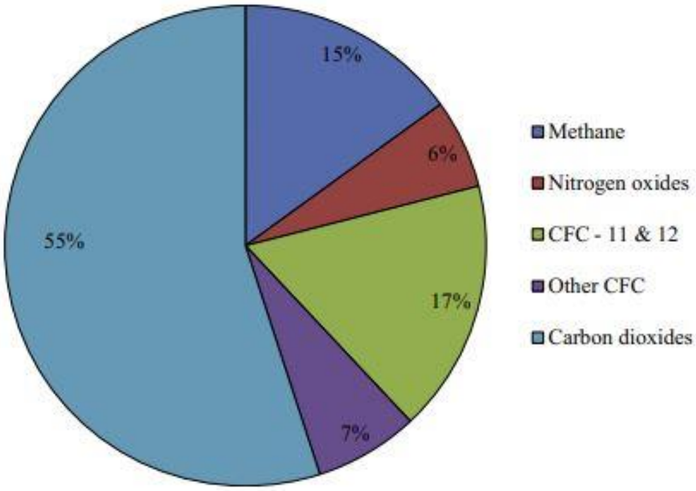


Figure 12.1:Different greenhouse gasses and their contribution to global warming[49]

Growing awareness concerning the environment roots for variety of environmental movements and regulations that aims at mitigating these harmful effects. Furthermore, they highlight the dire need to develop cleaner and safer energy alternatives. [70] However this transition still remains a dire challenge for governments to sustain their economies at the expense of deteriorating environment or saving environment at the expense of economy. [71]

In early 21st century there is a noticeable surge and investment in renewable fuel sources. Bio fuels introduced in early 2000's as an alternative to fossil fuels was not only due to the soaring high prices but also to their low COx, SOx and NOx emissions. They were cleaner alternatives but irony remains the same as they still produce substantial amounts of carbon emissions. [72, 73]Despite being expensive in comparison to its conventional rival i.e. crude oil conspicuous amount of funds are pouring into developing new and more sustainable fuel alternatives. Emerging technologies like wind, solar and hydropower are deployed to mature synergistic energy systems that are not only green but also increase energy independence. According to the Paris agreement of 2015 investment on renewable sources and environmental burden of oil exploration for developing countries like Kenya needs is to be shared by the world being a collateral environmental hostage. [74]

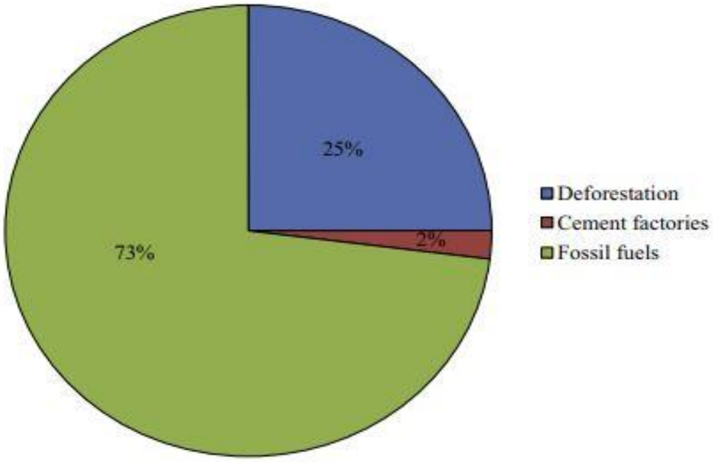


Figure 2.2:Pie chart of major CO_2 source [49]

World faces a monumental challenge while transitioning from economical fossil fuels to expansive sustainable fuel sources. Environment being the colossal opportunity cost of using economical fuel pose serious threat to the fate of our planet and the wellbeing of our generations to come.[75] Climate change, resource depletion, geopolitical tensions, growing world's fuel needs, and viability of economies underscore the perseverance of transitioning into renewable yet sustainable fuel alternatives. Nature of problem is more tumultuous than it seems apparently because of under pinning political economical currents as government supporting oil explorations and imports supports fossil oil backed economies however at the same time, government signed environmental treaties demands significant decrease in consumption and production of fossil fuels. [75, 76]

2.3 Renewable fuels

Diverse range of renewable fuels is available that offers variety of sustainable energy options that interns depends upon the end application. [77]Biofuels and bio gas were the earliest in renewable forefront and can be easily used in conventional vehicles with significantly lower carbon emissions and as a natural gas alternative respectively. Countries like Australia and Brazil have conducted numerous studies on shifting their domestic transport on biofuels. [78] Both alternatives were significantly criticized for having their carbon foot print furthermore bio fuels controversy of food versus fuel limits its sustainability.[76, 79]

One renewable source might not have capacity to power all fuel needs but their development and integration into existing energy system significantly reduces fossil fuel consumption and overall improving air quality index of metropolitan cities.[80] Geothermal energy, hydropower energy, wind energy and solar energy emerged as sustainable contenders for renewable energy alternatives.[81, 82]

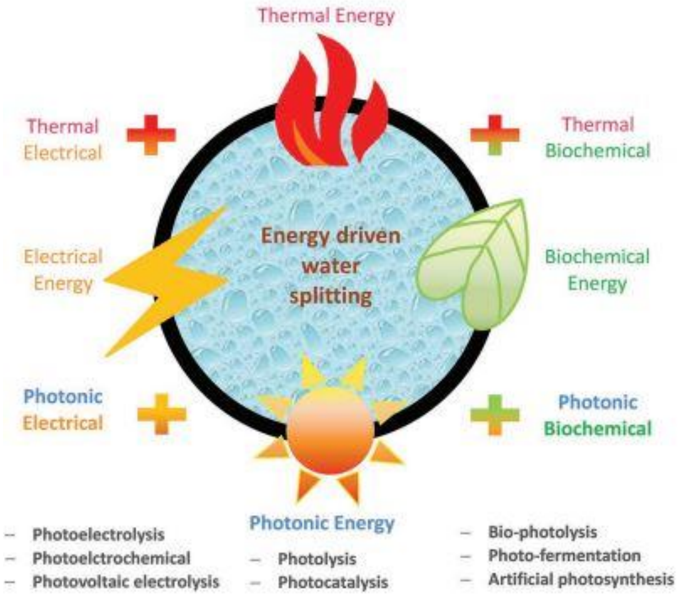


Figure 2.3:Schematics of water splitting systems with variety of energy drivers[14]

The new to this energy arena is hydrogen where hydrogen burning through fuel cells produces only one by product that is water and it is clean. If hydrogen is produced through some renewable source like wind or solar it has potential to be the future green and sustainable fuel. [54]

Studies have been conducted in shifting power generation systems of different countries by fuel cells that in turn are backed by hydrogen. Future trends and studies forecast towards major energy shift and it is towards hydrogen. [83]

2.3.1. Hydrogen fuel

In the global green energy landscape hydrogen status has been significantly elevated due to its small size and abundant availability. It is highly versatile energy alternative that can be incorporated into powering vehicles to generating electricity and heat. Energy storage nature of hydrogen also enables to store more renewable energy produced on fortunate days with high wind and sun exposure to be later used in less fortunate days. This added versatility and green nature gives hydrogen stardom in sustainable energy ecosystem.[84] Variety of hydrogen synthesis methods is available but a selection plays a crucial role in harnessing hydrogen for its applications like fuel cells, energy storage and industrial processes. All the synthesis methods are assessed on the basis of feed stocks, their energy inputs, overall emissions, cost assessment and overall environmental assessment.

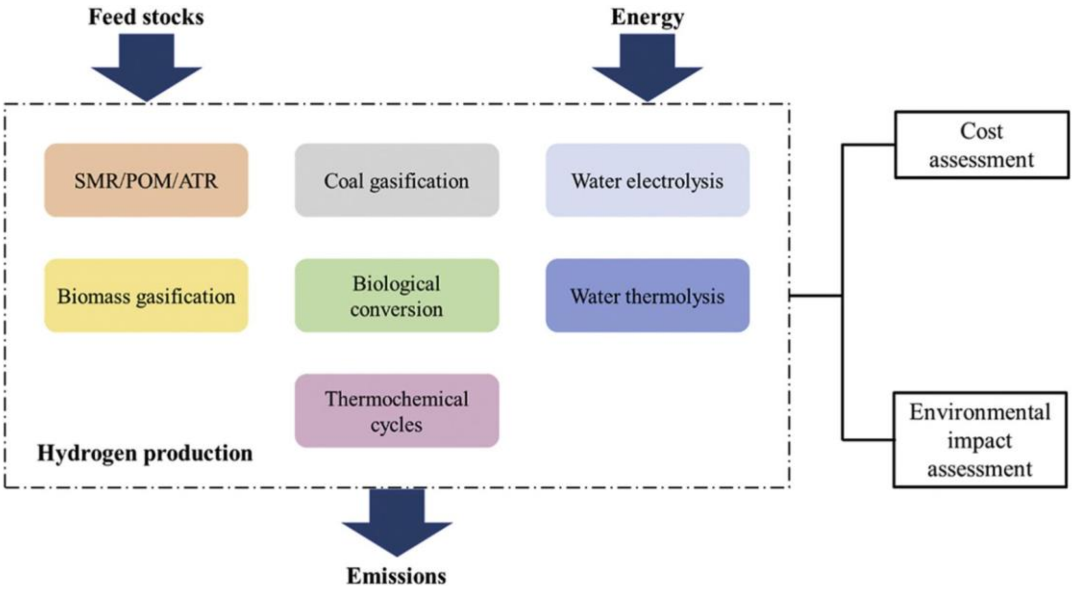


Figure 2.4 **:**Hydrogen production methods assessment in view of cost involvement and environmental output

Brief overview of hydrogen synthesis techniques is discussed below

2.3.2. Steam methane reforming (SMR)

Steam methane reforming (SMR) being the classical hydrogen synthesis method is used in variety of industries such as petrochemicals and fertilizer for over a century.it not only contributes to 98% of commercial hydrogen synthesis but also to the 50% CO2 share worldwide. The process involves reactions between methane (CH4) and water (H2O) producing hydrogen H2 and carbon mono oxide CO.[85] Although it is the most established and efficient hydrogen synthesis process however carbon dioxide CO2 produced as a byproduct contributes to greenhouse gas emissions that raise serious doubts about using SMR. Thus it overall makes the fuel cells powered by hydrogen from SMR a pseudo green technology and poses a serious hurdle towards powering vehicles.[86, 87]

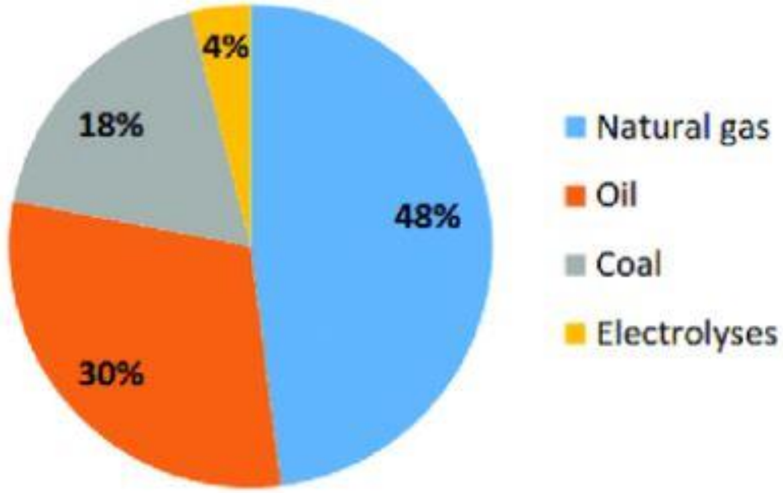


Figure 2.5:Pie chart of present H_2 production sources with maximum share of SMR fueled by natural gas[88]

2.3.3. Thermochemical hydrogen production

Thermochemical hydrogen production involves high temperature reactions using variety of feed stocks to produce minimal greenhouse gas emissions. It requires proper reactor design depending upon type and availability of feed stocks including water, sewerage water, biomass, industrial wastes and fossil oils.[89] Sludge pyrolysis, biomass incineration, sulfur-iodine cycle, hybrid sulfur cycle and partial oxidation of hydrocarbons are few examples with potential for high production efficiency. Complex control systems, reactor designs and expensive thermo-stable materials in addition residual carbon emissions makes it cleaner than SMR but still pose a serious challenge towards quest of green fuels.[90]

It has potential for large scale commercial production as researchers have proposed pilot plants with two step water splitting mechanisms. First, temperature is increased to reduce metal oxide using concentrated sunlight to tiger water redox reaction producing hydrogen and metal oxide gain. [91]

2.3.4. Biomass gasification:

Biomass gasification is much similar to coal gasification technology developed in WW-2 to meet military emergency fuel needs. Basically it converts hydrocarbons present in natural organic materials like wood, crop residues and sewerage wastes etc into a gaseous mixture containing hydrogen, carbon mono oxide, carbon dioxide and light weight hydrocarbons.[92] The process involves heating biomass in the absence of air to produce syngas that is a mixture of CO, H2 and other gases. However it produces less sulfur, ashes and releases way less carbon content in air.[93]

This technique has its own merits and demerits as it is overall energy intensive process that results into sizeable amount of energy wastage. It incorporates variety of feedstock and results into inconsistent impurities in syngas that requires an additional purification unit. On the whole it is more of a waste disposal technique that converts existing waste into value added fuel rather than being core Hydrogen source.[94] Significantly lower carbon foot print along with waste renewable nature and ease to be integrated into existing waste management systems, make it a potential candidate for cleaner secondary alternative that can be used in hybrid energy systems in the overall energy ecosystem.[95, 96]

2.3.5. Bio hydrogen production:

Significance of bio-hydrogen production methods can’t be ignored in view of its limited greenhouse emissions and low energy inputs. It employs variety of biological reaction like aerobic and anaerobic fermentation and photo-biological reactions by exploiting variety of microorganisms such as bacteria and algae.[97] These methods required high levels of precision and accuracy with respect to reaction conditions as biological reactions show high specificity towards reactions. They have an added advantage to be used with existing waste water management systems.[98] Low hydrogen yield, microbial strains and specific nature of reaction limits its commercial potential as a major clean alternative. Although it cannot replace proper industrial hydrogen needs but can be easily integrated as a charge for fuel cells. [99]

.

2.4 Electrolysis:

Before delving into hydrogen powered fuel alternatives it is imperative to develop new technologies that are based on fundamentals of renewable energy sources like wind or solar. In order to make a green transition sustainable and viable, all raw materials starting from scratch should be either environmental friendly in nature or are existing waste materials that need some waste treatment to make them ecofriendly. On the whole water splitting technologies are developed by utilizing solar or wind power to split water into hydrogen and oxygen with essentially no carbon emissions. It overall eliminates carbon emission that is considered hallmark pollutant of conventional techniques.[100]

Electrolysis is the first of the green hydrogen technologies and it also underpins a core concept to develop further cleaner technologies. Water electrolysis is a sustainable process that requires electric current to split water into its constituents i.e. hydrogen and oxygen in a specific ratio that can be used exactly in the same ratio in fuel cell.[101]

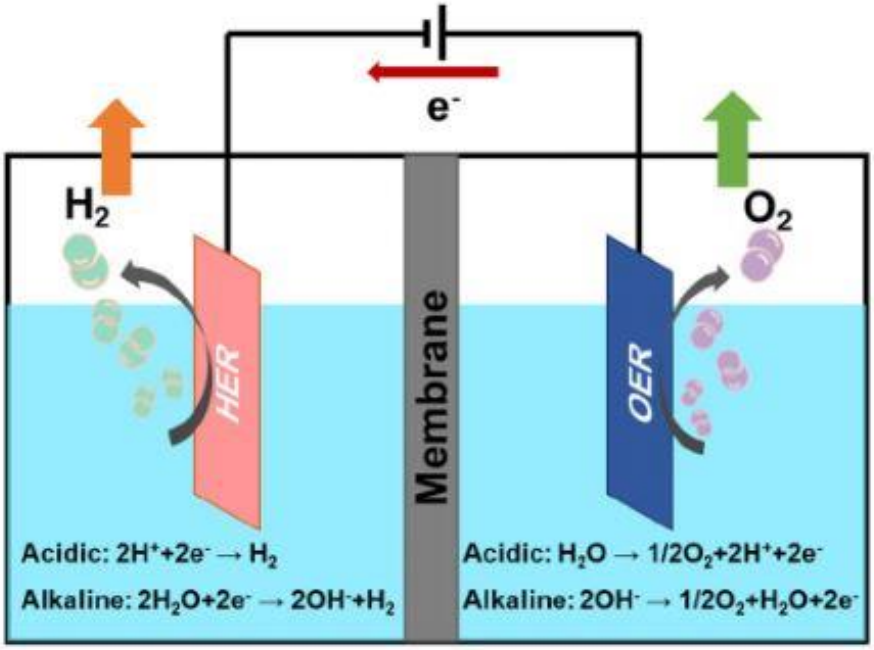


Figure 2.6: Hydrogen production methods todays and years to come[102]

Broadly two different type of electrolysis are used alkaline electrolysis and proton exchange membranes (PEM). Alkaline solution is used as an electrolyte in alkaline electrolysis and it considered as more robust but comparatively much cheaper than PEM electrolysis. On the other side PEM electrolysis uses solid polymer as an electrolyte that results into more efficient operations and much agility towards fluctuating loads.[103, 104]

It is a more advanced technology and produces hydrogen with much higher purity but requires a renewable energy source such as wind or solar to have cleaner hydrogen in the end. It also essentially requires much pure grade water like demineralized or deionized or distilled water to begin with. Furthermore high energy input and losses, use of expensive catalysts and materials especially in case of PEM electrolysis, infrastructure for distribution and storage, and finally scaling up to meet surging global energy needs limits the wide spread adoption of technology in view of its commercial potential. [105]Moreover the role of catalyst is the most crucial to the overall performance of water splitting reaction, it not only require careful selection but also structural and design engineering of catalytic matrix and catalyst itself is very crucial for optimum interfacial properties. [106]

2.5 Photo electrochemical water splitting:

The synergy between gelatin coatings and ferrite nanoparticles in drug delivery is an emerging research area. Preliminary studies by Smith et al. (2019) demonstrated that gelatin-coated ferrite nanoparticles could effectively encapsulate both hydrophilic and hydrophobic drugs, providing sustained release profiles. This suggests the potential for a multifunctional drug delivery platform that combines the biocompatibility of gelatin with the magnetic properties of ferrite nanoparticles.

Solar energy is the most abundant and versatile renewable source available and same solar energy can be used in variety of renewable process for generation of hydrogen. From green heating systems to power generation or production of synthetic fuel all depends upon ingenious process design.[1]

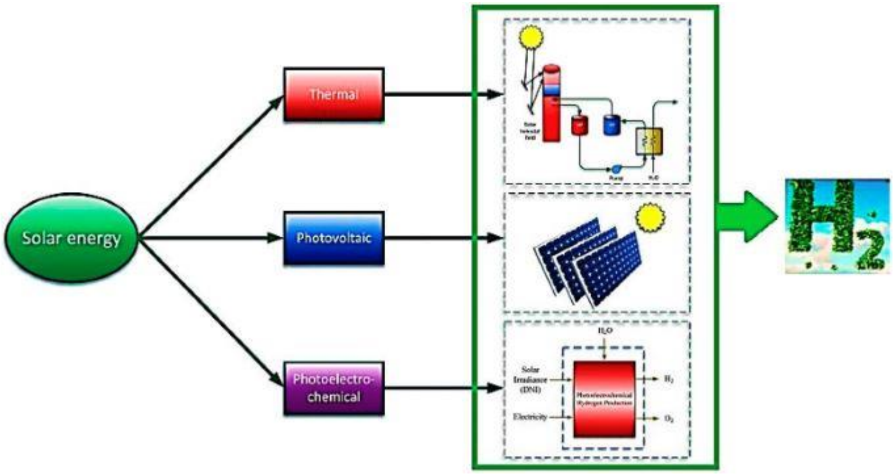


Figure 2.7:Various process powered by solar energy for hydrogen generation[1]

2.5.1. Mechanism

Photo electrochemical (PEC) water splitting is a sustainable technology to harness solar energy to produce green hydrogen. Its process is much similar to electrolysis but instead of using electricity to split water it utilizes combination of semiconductor material and solar energy. Photo irradiation of semiconductor materials generates electron hole pairs that initiate desired water splitting reactions.[107]

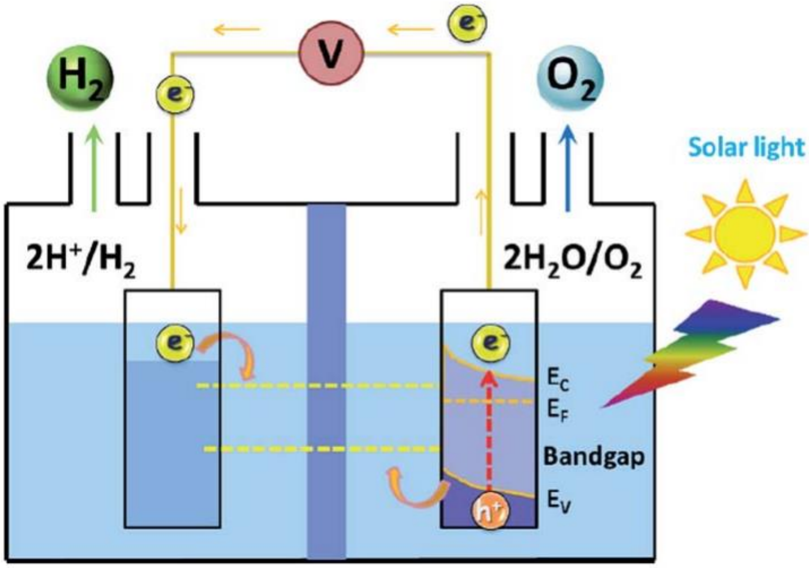


Figure 2.8:Various process powered by solar energy for hydrogen generation[108]

Essentially it involves photo electrodes immersed in electrolyte solution that converts solar energy into chemical energy by splitting water into its respective derivatives i.e. hydrogen and oxygen using electron hole pairs. Early PEC cells utilize mainly titanium dioxide TiO2, silicone and zinc oxide ZnO. They offer limited efficiency as a result of poor light absorption, proper band alignments and high charge recombination. Prompt research is required to design specialized engineering materials to spit water under sunlight while remain environmental friendly at the same time.[109]

2.5.2. Materials

The choice of photo electrode material plays a pivotal role in efficiency of PEC cell from early use of simple semiconductors as silicone to complex tandem cells today. Researchers have proposed four step strategies to overcome silicon inherent limitation and to harness its low band gap energy i.e. 1.1eV. Starting from surface morphology regulation to enhance light harvesting properties, band engineering to reduce charge recombination issue, addition of protective layer to reduce photo corrosion and lastly loading photo catalyst on silicon electrode. Later researchers also followed the similar trend for other materials to enhance their photo properties. [35]

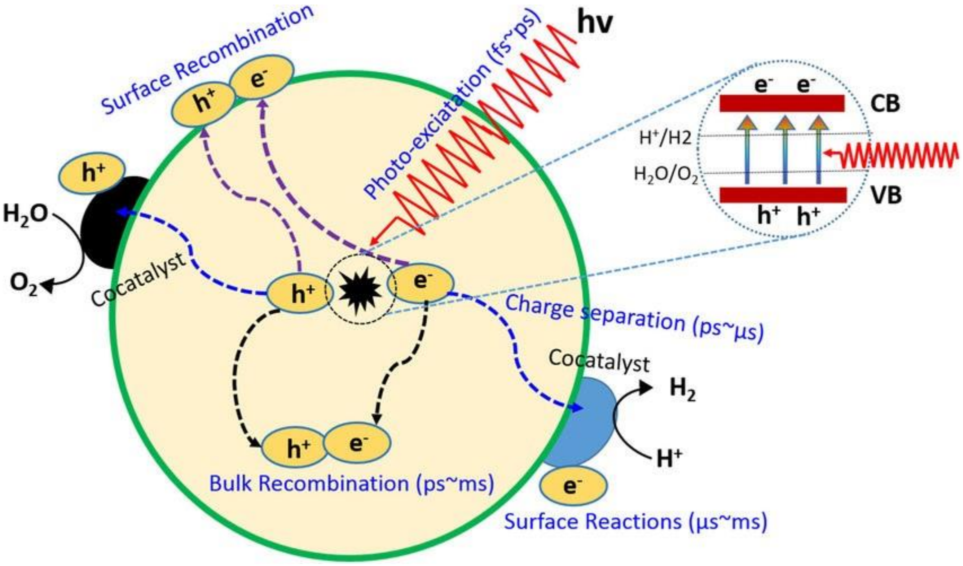


Figure 2.9:Schematics of Photo catalysis from photo excitations to charge separation and recombination followed by desired reactions[110]

UV active semiconductors show wider band gaps with higher charge recombination rates. On the other side, visible band gap semiconductor materials show narrower band gaps with compromised quantum efficiency and poor available surface area. Metal semiconductors are broadly susceptible to photo corrosion that further limits their use.[111] Binary semiconductors like layered materials with anisotropic nature like graphitic carbon nitride g-C3N4, RGO, black phosphorous and few chalcogenides like CdS etc have appropriate bang gaps but their high charge recombination limit their direct application as photo electrodes. Apart from new and more sophisticated materials more integrated and complex PEC systems are being constituted by incorporating photovoltaics PV into green hydrogen systems. [34]

Band edge and band gap of perovskite crystal structures can be engineered and custom tailored to make them visible light active for both solar cells and PEC cells. Perovskites can be categorized on the basis of their structure ABO_3, layered and ABX_3 type where doping either A or B sites have significant effect on band gaps and overall PEC cell output. New stride in doping luminescent materials like (Ho, Er, Eu and Nd etc) not only narrows the band gap but also reduces charge recombination rate.[112] Perovskites band edge can also be managed by making their composites with binary semiconductors resulting into hetero junction systems that are capable of producing hydrogen under visible light. This area has recently gained much attention as recently researchers have been exploring more and more visible light active composites, nano structures and their hybrids to enhance light absorption and reduce charge recombination. On the whole perovskite have gained a repute of wonder catalyst in the solar hydrogen production stage.[34]

Efficient photo catalysts are crucial for PEC water splitting systems and variety of materials broadly in the categories of metal oxides, perovskites, organic semiconductors and their hetero junctions have been investigated over years. However recent studies have shown significant emphasis on perovskites especially lead based iodides but their toxicity raise a serious objection on its application as a potent candidate for green hydrogen. Despite significant research in the field of PEC water splitting over decades it still faces several challenges that act as key milestones towards green hydrogen’s future. Restricted stability of photo electrodes under tough operating conditions like corrosion and photo corrosion limits the cyclic stability of the cell and their solutions have been core concern of recent researchers.[113]

Metals being excellent hydrogen catalysts are prone to metal oxidation under wet PEC cells whereas n-type semiconductors are prone to photo corrosion under prolonged light irradiation. In order to mitigate low efficiency effects of photo sensitive materials new strategies like coatings and surface passivation needs to be incorporated. Researchers have investigated new method of metal passivation without compromising catalysis by using triple catalytic mixture that is NiFeMo in CNTs framework. Overall system performs really well at 13.8% solar to hydrogen efficiency at 450mV over potential.[114]

2.5.3 Recent Advancements

Photo corrosion still remains a compelling challenge to PEC hydrogen systems. Variety of techniques apart from just advanced engineered materials have been employed that include coating stable protective layers, surface passivation techniques and strategically smart designed reactors that limits the contact between photo electrode and electrolyte. Similarly organic semiconductors and polymers as PEC are also less common due to their instability in water. However recent studies have investigated p-type polymers and n-type fullerene materials are passivized with Ni foils, Galn eutectic and layered doubled hydrates as model materials. [115]Perovskite materials being one of the key actors in PEC stage they are less prone to photo corrosion but their instability in water require certain surface treatments to mitigate their poor stability issue and improve longevity.

Nano materials like quantum dots and nano particles of higher order offer unique advantages in PEC schemes. Size and dimension dependent properties make them appropriate additive materials to decorate either binary semiconductors or make unique composites with other photo active materials. As a result hybrid materials offer much favorably positioned and tunable band gaps for desired application.[34]

Just like in photo voltaic concept of tandem cells can also be employed in PEC cells. Self-driven tandem cells offer solutions to eliminate external bias no matter how small external bias it is. Addition of photo voltaic PV component to PEC system makes overall system self-reliant.[116]

Photo electrode made with multiple photo sensitive materials varying in their band gaps have recently gained much attention because of their potential to improve overall cell efficiency. Depending on band gaps different materials absorb light from different regions of overall solar spectrum and by utilizing such materials it increases chances to absorb more light from different parts of solar spectrum. [76, 117]

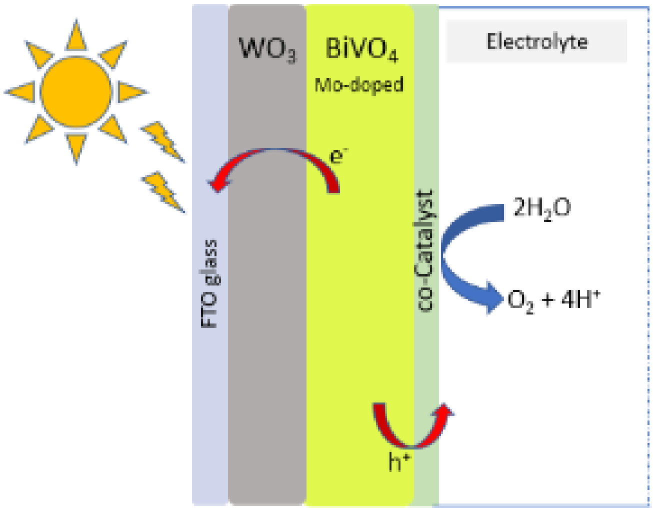


Figure 2.10: Schematics for heterojunction with $BiVO_4$ catalyst and WO_3 co-catalyst[117]

Tandem cells overall enhance light absorption and results in more charge generation that contribute to higher levels of hydrogen produced. The most critical parameter to evaluate PEC water splitting systems is it's solar to hydrogen efficiency. Solar to hydrogen efficiency beyond 10 % is quiet critical and require careful engineering to achieve.. Overall one junction responds to PV and other to PEC in turn making system self-reliant with no external bias.[34]

2.5.4 Integrated systems

Potential for further improvement lies solely in integration of advanced materials and prompts engineering solution. Single technique seems to lack in providing solution for such an intricate technology, commercialization of PEC is still far from happening due to complex nature of process, scalability and cost effectiveness. This PV assisted PEC technology has potential for making self-powered smart devices on the principle of artificial photosynthesis and variety of already tried and tested PV materials can be incorporated here as well. Researchers have explored potential of classic GaAs as PV solar cells in double junction PV-PEC system with InGaP as InGaP/GaAs with reported solar to hydrogen efficiency of 9%. [118] however recent advancement is breakthrough in this field where 20.8% efficiency is reported in July 2023 and is the most efficient photo electrochemical system reported so far. This type of PV-PEC system has used integrated halide perovskite based tandem cell that is a smart use of cheaper catalyst for expensive green technology. [115]

Sophisticated yet strategic nature of such technologies requires collaborations between academia, industry and governments to accelerate transition from lab to commercial scale. PEC has led a new stride in recent years and set the foundation of more sophisticated solar technologies in green fuel arena as artificial photosynthesis, artificial leaf, integrated solar fuel systems, photo catalysis, piezo photo catalysis and self-powering tribo electric nano generator TENG PEC systems. Continuous dedication of researchers in PEC commercialization and potential of its easy integration in existing energy landscape future seems to be positive for green hydrogen.[35, 119]

2.6 Photo catalysis:

Photo electro-catalytic (PECat) also called as photocatalysis PC for hydrogen production are basically modification of PEC production of hydrogen. Where both use semiconductor materials and light irradiation to produce electron hole pairs to carry out water splitting reactions. However the mechanism, design architecture, gas synthesis and end application of both technologies differs a lot. [120]

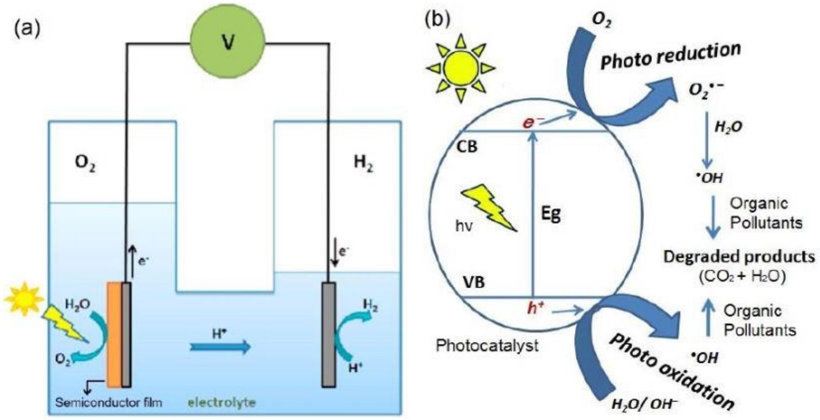


Figure 2.11:Schematics (a) Photo catalysis for water splitting and (b) photocatalysis for waste water and organic dye degradation[121]

In PEC cell we have pair of photo electrodes generally made with some semiconducting material that are immersed in an electrolyte. Photons are absorbed by photo electrodes resulting into respective electron hole e-h+ pair that migrate to the electrode electrolyte interface. Interface becomes very important for PEC cells as reaction takes place on interface and could contribute to serious impedance issues. At the anode interface oxidation reaction takes place and oxygen is released while electrons travel through an external circuit and reach cathode where they reduce protons to form hydrogen gas. Water oxidation results in the formation of oxygen gas, protons and electrons where electrons travel through an external circuit while protons travel through an electrolyte and both reach cathode where they combine to produce desired hydrogen gas. Both the gases are released at two different electrodes with high grade purity. [111, 122]The overall reaction can be represented as

Oxidation reaction

$$H_2O + \text{Photon} \rightarrow O_2\,(g) + e^- + H^+$$

Reduction reaction

$$H^+ + e^- \rightarrow H_2\,(g)$$

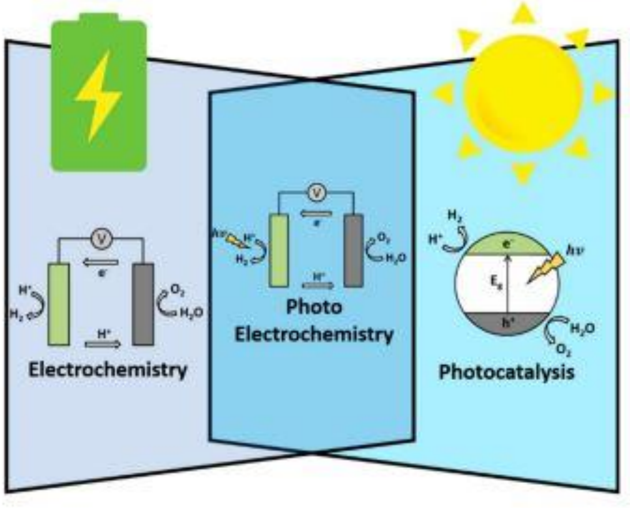


Figure 2.12:Schematics for comparison between three water splitting mechanisms Electrochemical, PEC and PECat[123]

On the other hand photo catalysis for water splitting uses photo catalyst (PC) that might and might not be a semiconductor material. Traditionally photo catalysts were metal nano particles or p-type semiconductors of either chalcogenide or metal oxide families such as TiO2 or CdS. PC is directly added to water reaction mixture that essentially holds few additives as sacrificial agents to facilitate reduction reaction. [124] Similar to PEC cells when PC are exposed to light they also generate e-h+ pair, however e-h+ can participate in multiple redox reactions in water and other reactants present in reaction mixture directly on the catalyst surface. It is one of the fundamental differences with respect to reaction mechanism as it requires no alternate pathways for e and h+ prior reduction reaction. Here catalyst surface is of great importance as it provides reaction sites for water splitting reactions.[109]

Nature of redox reactions in PECat reaction systems is much complex as compared to PEC reaction scheme. Variety of reactions apart from hydrogen evolution reaction (HER) takes place depending upon nature and type of both catalyst and reaction mixture. Oxygen evolution reaction (OER) is not always guaranteed as other oxidation reactions might take precedence. Researches have reported with perovskite halides formation of super oxide anion$O_2^{\bullet-}$ different oxidation reaction results into the formation of H_2O_2 instead of O_2. [125]

Especially in case of g-C_3N_4 imbedded with some metal nano particles. This technique allows more complex reactions along with OER and HER especially if reaction mixture is made from industrial waste water or some natural organic waste. Catalysis is highly specific in nature so same catalyst might produce different products at different yield depending upon nature and type of reaction mixture. [126] At the same time, instead of OER there are high chances for hydrogen peroxide H_2O_2 to be formed and left in spent reaction mixtures with same water samples by just changing a catalyst. Researchers have reported presence of nitrides in layered carbon sources and iodides, bromides and chlorides in perovskites not only alter oxidation reaction but also overall product mixture in the end that makes HER more complex. [30, 127]

Band energies refer to energy levels occupied by electrons where two energy levels are of significant importance for PC materials i.e. valance band (VB) and conduction band (CB). Band gap is the difference between two levels that dictates the electrical and optical properties of PC materials and is the most crucial factor in PECat water splitting. Researchers have investigated porous $BiFeO_3$ as photo anodes for water splitting they have tried to optimize band properties through interfacial engineering [128]

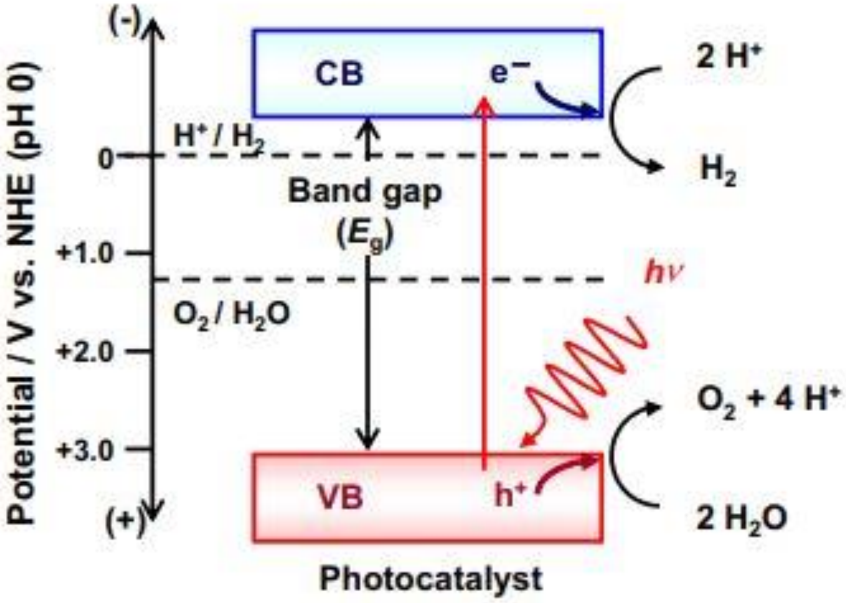


Figure 2.13:Band energy diagram for photo catalytic water splitting system[129]

Photon absorption contributing to $e^- h^+$ pair takes place only when energy of incident photon is equal or higher than the band gap energy of PC material. Apart from just band gap structuring researchers have investigated other techniques like surface passivation and junction improvement to suppress charge recombination. For example $BiFeO_3$ with Ar annealing improve charge mobility and further passivation with p-type polymer polyethylenedioxytheophene PEDOT reduces its surface defects and improve p-n junction that overall suppresses charge recombination. [130]

The two energy levels play a crucial role in redox reactions where excited electrons present in CB participate in reduction reactions while holes left in VB can trigger oxidation reactions. Efficient PECat for water splitting require materials with band energies that can be synchronized with thermodynamic potential of water splitting reactions i.e. 1.23eV theoretically. Materials with band gaps higher than 1.23eV can qualify as PC materials however band gaps with CB being more negatively and VB being more positively positioned with the same band gap are preferred.[131]

Solar spectrum reaching earth surface can be bifurcated into three main types depending upon their energy level as 4 to 5% UV, 45% visible and remaining 49 to 50% as IR. The thermodynamic potential of IR is less than 1eV and is less than minimum potential required for water splitting and disqualifies IR active materials though they have highest contribution to overall solar spectrum. [12]Although thermodynamic potential of UV is between 3 to 4eV that is quiet favorable and well above that of water splitting but UV contribution to overall solar spectrum is the lowest. That makes UV active photo catalysts poor choice for water splitting under direct sunlight exposure. Recent researchers have explored g-C_3N_4 as a potential visible light active photo catalyst through various pretreatments, doping methods, metal depositions, surface passivation and its composites with appropriate co-catalyst.[132]

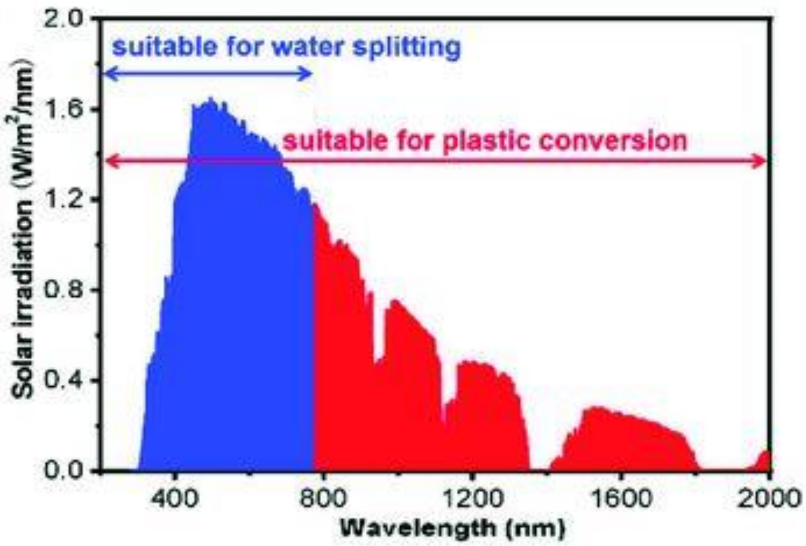


Figure 2.14:Band energy diagram for photo catalytic water splitting system[133]

However, visible light active photo catalysts hold great potential as not only their thermodynamic potential is above that of water splitting reaction but also they can make maximum use of broad range solar spectrum i.e. 45%. Furthermore, peak hours with max UV exposure on sunny days also improve efficiency by give higher yields. Generally 1.5 to 2.5eV band gap is considered to be ideal for PC materials used in sun driven water splitting as it is in perfect alignment with visible region potential.[134] In order to make TiO_2 more visibly active first its composite is made with visible light active CdS then is loaded with CoO as a co catalyst. Under visible light and 2% co-catalysts loading it results in 7% higher yield than TiO_2 alone. [135]

2.6.1. Materials

Early researchers have extensively investigated TiO_2, ZnO and their composites potential as PC material however having favorable band energy 3.2eV that is significantly higher than minimum requirement of 1.23eV it still remained a poor choice. Although it is efficient in e^- h^+ pair generation its band energies are not properly aligned with water splitting potential and results in low quantum efficiency. Researchers have investigated similar CdS with Au loading and find it much superior in water splitting in terms of hydrogen yield and quantum efficiency.[136]

Apart from water splitting TiO_2 has been proved as one of the most effective photo catalyst in waste water dye degradation and other renewable environmental remediation processes.[137] Previous findings also suggests several methods to enhance TiO_2 performance in water splitting reactions through doping, surface modification and band engineering to not only reduce band gap but also to improve band alignment.[138, 139]

Binary perovskites like Bismuth vanadate ($BiVO_4$) have not only been used in PEC tandem cells but also continues their stride in PECat systems due to their favorable band energies. Recent studies have shown great emphasis on speeding up slow OER reactions as they result in steady flow of electrons for much faster HER and $BiVO_4$ proved to accelerate photo catalytic activity of water oxidation reactions. Strategies such as heterojunction formation, cocatalyst decoration on $BiVO_4$ and forming layered structures with other charge mobile materials further enhance its performance and potential in PECat systems.

Chalcogenides and metal oxides is also another category of material that offers greater potential to be used in PECat systems. Researchers have explored potential of g-C_3N_4 as multifunctional photo catalyst by making its composites with metal oxides like WO3 and $BiVO_4$. It makes quiet a robust system that can also be deployed in PEC and PV-PEC systems.[140]

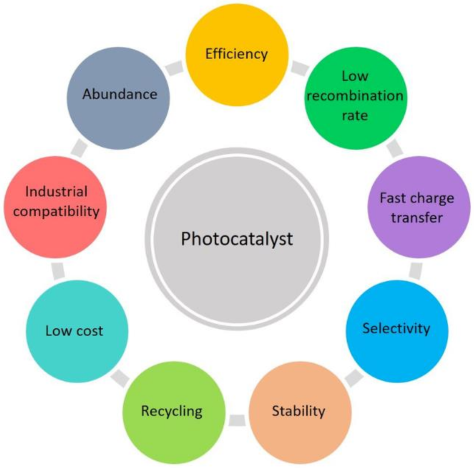


Figure 2.15:Schematics summarizes basic design requirements for high efficiency photo catalysts [141]

2.6.2 Recent advancements

Tandem photo catalysis is the most recent advancement in the line of PECat water splitting where the aim is to have controlled and stepwise generation of e^- h^+ pairs yet maximizing solar absorption. Different photo materials with varying band energies are combined not only to maximize utilization of solar spectrum but it also forms a heterojunction that significantly reduce charge recombination.[142] Heterojunctions promote efficient e and h+ transfer between different materials thus they overall reduce charge recombination and improve PECat water splitting. Studies shows already tried and tested perovskite materials with appropriate bands are combined giving entirely different yet optimized results in photo catalysis.[143] Researchers have explored wide range of s-scheme hetero-junction photo catalysts such as TiO_2, CdS, g-C_3N_4, COF-based graphdinyne based, ZnO, and $ZnIn_2S_4$. Their charge migration schemes in different material combinations along with their expected p-n junction are presented.[144] Metal free 2D polymer tandems with 1.8 to 2.8eV band gaps are also researcher's key area of interest as it offers more flexible and corrosion resistant systems. [145]

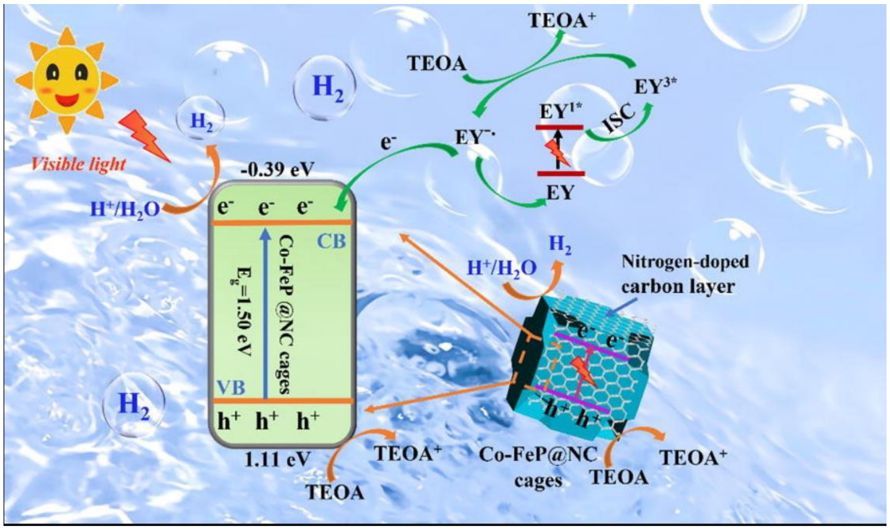


Figure 2.16:Schematics for PECat H_2 evolution using double s-scheme hetero junction[144]

Metal organic frameworks MOFs are a more recent trend in photo materials where MOFs acts as a medium for generated e-h+ pair to flow in and out of the matrix. Researchers have investigated MnO_x as co-catalyst added in Pt based MOF matrix resulting much higher hydrogen yield and enhanced charge separation. Here Pt acts as electron site contributing HER and MnO_x as h+ carring site promoting OER.[33]

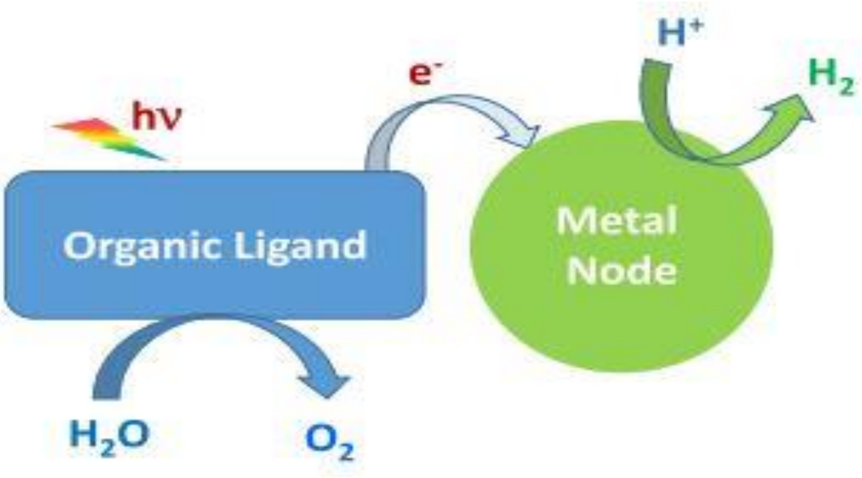


Figure 2.17:Schematics of MOF materials for photo catalytic water splitting[146]

Longer polymeric chains of MOFs give more stability to metals from under water oxidation and enhance longevity of metal nano particles that are embedded in their polymeric structure. [146] Researchers have also reported conjugated polymer frameworks loaded with IrO_2 as h^+ and Palladium as e carrier medium for efficient water splitting. MOFs can be effectively used for loading both metal and metal oxide nano particles to optimize HER and OER sites. [147]

2.7 Piezo catalysis

Piezo catalysis is more recent development in the catalysis realm where focus is on harnessing mechanical force or pressure to trigger chemical reactions. Mechanical energy is another abundant form of green energy available in nature as wind, tide, vibration, sonication and atmospheric pressure. Certain materials can harness this energy in to an electrical energy and are termed as piezo materials. [148]

2.7.1. Mechanism

This emerging branch of catalysis exploits unique properties of piezo electric materials that generate electric charge when subjected to mechanical stress and vice versa. Internal polarization caused by mechanical stress induces strain in the piezo catalyst thus altering its electronic configuration and facilitating charge carriers separation. [5] In piezo catalysis piezo materials are either used as catalysts or co-catalysts to improve both efficiency and selectivity of various chemical reactions. Strong internal current pulsations as an outcome of mechanical force it induces changes in electronic structure and surface properties thereby influencing catalysis that is completely surface dominated phenomenon. [149, 150] Piezo current produced inside material provides altered reaction pathways that not only lowers their activation energy barrier but also improve their reaction kinetics thus ultimately lead to water electrochemical splitting. It is an innovative approach that can be fine-tuned to various renewable systems from waste water treatment to energy storage and sustainable green fuels production. [151, 152]

Piezo catalysis can easily be incorporated into existing heterogeneous catalysis where harnessing mechanical energy yields into specific chemical and electrochemical reactions. In order to perform water splitting reaction piezoelectric activation is required by subjecting mechanical stress to the material. It generates electric charge at specific sites where these charges interact with water molecule adsorbed on piezo materials surface. [153] Efficiency of piezo catalysts is crucial to selective activation of catalytic sites on material surface. On these sites water molecules get physisorbed due to strong interaction between freshly produced electric charges and water. As a result catalytic activity of adsorbed sites improves and facilitates water splitting reaction. [154] Electron rich negative sites promote reduction reactions like dye degradation, chromium reduction and HER while positive sites facilitate OER or other oxidation reactions like formation of peroxides. The internal polarization as an outcome of mechanical stress generates two types of sites leading to a pair of redox reaction for water splitting. [155]

2.7.2 Materials

The most investigated piezo materials for catalysis are perovskites in the form of titanates such as lead zirconate titanate (PZT) and barium titanate $BaTiO_3$ with high piezoelectric coefficients d33. Piezo electric coefficient is a ratio whose value indicates mechanical to electrical conversion efficiency and vice versa. Higher the D33 values higher will be the piezo effect and faster reaction kinetics will be expected. Toxic nature of PZT limits its use in environment friendly technologies although it offers highest d33 value. [156] According to established data and environmental concern $BaTiO_3$ offers highest D33 value in lead free piezo materials. Researchers have reported $BaTiO_3$ with 10nm particle size under sonication alone producing 655 μmol g^{-1} h^{-1} hydrogen. [157] Researchers have also reported organic metal free polymeric piezo materials like polyvinylidene fluoride PVDF and PVDF-HFP as excellent materials for hydrogen production. Although premium cost for polymeric piezo materials still opens a quest for finding efficient yet economical alternatives. [20]

In order to improve efficiency of piezo catalysts classic metal catalysts are either deposited on piezo materials or embedded in their polymeric structure. Catalysts like platinum Pt, iridium Ir and ruthenium Ru are commonly used due to their superb catalytic activity under room conditions. [5] Nano materials are most widely used to enhance piezo catalysis efficiency and recent research trend shows use of metal nano particles like Pt deposition on nano scale piezo electric to create highly efficient piezo catalytic systems. Researchers most commonly used piezo material $BaTiO_3$ performance is reported to be enhanced by using Ag nano particles.[158] [11]

Piezo catalysis is more advanced catalysis and offers great potential to be integrated with any other green hydrogen system such as PEC or PECat system. Such integrated systems open a way for semiconducting materials to be used in piezo catalysis.[159] Especially in the nano range they have admirable ability to absorb piezo generated charges and stimulating surface reactions crucial to water splitting. Common semiconductors used in PECat systems like ZnO, TiO_2 and WO_3 can also be used in piezo catalysis systems under nano range with or without carbon loadings.[160]

2.7.3 Recent advancements

Integration of PECat systems with piezo systems result into powerful catalysts for sustainable water splitting systems. Perovskite oxides are versatile materials with diverse chemical composition and tunable band gaps through doping. Broad range applications of these materials made them ideal choice for clean energy storage such as solar cells and supercapacitors and green fuel synthesis systems like PECat and piezo catalysis systems.[16] Materials like bismuth ferrite $BiFeO_3$, strontium titanate $SrTiO_3$ and barium titanate $BaTiO_3$ exhibit both piezoelectric and semiconducting properties that not only make them ideal choice for charge generation but also for catalyzing water splitting. [12, 13, 161]

Growing research is especially inclined towards 2D materials due to their diverse and unique electrical and mechanical properties. Researchers have reported huge potential in group three Ga, In and Se dichalcogenides and Ga holds more attention as other researchers have also explored its nitrides potential for piezo catalysis as well. [162, 163] Commonly used 2D materials encompasses transition metal dichalcogenides (TMDs) like molybdenum di sulfide MoS2 and cadmium sulfide CdS and graphene derivatives like RGO and g-C_3N_4. Conventional charge recombination issue is much catered by piezo induced polarization inside material layers. [164]

To harness synergistic effects of multiple materials researchers over time have developed hybrid materials. Their combinations include piezoelectric materials coupled with electro catalysts, semiconductors, layered 2D sheets, dual nature materials like perovskites and metal nano particles. [18]However along with advantages of such systems it can also hampers overall performance as more actors take part in reactions. Interfaces formed around variety of materials provide alternative energy paths inside material matrix that might reduce charge recombination but also reduces charge mobility inside material that is crucial for reaction kinetics.[21]

2.8 Piezo-photo catalysis:

Piezo photo catalysis is ingenuous technique that combines both piezo catalysis and photo catalysis in one catalytic system. Their synergic effect can produce more hydrogen by reducing charge recombination issues enhancing charge mobility inside catalyst due to internal polarization. Material with compromised either side can be made efficient by the dual effect of both powerful catalytic systems.

2.9 Future Directions

The challenges in the research on cobalt-substituted zinc ferrites revolve around achieving a balance between specific capacitance and cycling stability. The choice of substitution ratio is critical, as excessive substitution can lead to decreased cycling stability, while insufficient substitution may limit specific capacitance. The optimization of these parameters remains a challenge and requires a deep understanding of the materials' electrochemical behavior[30].

Additionally, the environmental impact and sustainability of these materials are important considerations in the context of modern energy storage systems. Researchers are increasingly focused on developing environmentally friendly electrode materials with minimal environmental footprint. Future directions in this area should explore the development of sustainable synthesis methods and the use of eco-friendly precursors[31].

Moreover, future research should aim to explore novel synthesis routes and advanced characterization techniques that can further enhance the performance of cobalt-substituted zinc ferrites. Incorporating nanoscale engineering and other innovative approaches may lead to breakthroughs in material design and energy storage technology.

Ferrites, both cobalt and zinc-substituted, have shown promise as HER and OER electrode materials, with the potential to outperform traditional choices in terms of overpotential and stability. However, a comprehensive comparative study that directly compares these materials and assesses their performance in practical.

Water splitting applications is currently lacking. The forthcoming research aims to address this gap and provide valuable insights into material selection for piezo-photo water splitting systems.

2.10 Research Gap and Rationale

The research gap identified in the existing literature is the absence of a comprehensive comparative study between cobalt and nickel-substituted zinc ferrites for water splitting applications. While individual studies have explored the electrochemical behavior of these materials, a direct comparison that considers factors such as OER/HER over potential, cycling stability, and hydrogen production is necessary. This gap is significant because it impedes researchers and engineers from making informed decisions about which material is best suited for specific water splitting applications.

The rationale for this comparative study is rooted in the need for a systematic evaluation of these materials' performance. Such a study can provide insights into their strengths and weaknesses, ultimately aiding in material selection and the design of high-hydrogen and oxygen yielding electrodes. Additionally, understanding how cobalt and zinc substitution affects these materials' electrochemical behavior can contribute to the broader knowledge of electrode materials for water splitting and energy storage applications..

CHAPTER 3: MATERIALS AND METHODS

3.1 Synthesis Route:

This study aims to synthesize binary zinc cobalt ferrite for water splitting through piezo-photo-catalysis. This study includes

- Synthesis of mono ferrites through co-precipitation method.
- Synthesis of binary ferrite through one step co-precipitation method with sonication
- Characterization of mono ferrite and composite material.
- Reaction set up and successful gas collection
- Testing of collected gas using gas chromatograph

3.2 Materials Required

- Iron Nitrate $Fe (NO_3)_2. 9H_2O$
- Zinc Nitrate $Zn(NO_3)_2$
- Cobalt Nitrate $Co (NO_3)2.6H_2O$
- Sodium Hydroxide NaOH
- Ethanol
- Distilled water
- Deionized water
- Triethanol amine

- Philips bulb(add specs)
- Apparatus Used
- Media bottles
- Weighing balance
- Drying oven/vacuum oven/furnace
- Beakers
- Thermometer
- Magnetic stirrer
- Hot plate
- Petri dish/ceramic boats/crucibles
- Centrifuge
- pH meter

3.3 Synthesis of $ZnFe_2O_4$ Nanoparticles

These methods, The synthesis of magnetic nanoparticles of ZnFe2O4 was accomplished using the co-precipitation method, a widely employed technique for producing nanoparticles with controlled properties. The process began by preparing a precursor solution. In this step, 16.00 grams of iron (III) nitrate nonahydrate (Fe (NO3)3·9H2O) and 2.97 grams of zinc (II) nitrate tetrahydrate (Zn (NO3)2·4H2O) were meticulously dissolved in 400 milliliters of deionized water.

To initiate the co-precipitation reaction Sodium hydroxide was then slowly added dropwise to the solution while vigorously stirring, and the pH was raised to 13 by the end of the process. The reaction was carried out at a constant temperature of 80°C for 1 hour. After cooling, the magnetic nanoparticles were washed several times with deionized water and ethanol through centrifugation and then sintered at 800°C for 3 hours for further analysis.

Upon completion of the reaction, the resulting magnetic nanoparticles were allowed to cool. Subsequently, they underwent thorough washing with deionized water and ethanol in order to remove any impurities or residual reactants. This purification process ensured the attainment of highly pure ZnFe2O4 nanoparticles.

The final step in the synthesis process involved sintering the purified nanoparticles at a temperature of 800°C for a duration of 3 hours. This high-temperature treatment is critical for the consolidation of nanoparticles, facilitating crystal growth and enhancing the material's overall properties.

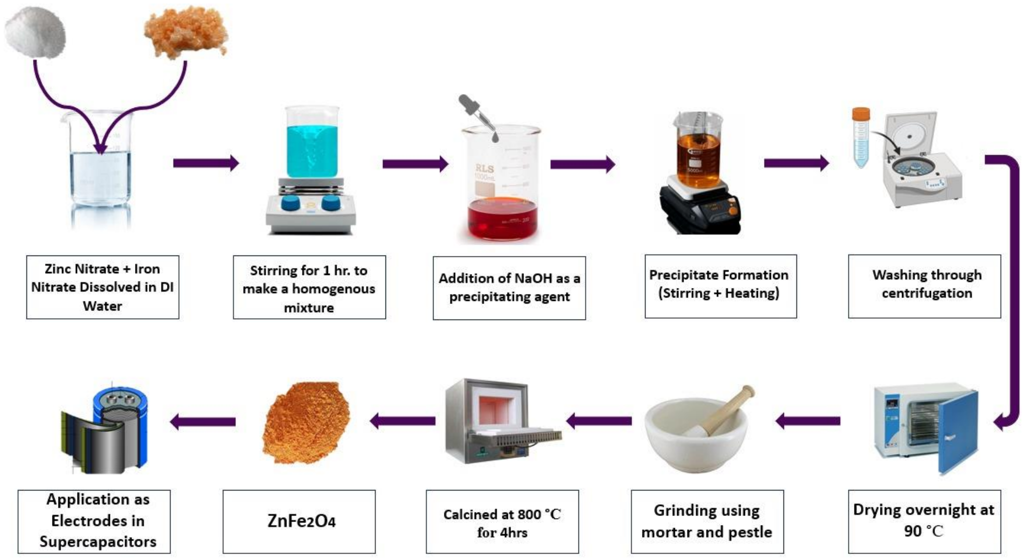


Figure 3.1: Schematic diagram of the synthesis of ZnFe2O4

3.4 Synthesis of Synthesis of Zn0.5Co0.5Fe_2O_4 Nanoparticles

The materials of high purity Fe $(NO_3)_2$. $9H_2O$, Mn $(NO_3)_2.6H_2O$, Co $(NO_3)_2.6H_2O$, NaOH were used according to their stoichiometric proportion for synthesis of $MnFe_2O_4$ and $CoFe_2O_4$ nanoparticles. All the salt was from Sigma Aldrich. Gelatin polymers were used to coat the nanoparticles. Acetic acid was used as a dispersive medium for making nanocomposites. Ciprofloxacin drug was used for drug loading experiments.

The synthesis of substituted Zinc nano ferrite, Zn0.5Co0.5Fe2O4, followed a similar co-precipitation approach. However, in this case, divalent metal cation cobalt (Co), was incorporated into the crystal structure.

For the synthesis of Zn0.5Co0.5Fe$_2$O$_4$, 2.91 grams of cobalt (II) nitrate hexahydrate (Co(NO3)2·6H2O was included in the precursor solution. The remainder of the co-precipitation method mirrored the process employed for ZnFe$_2$O$_4$, including the gradual addition of NaOH, maintaining the pH at 13, and conducting the reaction for 1 hour at a constant temperature of 80°C.

Upon the completion of the co-precipitation reaction, the resulting Zn0.5Co0.5Fe$_2$O$_4$ nanoparticles were subjected to the same purification steps involving multiple washes with deionized water and ethanol. This thorough purification process ensured that the substituted nanoparticles were of high purity.

As with ZnFe$_2$O$_4$, the final step for Zn0.5Co0.5Fe$_2$O$_4$ synthesis involved sintering the purified nanoparticles. They were heated to 800°C and maintained at this temperature for a duration of 3 hours. This post-synthesis sintering process allowed for further crystallization and optimization of the nanoparticles' properties, making them suitable for subsequent characterization and analysis.

These synthesized materials, ZnFe$_2$O$_4$ and Zn0.5Co0.5Fe$_2$O$_4$, are essential components for further characterization and analysis in various applications, including their potential use as material for water splitting and hydrogen production.

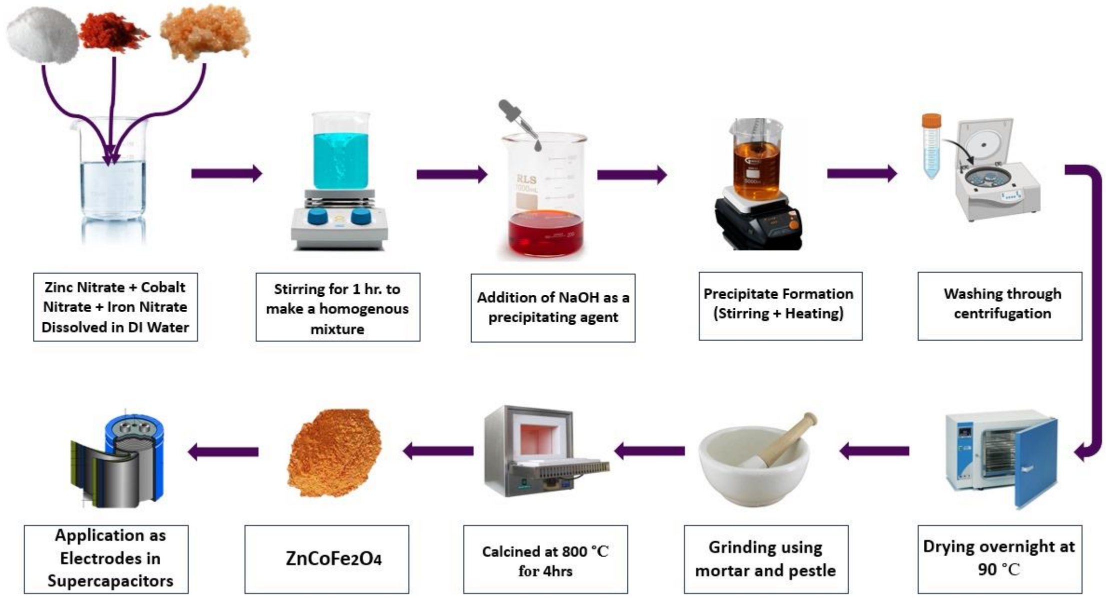


Figure 3.2: Schematic diagram of the synthesis of Zn0.5Co0.5Fe2O4

We have designed our own gas collection system with photo chamber using Philips 635nm bulb and two blowers to remove heat from the system. Sonicator is placed inside chamber and 100ml flask was placed inside with skewers system to keep reaction flask in place. Round bottom reaction flask was covered with rubber septum in order to seal entire reaction system. 10ml syringe was used to collect gas sample to be injected in GC for chromatography.

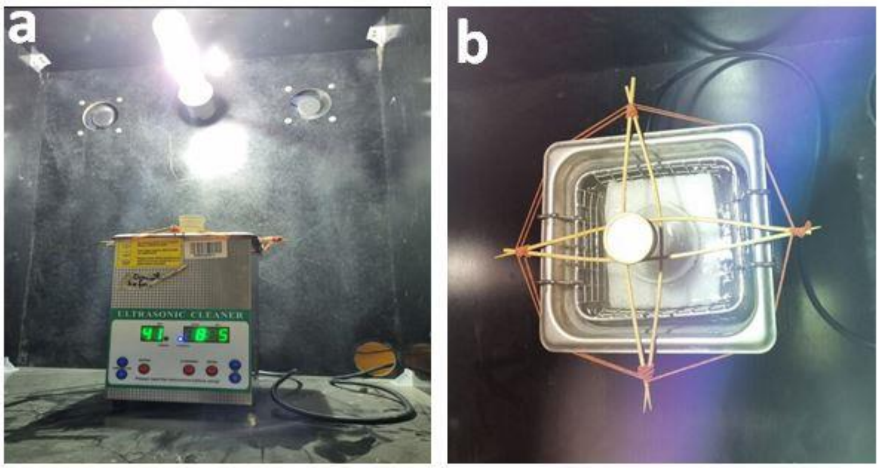


Figure 3.3 a) Experimental setup for reaction and gas collection and b) Skewer arrangement to keep reaction flask upright

We have GC and reading is given in percentage. Sample is extracted in fixed volume and then moles are calculated from standard molar volumes formula

$n=V/V_m$

Where V stands for volume of a gas extracted from a collected sample and V_m for molar volume that is $22.4dm^3$ at STP.

3.5 Sample Preparation for Characterizations

A controlled and systematic approach was undertaken to synthesize composite materials comprising manganese ferrite ($MnFe_2O_4$) and cobalt ferrite ($CoFe_2O_4$) nanoparticles, embedded within a polymer matrix. To achieve this, 20 mg of each ferrite type was individually dispersed in 10 ml of distilled water and subjected to ultrasonic agitation for a duration of 20 minutes. Concurrently, 10 mg of polymer particles were meticulously dispersed using a magnetic mixer within 20 ml of an acetic acid solution, and this process was replicated for both $MnFe_2O_4$ and $CoFe_2O_4$ ferrite types.

3.5.1 XRD:

Grind the synthesized ferrite powder into a fine powder using a mortar and pestle. Place the powder onto a sample holder, ensuring a smooth and level surface. Perform the XRD analysis to obtain diffraction patterns for phase identification and crystallite size calculation.

3.5.2 SEM:

Disperse a small amount of ferrite powder in ethanol and ultrasonicate for uniform suspension. Drop-cast the suspension onto a conductive substrate, allow it to dry, and sputter-coat with a thin layer of gold if necessary. Analyze the sample for surface morphology and particle size.

3.5.3 RAMAN:

Place a small quantity of ferrite powder on a clean glass slide or suitable substrate.

Focus the Raman laser on the sample and collect the spectra to identify vibrational modes and structural information.

3.5.4 FTIR:

Mix the ferrite powder with potassium bromide (KBr) and press it into a pellet using a hydraulic press. Place the pellet in the FTIR sample holder and collect spectra to identify functional groups and bonding characteristics.

3.5.5 Electrode Preparation for Electrochemical Analysis

The slurry was prepared with the activated material $Zn0.5Co0.5Fe_2O_4$, polyvinylidene (PVDF) as a binder and Carbon black to increase conductivity with a ratio of 85:05:10 respectively. Further 2 to 3 drops of N-methyl-2-pyrrolidone (NMP) solvent were added and sonicated until a homogenous suspension formed. Subsequently, Nickel foam (1cm x 1cm) is utilized as the current collector rinsed with Hydrochloric acid (HCl) for 5 minutes to remove the oxide layer then washed with deionized water (DI) and Ethanol for 10 minutes. Then dried in the oven at 60°C for 20 minutes. After this, the prepared slurry was deposited into Ni-foam then uniformly coated in Ni- foam and dried in a vacuum oven at 60°C overnight then it was pressed at 5Mpa for 5 mins. $ZnFe_2O_4$ and $CoFe_2O_4$ electrodes were also prepared by using the same method.

CHAPTER 4: RESULTS AND DISCUSSION

To comprehensively examine the properties of the synthesized material, a range of characterization techniques were employed. This chapter provides an in-depth analysis of each technique, offering detailed insights into the observed effects. The focus of this thesis centers on exploring the applications of cobalt ferrite, zinc ferrite and its composites, specifically in the field of piezo-photo catalytic water splitting.

4.1 X-Ray Diffraction (XRD)

The crystal structure of synthesized, $ZnFe_2O_4$, $CoFe_2O_4$ and $Zn_{0.5}Co_{0.5}Fe_2O_4$, composite was characterized by X-ray diffractometer with Cu/Kα radiation. The performed diffractograms spread over the 2θ values from 20^0 to 70^0 and scan time was 45min.

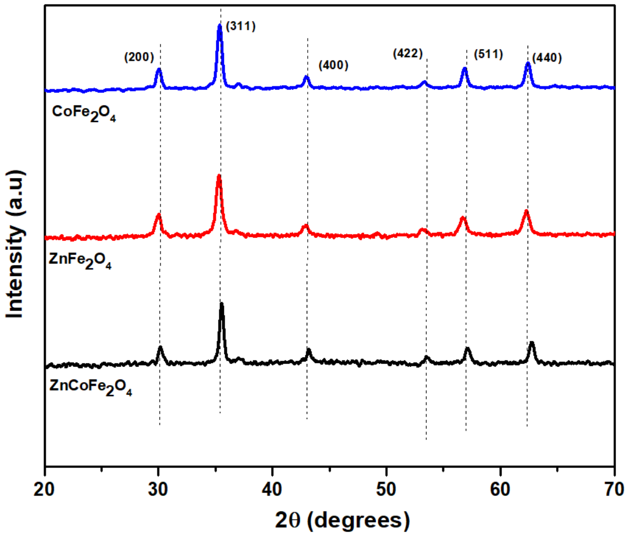


Figure 4.1: Shows The X-Ray diffraction Pattern of $ZnFe_2O_4$, $CoFe_2O_4$ and $Zn0.5Co0.5Fe_2O_4$ Nanoparticles.

The following equation was used to calculate the lattice parameter values,

$$\sin^2 \theta = (\lambda^2/a^2)(h^2 + k^2 + l^2)$$

Where λ is the X-ray wavelength (1.540 Å), a is the lattice constant, h k l are the miller indices of the reflection planes, and θ is the angle of diffraction. $ZnFe_2O_4$ has a lattice parameter value of 8.4310, $CoFe_2O_4$ has a lattice parameter value of 8.36, whereas $ZnCoFe_2O_4$ has a value of 8.4250. $ZnFe_2O_4$ sample crystallite size was found to be 19.26 nm, $CoFe_2O_4$ to be 32.00 nm, and $ZnCoFe_2O_4$ to be 34.20 nm. Using Debye- Scherrer's formula, the diameters of the samples' crystallites were determined as follows [20]

$$D = K\lambda/ (\beta \cos \theta) \text{ --(i)}$$

Where λ is the X-ray wavelength, t is the crystallite size, β is the FWHM and θ is the angle of diffraction.

The Bragg equation, on the other hand, enabled us to calculate the d-spacing of the XRD peaks and is represented as:

$$d = \lambda/(2 \sin \theta) \text{--(ii)}$$

where d is the d-spacing, λ is the X-ray wavelength, and θ is the Bragg angle.

The ZnFe2O4 sample's x-ray density was determined to be 5.42 g/cm3, $CoFe_2O_4$'s density was 5.32 g/cm3, and $ZnCoFe_2O_4$'s density was 4.90 g/cm3. $ZnFe_2O_4$ was found to have a unit cell volume of 599.29, $CoFe_2O_4$ of 593.34, and $ZnCoFe_2O_4$ of 598.01. The co-precipitation process is a great way to synthesize the necessary-sized nanoparticles, as shown by the XRD results [21].

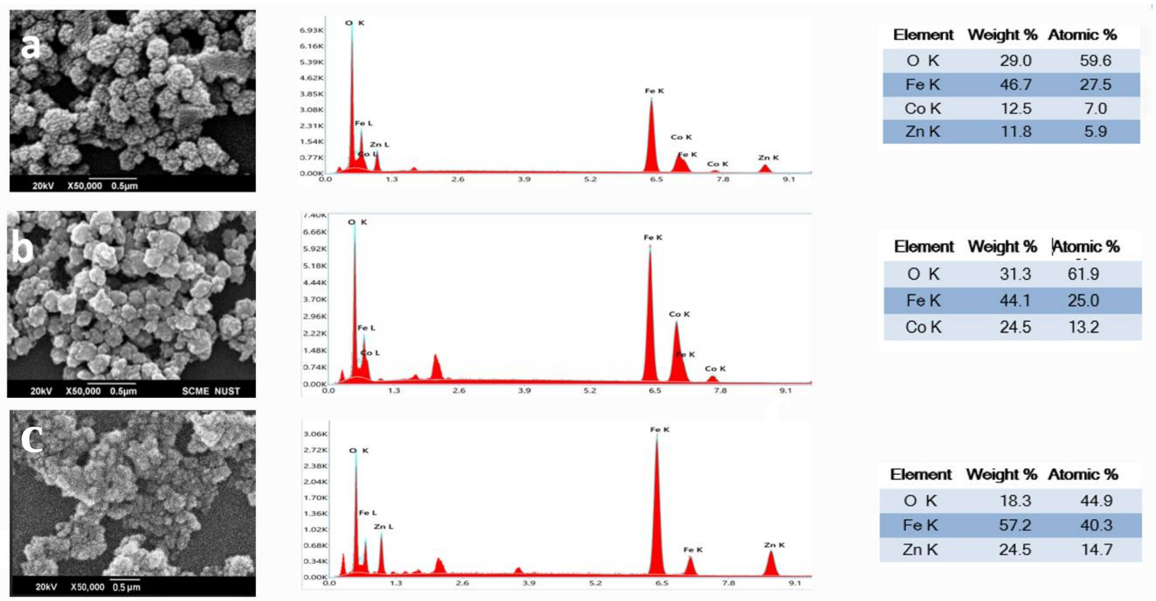
Table 4.1: Crystallographic Properties of $CoFe_2O_4$, $MnFe_2O_4$, and Gelatin-Coated $CoFe_2O_4$ and $MnFe_2O_4$ Nanoparticles

Sample	**Crystallite Size (nm)**	**FCC Crystal Structure**	**Lattice Constant (Å)**	**Strain (%)**
$CoFe_2O_4$	32	Yes	8.36	0.01

$ZnFe_2O_4$	36	Yes	8.43	0.02
$ZnCoFe_2O_4$	35	Yes	8.425	0.01

4.2 Scanning Electron Microscopy (SEM)

The The FE-SEM analysis was used to regulate the morphology and average size of the $ZnCoFe_2O_4$, $CoFe_2O_4$ and $ZnFe_2O_4$ NPs. Spherical nanometric particles of cobalt ferrites could be observed in Fig 30 a,b,c and d . A slight particle agglomeration is suggestive of dipole dipole interaction between the nanoparticles.[81] The average particle sizes obtained were 20-30 nm, approximately.



Element	Weight %	Atomic %
O K	29.0	59.6
Fe K	46.7	27.5
Co K	12.5	7.0
Zn K	11.8	5.9

Element	Weight %	Atomic %
O K	31.3	61.9
Fe K	44.1	25.0
Co K	24.5	13.2

Element	Weight %	Atomic %
O K	18.3	44.9
Fe K	57.2	40.3
Zn K	24.5	14.7

Figure 4.2: Shows SEM images of (a) $ZnCoFe_2O_4$ and (b) $CoFe_2O_4$ and (c) $ZnFe_2O_4$ Nanoparticles

The images are all at the same magnification of 500,000x and have a scale bar of 0.5 micrometers. The images were taken at 20kV, which is the voltage applied to the electron beam in the microscope. Scanning electron microscopy (SEM) provides estimations of the information regarding the surface morphology, shape, and size of grains. Synthesized ferrites had well-crystalline grains, according to SEM pictures. Both particle size and morphology were significantly impacted by the replacement of cations. The SEM micrograph shows the precise geometry of the grain size. When the resolution is raised, the buildup is also visible in the most recent sample.[165] Intergranular porosity and variations in grain size distribution can be seen in SEM pictures.

4.3 FT-IR Spectroscopy

In this research, The obtained FTIR spectra from the distinct ferrite samples—Zinc

Ferrite, Cobalt Ferrite and Zinc Cobalt Ferrite—reveal distinct features characterized by three primary peaks, each providing unique insights into the vibrational behavior of chemical bonds within the samples

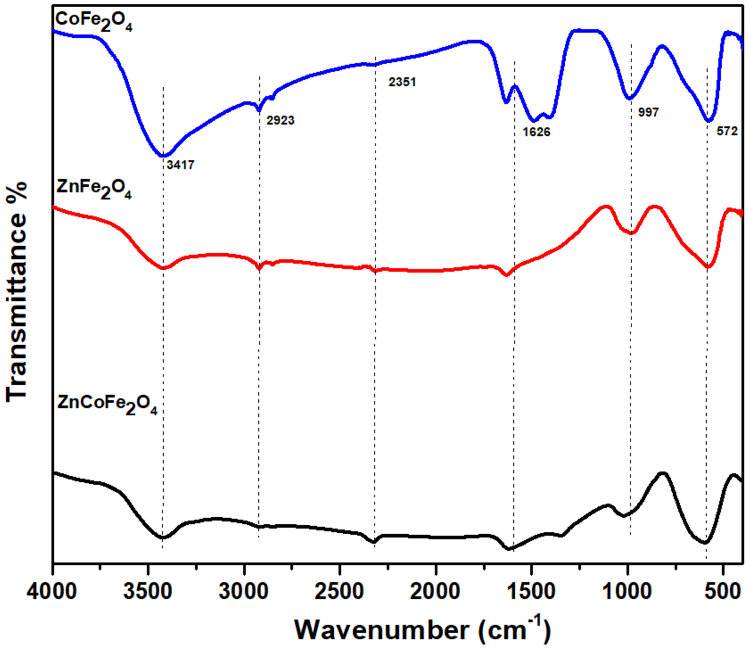


Figure 4.3: The FTIR pattern of ZnFe2O4, CoFe2O4 and Zn0.5Co0.5Fe2O4 Nanoparticles

Firstly, a notable peak positioned at approximately 3417 cm-1 signifies the stretching vibration of O-H bonds present in water molecules. This common peak is observed consistently across all three samples, attributed to their exposure to ambient air before measurement.

A significant peak around 1626 cm-1 is ascribed to the stretching vibration of Fe-O bonds in the tetrahedral sites of the lattice structure. This peak's frequency subtly differs among the samples, being slightly higher in Zinc Cobalt Ferrite compared to Zinc Ferrite. This disparity implies enhanced Fe-O bond strength in the former samples due to the greater valence electronegativity of cobalt and ions, resulting in a stronger attraction of oxygen atoms.

Furthermore, a peak around 997 cm-1 corresponds to the bending vibration of Fe-O bonds within the octahedral sites. Analogously, this peak appears at slightly elevated frequencies in Zinc Cobalt Ferrite, attributed once again to the augmented bonding strength facilitated by cobalt ions. [27, 28]

Concurrently, secondary peaks emerge from the spectra due to vibrations within other chemical bonds present in the ferrites, involving Zn-O and Co-O bonds.When we carefully look at the spectra, we notice that they are quite similar. This is because all three samples share a basic structure called a spinel. The main difference is in the tiny spaces within the structure where metal ions sit. In Zinc Ferrite, only zinc ions are in these spaces, while in Zinc Cobalt Ferrite, there's a mix of zinc and cobalt ions. [29]

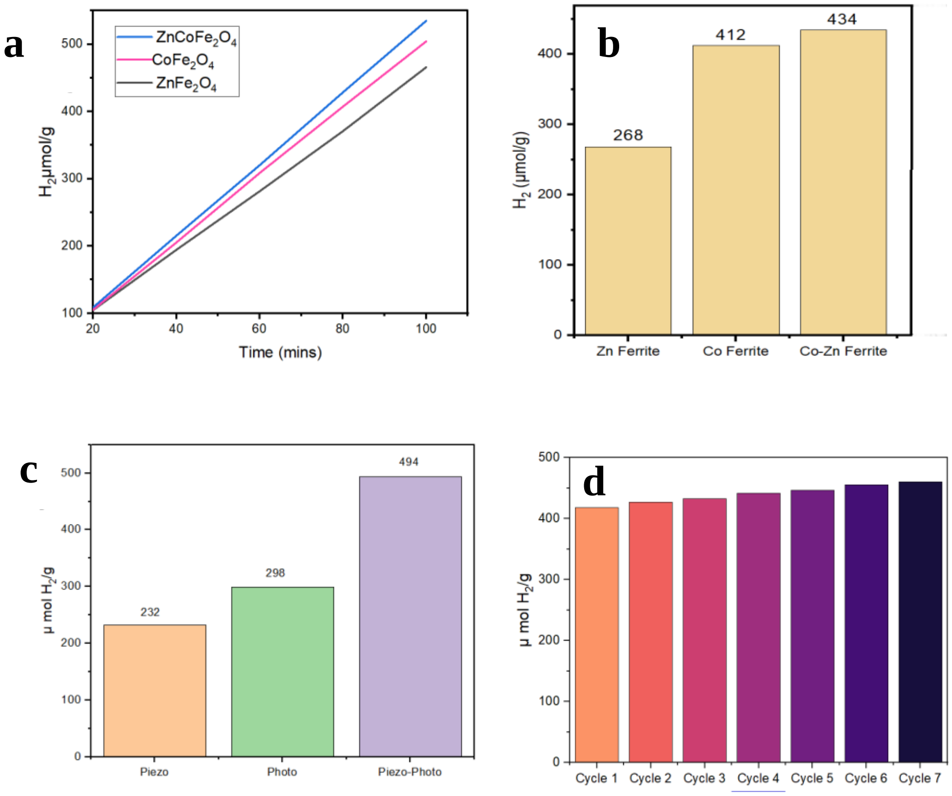
This difference in the metal ions in these spaces affects how strong certain bonds are between iron (Fe) and oxygen (O) atoms. This, in turn, affects the heights of the peaks we see in the FTIR measurements. That's why we see slightly higher peaks in Zinc Cobalt Ferrite compared to Zinc Ferrite and cobalt ferrite. It's like a small bump in the music of the spectra.

To put it simply, even though the spectra look alike, the types of metal ions in the structure cause some vibrations to be a bit stronger, making those peaks a bit taller in Zinc Cobalt Ferrite when compared to Zinc Ferrite. [30].In addition, the peak centered around 600 cm-1 corresponds to the stretching vibration of Zn-O bonds in the tetrahedral sites. Remarkably, this peak is consistent in all three samples due to the presence of zinc ions within their respective tetrahedral sites. Slight frequency fluctuations are noticeable in Zinc Cobalt Ferrite, aligning with the trends detected in preceding peaks.

The higher peak frequencies observed in Zinc Cobalt Ferrite spectra compared to Zinc Ferrite indicate stronger Fe-O bonds, a favorable trait for supercapacitor electrodes due to potentially higher specific capacitance. The presence of the peak around 600 cm-1 across all samples signifies Zn-O bonds in tetrahedral sites, beneficial for electrochemical energy storage. The similarities in the spectra suggest these ferrites could be candidates for supercapacitor electrodes [29]

4.4 Gas Chromatography

In order to demonstrate the effect of piezo-photocatalytic, H_2 production performance of prepared samples was first investigated by both light and sonication. 100ml reaction mixture with 25mg catalyst is constituted with distilled water (DI).



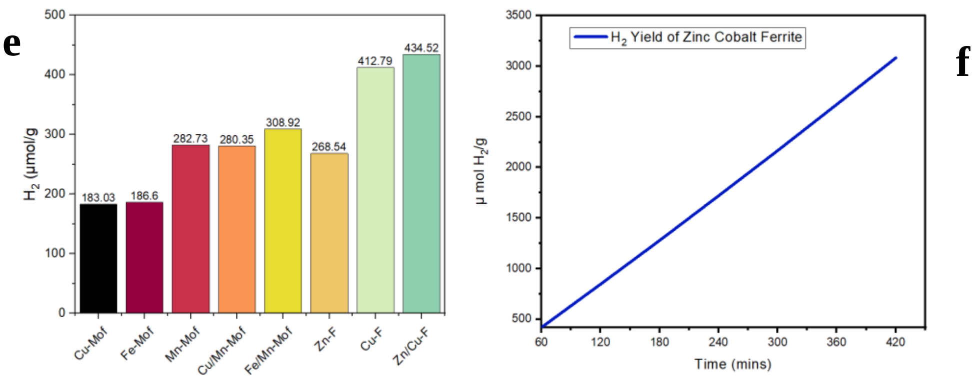


Figure 4.4 (a) Shows best compositions for H_2 yield, (b) shows H_2 accumulated amount against each composition, (c) Photo, piezo and their synergistic effect on H_2 evolution, (d) Cyclic stability /cyclic strength of catalyst and (e) Comparison between our best composition and other materials

Fig. 4.4 (a) and (b) illustrates hydrogen production rate of all samples where $ZnFe_2O_4$, $CoFe_2O_4$ and $ZnCoFe_2O_4$ deliver H_2 at the rate of 268 μmol/g-h , 412 μmol/g-h and 434 μmol/g-h respectively. The highest H_2 activity 412 μmol/g-h is observed in composite with Zn0.5Co0.5-Fe_2O_4 loading that is nearest to RGO-Co_3O_4. Excessive co-catalyst loadings beyond 5% reduce H_2 activity [135, 166].

In order to investigate piezo, photo and its synergistic effects on water splitting reactions, three set of experiments were performed on the catalyst as shown in fig.33 (c). One hour reaction was performed under sonication alone and it nearly produces 232 μmol/g-h hydrogen. Another reaction was performed under light alone and it produces hydrogen around 298 μmol/g-h. In the end one hour reaction was carried out under both sonication and light irradiation with hydrogen yield around 494 μmol/g-h. Although there isn’t significant difference between piezo and photo catalysis alone however it still confirms materials photo effect is stronger than piezo strain that also confirms well with literature as it happens with few materials.[166] Under dual application of both piezo and photo effects significant increase in hydrogen production was observed as a result of their synergistic effect.

Cyclic stability of pristine catalyst is studied over 7 cycles of 1 hour as shown in fig 33 (d) and appears to be stable. Slight increase is seen upto seven cycles that is from

418 µmol/g-h to 460 µmol/g-h and. On the whole catalyst it is estimated to be stable under consecutive 7 hours of H_2 activity.

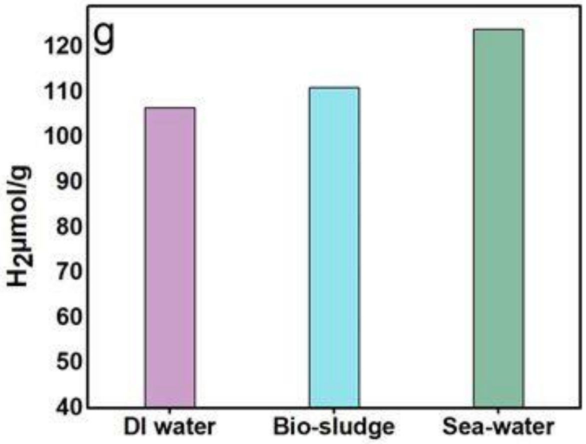


Figure 4.5: Shows solvent effect on H_2 evolution with same catalyst

For comparison Cu-MOF , Fe-MOF ,Mn-MOF and their binary metal composites were also used to investigate H_2 activity as shown in fig 41 (e) where MOFs were selected due to their prolonged stability under moist conditions. H_2 production rate of Cu-MOF and Fe-MOF are 183 µmol/g-h and 187 µmol/g-h of H_2 respectively.

Moreover potential of catalyst for different mediums is also tested for H_2 activity as shown in fig 42 (g). Sea water and manure solutions were used without sacrificial agent and produces nearly 123 µmol/g-h and 123 µmol/g-h H_2 respectively. It nearly produces 12.8% more H_2 for sea water as compared to 1.8% more H_2 in case of manure. We can conclude sea water has much better potential to be used instead of DI water.

4.6 Electrochemical Testing

The slurry was prepared with the activated material Zn0.5Co0.5Fe_2O_4, polyvinylidene (PVDF) as a binder and Carbon black to increase conductivity with a ratio of 85:05:10 respectively. Further 2 to 3 drops of N-methyl-2-pyrrolidone (NMP) solvent were added and sonicated until a homogenous suspension formed. Subsequently, Nickel foam (1cm x

1cm) is utilized as the current collector rinsed with Hydrochloric acid (HCl) for 5 minutes to remove the oxide layer then washed with deionized water (DI) and Ethanol for 10 minutes. Then dried in the oven at 60°C for 20 minutes. After this, the prepared slurry was deposited into Ni-foam then uniformly coated in Ni- foam and dried in a vacuum oven at 60°C overnight then it was pressed at 5Mpa for 5 mins. $ZnFe_2O_4$ and $CoFe_2O_4$ electrodes were also prepared by using the same method

4.6.1 Linear Sweep Voltammetry:

The At room temperature, all electrochemical testing was carried out using the three-electrode setup of the electrochemical workstation GAMRY B110. Ag/AgCl electrode saturated with 3.5M KCl is employed as a reference electrode, the counter electrode is Platinum wire and the electrocatalyst cast in Ni-foam is utilized as a substrate for a current collector to act as a working electrode allowing electrons and mass to be transferred quickly. Each measurement was performed in 1M KOH (pH=14). The hydrogen evolution and oxygen evolution were investigated by using Linear Sweep Voltammetry at 10 mVs^{-1} scan rate where the voltage window for OER is from 0V to 1.4V while for HER it is 0V to -1.4V. The OER and HER were carried out under the same circumstances.

To find the kinetic performance of the prepared catalyst, the Tafel slope is calculated by using the equation[66] $\eta = a + b \log j$, b is the Tafel slope, and η is overpotential. Electrochemical Impedance spectroscopy (EIS) was conducted in the range of 20 kHz to 0.1 Hz. Chronoamperometry was acquired for a long-term stability test at a constant applied voltage of 0.6V. The potential against Ag/AgCl was transformed into reversible hydrogen electrode potential (RHE) to conduct further calculations by employing.

$$E_{RHE} = E_{Ag/AgCl} + 0.1976 + 0.059\ pH$$

4.6.2 OER Catalytic Activity

Fig.36a exhibits the comparison OER polarization curves of $Zn0.5Co0.5Fe_2O_4$, $ZnFe_2O_4$ and $CoFe_2O_4$ electrocatalysts respectively. $ZnFe_2O_4$ showed a higher overpotential and lower catalytic activity than $Zn0.5Co0.5Fe_2O_4$ and $CoFe_2O_4$ for OER where both acted to lower the activation energy respectively. It demonstrates that $Zn0.5Co0.5Fe_2O_4$ has exhibited enhanced activity and less overpotential than pristine $CoFe_2O_4$ and $ZnFe_2O_4$ to attain current density at 415 mV@η_{10}. Furthermore, the nickel foam has little activity in both the Oxygen Evolution Reaction (OER) and the Hydrogen Evolution Reaction (HER), indicating that it has little impact on the overall water-splitting process. The Tafel slope values were also determined, and the linear- fitted curves are shown in Fig. 36 b where $Zn0.5Co0.5Fe_2O_4$ with a Tafel slope of 167 mV dec^{-1}, the $CoFe_2O_4$ has 260 mV dec^{-1} and $ZnFe_2O_4$ has 300 mV dec^{-1} which shows a slower kinetic catalytic activity of electrocatalysts than $Zn0.5Co0.5Fe_2O_4$. Composite of zinc and cobalt ferrite results in the formation of more active sites on the surface [67] which is confirmed by XRD analysis as the c-lattice parameter increases from 8.36 Å to 8.43 Å. When compared to zinc and cobalt monoferrites .It demonstrates that the high performance of $Zn0.5Co0.5Fe_2O_4$ as an electrocatalyst lowers the overpotential which improves the overall efficiency.

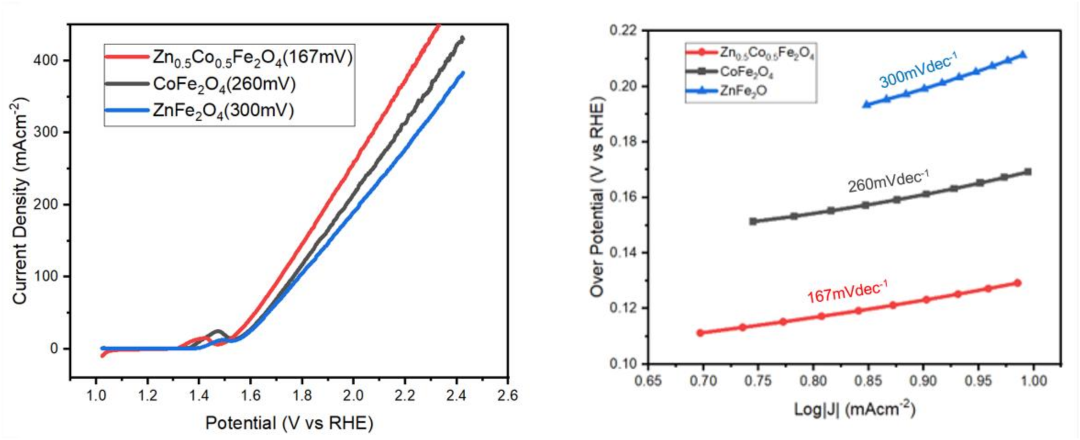


Figure 4.6: Polarization curves $Zn0.5Co0.5Fe_2O_4$, $ZnFe_2O_4$ and $CoFe_2O_4$ (b) Tafel Slope

4.6.3 *HER Catalytic Activity:*

The Fig. 4.7 a exhibits the comparison of HER polarization curves of Zn0.5Co0.5Fe_2O_4, $ZnFe_2O_4$ and $CoFe_2O_4$ electrocatalysts respectively. The Tafel slope provides a mechanism for the electrocatalytic process illustrated in Fig. 4.7b

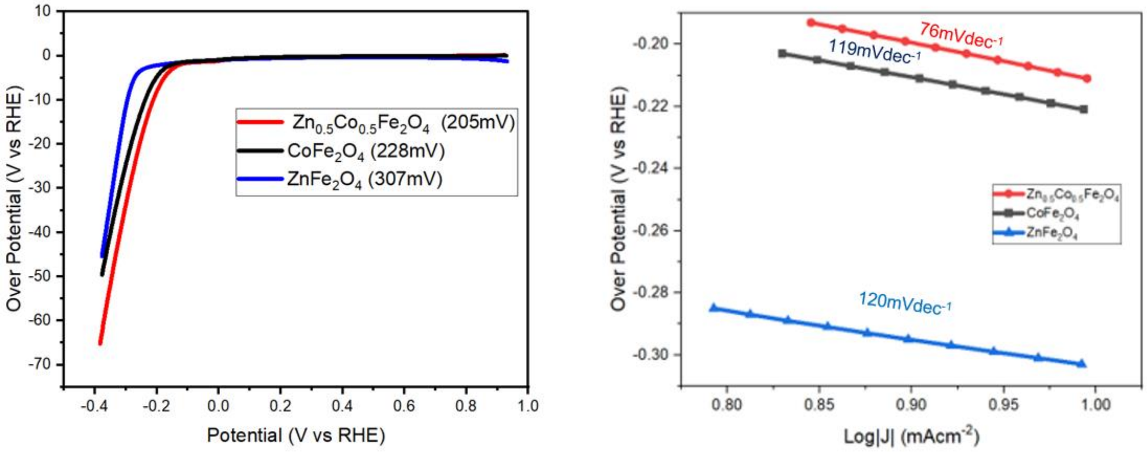


Figure 4.7: Polarization Zn0.5Co0.5Fe_2O_4, $ZnFe_2O_4$ and $CoFe_2O_4$ (b) Tafel Slope

A lower Tafel slope is usually accepted to imply more favourable kinetics for the Hydrogen Evolution Reaction (HER). The synergistic effect zinc and cobalt in the Zn0.5Co0.5Fe_2O_4 develops as a lower Tafel slope, indicating improved kinetics. The N-doped Nb2CTx MXene follows the Volmer-Heyrovsky pathway for the HER process during the rate-determining step (RDS) according to the literature as well as indicated by its slope value.

The Tafel slopes for the prepared catalysts were calculated as 205, 228, 238mV $dec^{-1}$for Zn0.5Co0.5Fe_2O_4, $CoFe_2O_4$ and $ZnFe_2O_4$ respectively. HER refers to the process of producing hydrogen (H_2) gas from hydrogen ions (H^+) and electrons (e^-) at the electrochemical cathode. Cobalt incorporation by doping has a significant influence on the kinetics of the Hydrogen Evolution Reaction (HER) by lowering the energy barriers associated with distinct reaction stages. For overall bifunctional water-splitting electrolysis with the ability to minimize application costs, a bifunctional water-splitting electrolyzer can act efficiently as both OER and HER electrodes.

4.6.4 Chronoamperometry Test:

The stability of the catalyst is essential to its commercialization. The electrode was subjected to 14 hours of chronoamperometry testing (I-t curve) for HER at a constant applied voltage of 0.6 V to verify the long-term durability. The Zn0.5Co0.5Fe_2O_4 as displayed in Fig. 5.9. had a current stability retention of 94% after 14 hours of testing. It shows that the cobalt doped zinc ferrite catalysts are stable and long-lasting. Moreover, during chronoamperometry testing, the decreased ion diffusion resistance at the electrode-electrolyte interface enhances rapid ion penetration by active sites generated by electrochemical activation of as-prepared material. The overall water splitting test was carried out in a 1 M KOH solution .

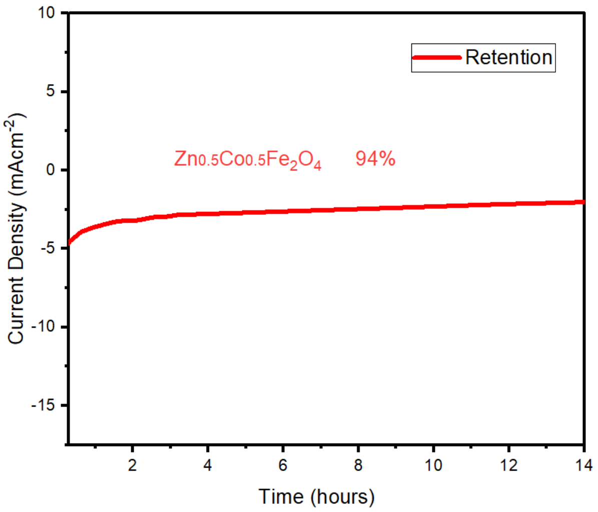


Figure 4.8: Chronoamperometric curves of $Zn0.5Co0.5Fe_2O_4$ for 14 h.

The results show that the $Zn0.5Co0.5Fe_2O_4$ sample's increased HER and OER activity can be due to its available active sites and strong charge transfer capabilities.

4.6.5 Cyclic Voltammetry:

CV cycles of mono and binary ferrites were recorded from the voltage window of 0.00 V to 0.60 V. The specific capacitance is calculated as per weight of active material 2 mg. Figure 38 shows the CV plots of $Zn0.5Co0.5Fe_2O_4$, $CoFe_2O_4$ and $ZnFe_2O_4$, voltage windows for the composite are increased. All the measurements were done in 1M KOH electrolyte. Scan rates were taken from 100 to 5 mV s-1 and an increase in specific capacitance was observed.

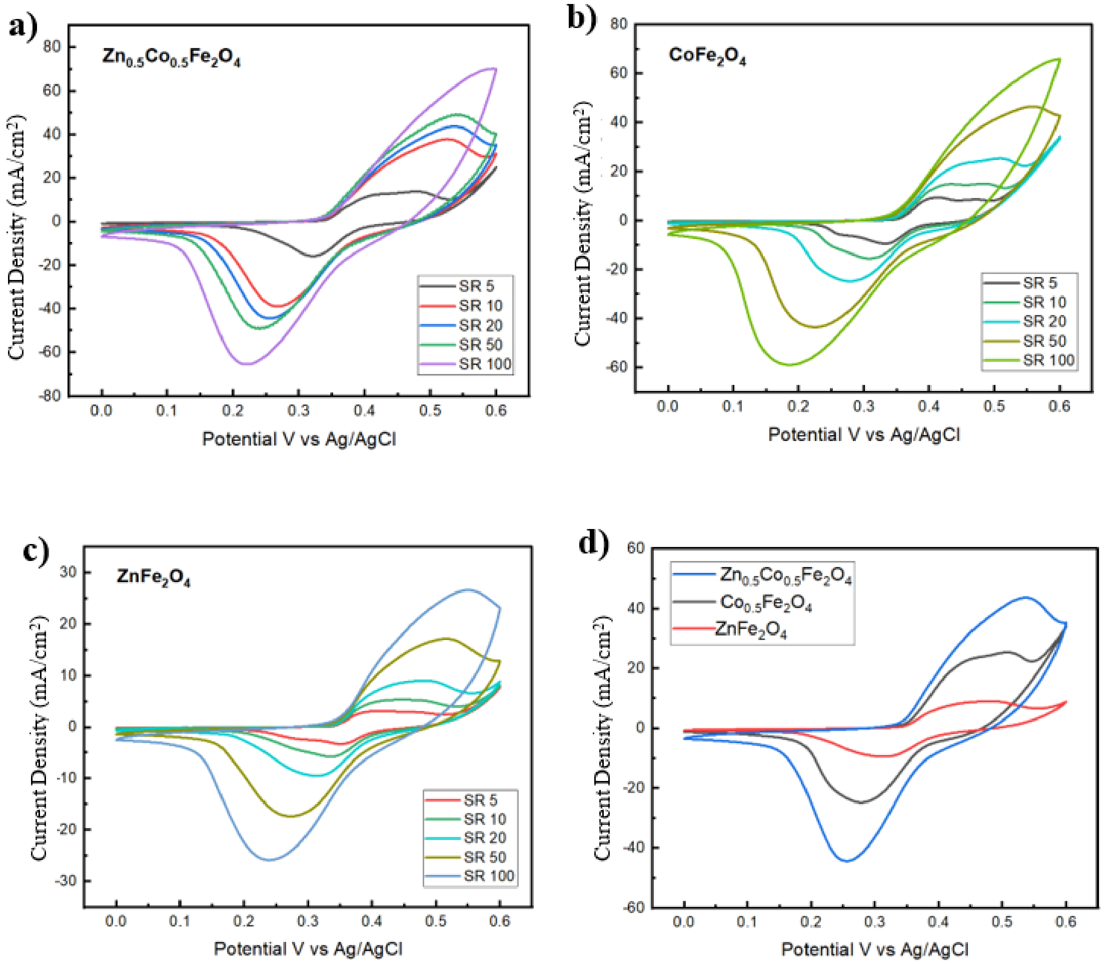


Figure 4.9 : (a)CV voltammogram of Zn0.5Co0.5Fe_2O_4, (b) CV voltammogram of $CoFe_2O_4$ (c) CV voltammogram of $ZnFe_2O_4$ (d) Comparison of CV Voltammogram @20 SR

4.6.6 Electrochemical Impedance Spectroscopy (EIS):

Electron impedance spectroscopy involves measuring a system's impedance response to an applied AC signal at various frequencies, and the resulting impedance spectrum is frequently depicted visually in a Nyquist plot. It also gives fundamental information about the internal resistance of the electrode material as well as the resistance between the electrode and the electrolyte interface.

It was used to investigate the electron transport mechanism between electrode and electrolyte. Fig. 39 displays the EIS spectra plot between Z_{real} on x-axis and $Z_{impedance}$ on the y-axis for $Zn0.5Co0.5Fe_2O_4$, $CoFe_2O_4$ and $ZnFe_2O_4$ with a fitted model. CPE (Constant phase element) diffusion along with Warburg is utilized.

Solution resistance (Rs) corresponds with the electrolyte solution present between the electrodes in the cell where the charge transfer resistance (Rct) is associated with the electrolyte interface in an electrochemical context.

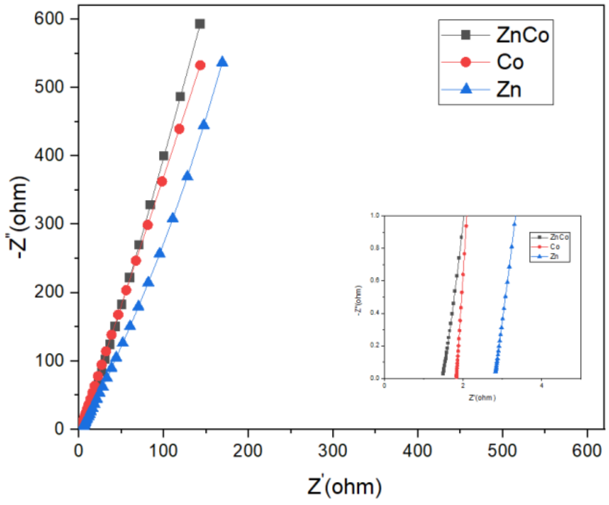


Figure 4.10 :EIS of $Zn0.5Co0.5Fe_2O_4$, $CoFe_2O_4$ and $ZnFe_2O_4$

Table 4.10 exhibits the fitting parameters value of EIS data of Zn0.5Co0.5Fe_2O_4, $CoFe_2O_4$ and $ZnFe_2O_4$.. Reduced solution resistance significantly shows the decrease in the impedance generated by the electrolyte solution within the electrochemical system while the decrease in charge transfer resistance (RCT) and solution resistance has indicated improved electrochemical kinetics and increased conductivity. A decrease in Warburg impedance from 0.233 $S * s^{1/2}$ to 0.158 $S * s^{1/2}$ indicates that reactants or products from the electrolyte are diffusing faster toward the electrode. As a result, the EIS data is also compatible with our previously stated OER and HER findings.

Table 4.2: Solution Resistance and charge transfer resistance of Zn0.5Co0.5Fe_2O_4, $CoFe_2O_4$ and $ZnFe_2O_4$

Materials	**R_S (Ω)**	**W ($S * s^{1/2}$)**
Zn0.5Co0.5Fe_2O_4	1.58	158.9e-3
$CoFe_2O_4$	1.83	200.7e-3
$ZnFe_2O_4$	2.96	233.0e-3

CHAPTER 5: CONCLUSIONS AND FUTURE RECOMMENDATION

5.1 Conclusion

In this research, I have successfully optimized the synthesis of binary ferrite composite Zn0.5Co0.5Fe_2O_4. where its structural properties using XRD, morphology using SEM and elemental concentration by using EDX was also studied. For electrochemical study, 1M KOH was used as an electrolyte. The electrode was prepared by deposition of material on Ni-foam by making a slurry in NMP using carbon black and PVDF as a binder. For water splitting application the Zn0.5Co0.5Fe_2O_4 has displayed an overpotential of 167 mV (vs. RHE) and a Tafel slope of 62 mV/dec for the Oxygen Evolution Reaction (OER) it also has displayed a 205mV overpotential (vs. RHE) and a Tafel slope of 76 mV/dec for the Hydrogen Evolution Reaction (HER). Similarly, for 14 hours binary ferrite composite Zn0.5Co0.5Fe_2O_4 retained 94% in the chronoamperometry making it a promising electrode material for supercapacitor applications. All of the electrochemical results strongly support the 434 μmol/g-h of hydrogen yield by the binary metal ferrite $ZnCoFe_2O_4$ .Piezo-photo catalysis shows a synergistic effect between piezo-catalysis and photocatalysis. After introduction of simultaneous photo and piezoelectric potential by using ultrasonicator H_2 evolution is much enhanced 494 μmol/g-h surpassing individual piezo catalysis 232 μmol/g-h and photo catalysis 298 μmol/g-h. Moreover, it was also found that catalyst performs significantly well without sacrificial agents.

5.2 Future Recommendations

Moreover, future research should aim to explore novel synthesis routes and advanced characterization techniques that can further enhance the performance of cobalt-substituted zinc ferrites. Incorporating nanoscale engineering and other innovative approaches may lead to breakthroughs in material design and energy storage technology.

Ferrites, both cobalt and zinc-substituted, have shown promise as HER and OER electrode materials, with the potential to outperform traditional choices in terms of overpotential and stability.

REFERENCES

[1] S. K. Dash, S. Chakraborty, and D. Elangovan, "A Brief Review of Hydrogen Production Methods and Their Challenges," *Energies,* vol. 16, no. 3, 2023.

[2] J. L. Holechek, H. M. E. Geli, M. N. Sawalhah, and R. Valdez, "A Global Assessment: Can Renewable Energy Replace Fossil Fuels by 2050?," *Sustainability,* vol. 14, no. 8, 2022.

[3] M. Cheng *et al.*, "Hydroxyl radicals based advanced oxidation processes (AOPs) for remediation of soils contaminated with organic compounds: A review," *Chemical Engineering Journal,* vol. 284, pp. 582-598, 2016.

[4] Z. Zhou *et al.*, "Persulfate-based advanced oxidation processes (AOPs) for organic-contaminated soil remediation: A review," *Chemical Engineering Journal,* vol. 372, pp. 836-851, 2019.

[5] Z. Liang, C.-F. Yan, S. Rtimi, and J. Bandara, "Piezoelectric materials for catalytic/photocatalytic removal of pollutants: Recent advances and outlook," *Applied Catalysis B: Environmental,* vol. 241, pp. 256-269, 2019.

[6] H. Yan, J. Zhang, C. You, Z. Song, B. Yu, and Y. Shen, "Influences of different synthesis conditions on properties of Fe3O4 nanoparticles," *Materials Chemistry and Physics,* vol. 113, no. 1, pp. 46-52, 2009/01/15/ 2009.

[7] S. Tasleem and M. Tahir, "Recent progress in structural development and band engineering of perovskites materials for photocatalytic solar hydrogen production: A review," *International Journal of Hydrogen Energy,* vol. 45, no. 38, pp. 19078-19111, 2020.

[8] T. Puangpetch, T. Sreethawong, S. Yoshikawa, and S. Chavadej, "Hydrogen production from photocatalytic water splitting over mesoporous-assembled SrTiO3 nanocrystal-based photocatalysts," *Journal of Molecular Catalysis A: Chemical,* vol. 312, no. 1-2, pp. 97-106, 2009.

[9] N. Denisov, J. Yoo, and P. Schmuki, "Effect of different hole scavengers on the photoelectrochemical properties and photocatalytic hydrogen evolution performance of pristine and Pt-decorated TiO2 nanotubes," *Electrochimica Acta,* vol. 319, pp. 61-71, 2019.

[10] F. E. Osterloh and B. A. Parkinson, "Recent developments in solar water-splitting photocatalysis," *MRS Bulletin,* vol. 36, no. 1, pp. 17-22, 2011.

[11] L. Pan *et al.*, "Advances in Piezo-Phototronic Effect Enhanced Photocatalysis and Photoelectrocatalysis," *Advanced Energy Materials,* vol. 10, no. 15, 2020.

[12] J. Tang, T. Liu, S. Miao, and Y. Cho, "Emerging Energy Harvesting Technology for Electro/Photo-Catalytic Water Splitting Application," *Catalysts,* vol. 11, no. 1, 2021.

[13] X. Li *et al.*, "Water Splitting: From Electrode to Green Energy System," *Nanomicro Lett,* vol. 12, no. 1, p. 131, Jun 17 2020.

[14] S. Y. Tee *et al.*, "Recent Progress in Energy-Driven Water Splitting," *Adv Sci (Weinh),* vol. 4, no. 5, p. 1600337, May 2017.

[15] Y. Zhang *et al.*, "High Efficiency Water Splitting using Ultrasound Coupled to a BaTiO(3) Nanofluid," *Adv Sci (Weinh),* vol. 9, no. 9, p. e2105248, Mar 2022.

[16] R. Su *et al.*, "Strain-Engineered Nano-Ferroelectrics for High-Efficiency Piezocatalytic Overall Water Splitting," *Angew Chem Int Ed Engl,* vol. 60, no. 29, pp. 16019-16026, Jul 12 2021.

[17] P. Wu *et al.*, "Electronic, Optical, piezoelectric properties and photocatalytic water splitting performance of Two-dimensional group IV-V compounds," *Applied Surface Science,* vol. 627, 2023.

[18] Y. Feng *et al.*, "Engineering spherical lead zirconate titanate to explore the essence of piezo-catalysis," *Nano Energy,* vol. 40, pp. 481-486, 2017.

[19] L. Chen *et al.*, "Facile preparation of Ag2S/KTa0.5Nb0.5O3 heterojunction for enhanced performance in catalytic nitrogen fixation via photocatalysis and piezo-photocatalysis," *Green Energy & Environment,* vol. 8, no. 6, pp. 1630-1643, 2023.

[20] L. Song, S. Sun, S. Zhang, and J. Wei, "Hydrogen production and mechanism from water splitting by metal-free organic polymers PVDF/PVDF-HFP under drive by vibrational energy," *Fuel,* vol. 324, 2022.

[21] S. Tu *et al.*, "Piezocatalysis and Piezo-Photocatalysis: Catalysts Classification and Modification Strategy, Reaction Mechanism, and Practical Application," *Advanced Functional Materials,* vol. 30, no. 48, 2020.

[22] X. Zhou, F. Yan, S. Wu, B. Shen, H. Zeng, and J. Zhai, "Remarkable Piezophoto Coupling Catalysis Behavior of BiOX/BaTiO(3) (X = Cl, Br, Cl(0.166) Br(0.834)) Piezoelectric Composites," *Small,* vol. 16, no. 26, p. e2001573, Jul 2020.

[23] S. A. Ali and T. Ahmad, "Treasure trove for efficient hydrogen evolution through water splitting using diverse perovskite photocatalysts," *Materials Today Chemistry,* vol. 29, 2023.

[24] M. L. Xu *et al.*, "Piezo-Photocatalytic Synergy in BiFeO(3) @COF Z-Scheme Heterostructures for High-Efficiency Overall Water Splitting," *Angew Chem Int Ed Engl,* vol. 61, no. 44, p. e202210700, Nov 2 2022.

[25] M. Irshad *et al.*, "Photocatalysis and perovskite oxide-based materials: a remedy for a clean and sustainable future," *RSC Adv,* vol. 12, no. 12, pp. 7009-7039, Mar 1 2022.

[26] X. Zhou, Q. Sun, D. Zhai, G. Xue, H. Luo, and D. Zhang, "Excellent catalytic performance of molten-salt-synthesized Bi0.5Na0.5TiO3 nanorods by the piezo-phototronic coupling effect," *Nano Energy*, vol. 84, 2021.

[27] Y. H. Chen, B. K. Wang, and W. C. Hou, "Graphitic carbon nitride embedded with graphene materials towards photocatalysis of bisphenol A: The role of graphene and mediation of superoxide and singlet oxygen," *Chemosphere*, vol. 278, p. 130334, Sep 2021.

[28] S. Singh and N. Khare, "Coupling of piezoelectric, semiconducting and photoexcitation properties in NaNbO 3 nanostructures for controlling electrical transport: Realizing an efficient piezo-photoanode and piezo-photocatalyst," *Nano Energy,* vol. 38, pp. 335-341, 2017.

[29] Y. Jiang *et al.*, "Efficient Cocatalyst-Free Piezo-Photocatalytic Hydrogen Evolution of Defective BaTiO3–x Nanoparticles from Seawater," *ACS Sustainable Chemistry & Engineering,* vol. 11, no. 8, pp. 3370-3389, 2023.

[30] M. Zelisko *et al.*, "Anomalous piezoelectricity in two-dimensional graphene nitride nanosheets," *Nat Commun,* vol. 5, p. 4284, Jun 27 2014.

[31] J. Wang *et al.*, "Energy and environmental catalysis driven by stress and temperature-variation," *Journal of Materials Chemistry A,* vol. 9, no. 21, pp. 12400-12432, 2021.

[32] Z. Zhao *et al.*, "Exclusive enhancement of catalytic activity in Bi0.5Na0.5TiO3nanostructures: new insights into the design of efficient piezocatalysts and piezo-photocatalysts," *Journal of Materials Chemistry A,* vol. 8, no. 32, pp. 16238-16245, 2020.

[33] J. Zhang *et al.*, "Metal-Organic-Framework-Based Photocatalysts Optimized by Spatially Separated Cocatalysts for Overall Water Splitting," *Adv Mater,* vol. 32, no. 49, p. e2004747, Dec 2020.

[34] A. M. K. Fehr *et al.*, "Integrated halide perovskite photoelectrochemical cells with solar-driven water-splitting efficiency of 20.8," *Nat Commun,* vol. 14, no. 1, p. 3797, Jun 26 2023.

[35] R. Li, "Latest progress in hydrogen production from solar water splitting via photocatalysis, photoelectrochemical, and photovoltaic-photoelectrochemical solutions," *Chinese Journal of Catalysis,* vol. 38, no. 1, pp. 5-12, 2017.

[36] A. Wei *et al.*, "Triboelectric Nanogenerator Driven Self-Powered Photoelectrochemical Water Splitting Based on Hematite Photoanodes," *ACS Nano,* vol. 12, no. 8, pp. 8625-8632, Aug 28 2018.

[37] Q. Fu *et al.*, "Improved Capture and Removal Efficiency of Gaseous Acetaldehyde by a Self-Powered Photocatalytic System with an External Electric Field," *ACS Nano,* vol. 15, no. 6, pp. 10577-10586, Jun 22 2021.

[38] M. Mumtaz, M. Hassan, S. Ullah, and Z. J. C. Ahmad, "Nanohybrids of multi-walled carbon nanotubes and cobalt ferrite nanoparticles: High performance anode material for lithium-ion batteries," vol. 171, pp. 179-187, 2021.

[39] S. Arcaro, J. Venturini, S. Arcaro, J. J. M. F. i. E. S. Venturini, Processing, and C.-E. Applications, "A Brief History of Ferrites," pp. 1-4, 2021.

[40] J. Sánchez-Martín *et al.*, "High-Pressure X-ray Diffraction and DFT Studies on Spinel FeV2O4," vol. 13, no. 1, p. 53, 2022.

[41] W. Zhang *et al.*, "Structural and magnetic properties of Ni–Cu–Co ferrites prepared from sol-gel auto combustion method with different complexing agents," vol. 816, p. 152501, 2020.

[42] J. J. E. Coey, "Perspective and prospects for rare earth permanent magnets," vol. 6, no. 2, pp. 119-131, 2020.

[43] C. de Julian Fernandez, C. Sangregorio, J. De La Figuera, B. Belec, D. Makovec, and A. J. J. o. P. D. A. P. Quesada, "Progress and prospects of hard hexaferrites for permanent magnet applications," vol. 54, no. 15, p. 153001, 2021.

[44] S. B. Narang, K. J. J. o. M. Pubby, and M. Materials, "Nickel spinel ferrites: a review," vol. 519, p. 167163, 2021.

[45] L. N. Warr and G. H. Grathoff, "Geoscientific Applications of Particle Detection and Imaging Techniques with Special Focus on Monitoring Clay Mineral Reactions," in *Handbook of Particle Detection and Imaging*: Springer, 2021, pp. 945-962.

[46] S. C. Tolani, A. Golhar, and K. Rewatkar, "A review of morphological, structural behaviour and technological applications of ferrites," in *AIP Conference Proceedings*, 2019, vol. 2104, no. 1, p. 030032: AIP Publishing LLC.

[47] V. V. Jadhav, R. S. Mane, P. V. Shinde, V. V. Jadhav, R. S. Mane, and P. V. J. B.-F.-B. E. S. Shinde, "Basics of Ferrites: Structures and Properties," pp. 37-45, 2020.

[48] I. Unit, "Orthogonality. Laguerre functions: Laguerre and associated Lauguerre polynomials, recursion relations; Orthogonality. Applications of special functions to problems in physics."

[49] G. Nicoletti, N. Arcuri, G. Nicoletti, and R. Bruno, "A technical and environmental comparison between hydrogen and some fossil fuels," *Energy Conversion and Management*, vol. 89, pp. 205-213, 2015.

[50] N. A. Owen, O. R. Inderwildi, and D. A. King, "The status of conventional world oil reserves—Hype or cause for concern?," *Energy Policy*, vol. 38, no. 8, pp. 4743-4749, 2010.

[51] M. Guo, W. Song, and J. Buhain, "Bioenergy and biofuels: History, status, and perspective," *Renewable and Sustainable Energy Reviews*, vol. 42, pp. 712-725, 2015.

[52] Z. Iqbal, Sonadia, W. Miran, A. Ul-Hamid, M. Sohail, and F. Azad, "Tailored Flower-Like Ni-Fe-MOF-Derived oxide Composites: Highly active and durable electrocatalysts for overall water splitting," *Fuel,* vol. 372, p. 132112, 2024/09/15/ 2024.

[53] F. Liu *et al.*, "Prehistoric firewood gathering on the northeast Tibetan plateau: environmental and cultural determinism," *Vegetation History and Archaeobotany,* vol. 31, no. 4, pp. 431-441, 2021.

[54] A. Syed, S. A. Zahra, A. Nasir, M. Yousaf, and S. Rizwan, "Improved electrocatalytic efficiency of nitrogen-doped Nb2CTx MXene in basic electrolyte for overall water splitting," *International Journal of Hydrogen Energy,* vol. 83, pp. 39-50, 2024/09/19/ 2024.

[55] L. J. R. Nunes, M. Casau, J. C. O. Matias, and M. F. Dias, "Coal to Biomass Transition as the Path to Sustainable Energy Production: A Hypothetical Case Scenario with the Conversion of Pego Power Plant (Portugal)," *Applied Sciences,* vol. 13, no. 7, 2023.

[56] J. Gasparotto and K. Da Boit Martinello, "Coal as an energy source and its impacts on human health," *Energy Geoscience,* vol. 2, no. 2, pp. 113-120, 2021.

[57] R. Fouquet, "The slow search for solutions: Lessons from historical energy transitions by sector and service," *Energy Policy,* vol. 38, no. 11, pp. 6586-6596, 2010.

[58] E. Ostadzadeh, A. Elshorbagy, M. Tuninetti, F. Laio, and A. Abdelkader, "Who will dominate the global fossil fuel trade?," *Economic Systems Research,* vol. 35, no. 3, pp. 354-375, 2023.

[59] T. Haas, "Comparing energy transitions in Germany and Spain using a political economy perspective," *Environmental Innovation and Societal Transitions,* vol. 31, pp. 200-210, 2019.

[60] R. Vakulchuk, I. Overland, and D. Scholten, "Renewable energy and geopolitics: A review," *Renewable and Sustainable Energy Reviews,* vol. 122, 2020.

[61] L. C. Stokes and H. L. Breetz, "Politics in the U.S. energy transition: Case studies of solar, wind, biofuels and electric vehicles policy," *Energy Policy,* vol. 113, pp. 76-86, 2018.

[62] T. O. Ogundipe *et al.*, "Nickel-cobalt phosphide terephthalic acid nano-heterojunction as excellent bifunctional electrocatalyst for overall water splitting," *Electrochimica Acta,* vol. 421, p. 140484, 2022/07/20/ 2022.

[63] B. Shabbir *et al.*, "Facile synthesis of Er-MOF/Fe2O3 nanocomposite for oxygen evolution reaction," *Materials Chemistry and Physics,* vol. 292, p. 126861, 2022/12/01/ 2022.

[64] Z.-b. Cai, Z.-y. Li, M.-g. Yin, M.-h. Zhu, and Z.-r. Zhou, "A review of fretting study on nuclear power equipment," *Tribology International,* vol. 144, 2020.

[65] M. Zeng, S. Wang, J. Duan, J. Sun, P. Zhong, and Y. Zhang, "Review of nuclear power development in China: Environment analysis, historical stages, development status, problems and countermeasures," *Renewable and Sustainable Energy Reviews,* vol. 59, pp. 1369-1383, 2016.

[66] J. M. Pearce, "Limitations of Nuclear Power as a Sustainable Energy Source," *Sustainability,* vol. 4, no. 6, pp. 1173-1187, 2012.

[67] J. Skovgaard and H. van Asselt, "The politics of fossil fuel subsidies and their reform: Implications for climate change mitigation," *WIREs Climate Change,* vol. 10, no. 4, 2019.

[68] J. Syvitski *et al.*, "Extraordinary human energy consumption and resultant geological impacts beginning around 1950 CE initiated the proposed Anthropocene Epoch," *Communications Earth & Environment,* vol. 1, no. 1, 2020.

[69] Y. F. Makogon, "Natural gas hydrates – A promising source of energy," *Journal of Natural Gas Science and Engineering,* vol. 2, no. 1, pp. 49-59, 2010.

[70] J. Curtin, C. McInerney, B. Ó Gallachóir, C. Hickey, P. Deane, and P. Deeney, "Quantifying stranding risk for fossil fuel assets and implications for renewable energy investment: A review of the literature," *Renewable and Sustainable Energy Reviews,* vol. 116, 2019.

[71] M. Lockwood, C. Kuzemko, C. Mitchell, and R. Hoggett, "Historical institutionalism and the politics of sustainable energy transitions: A research agenda," *Environment and Planning C: Politics and Space,* vol. 35, no. 2, pp. 312-333, 2016.

[72] D. Shindell and C. J. Smith, "Climate and air-quality benefits of a realistic phase-out of fossil fuels," *Nature,* vol. 573, no. 7774, pp. 408-411, Sep 2019.

[73] K. Bhattarai, W. M. Stalick, S. McKay, G. Geme, and N. Bhattarai, "Biofuel: an alternative to fossil fuel for alleviating world energy and economic crises," *J Environ Sci Health A Tox Hazard Subst Environ Eng,* vol. 46, no. 12, pp. 1424-42, 2011.

[74] K. Bos and J. Gupta, "Climate change: the risks of stranded fossil fuel assets and resources to the developing world," *Third World Quarterly,* vol. 39, no. 3, pp. 436-453, 2017.

[75] N. Scovronick *et al.*, "Air Quality and Health Impacts of Future Ethanol Production and Use in Sao Paulo State, Brazil," *Int J Environ Res Public Health,* vol. 13, no. 7, Jul 11 2016.

[76] V. Shakeel, I. Hussain Gul, P. John, and A. Bhatti, "Biocompatible gelatin-coated ferrite nanoparticles: A magnetic approach to advanced drug delivery," *Saudi Pharmaceutical Journal,* vol. 32, no. 6, p. 102066, 2024/06/01/ 2024.

[77] K. Moustakas, M. Loizidou, M. Rehan, and A. S. Nizami, "A review of recent developments in renewable and sustainable energy systems: Key challenges and future perspective," *Renewable and Sustainable Energy Reviews,* vol. 119, 2020.

[78] A. K. Azad, M. G. Rasul, M. M. K. Khan, S. C. Sharma, and M. A. Hazrat, "Prospect of biofuels as an alternative transport fuel in Australia," *Renewable and Sustainable Energy Reviews*, vol. 43, pp. 331-351, 2015.

[79] P. A. Owusu, S. Asumadu-Sarkodie, and S. Dubey, "A review of renewable energy sources, sustainability issues and climate change mitigation," *Cogent Engineering,* vol. 3, no. 1, 2016.

[80] H. A. Kazem and M. T. Chaichan, "Status and future prospects of renewable energy in Iraq," *Renewable and Sustainable Energy Reviews*, vol. 16, no. 8, pp. 6007-6012, 2012.

[81] P. A. Østergaard, N. Duic, Y. Noorollahi, and S. Kalogirou, "Renewable energy for sustainable development," *Renewable Energy,* vol. 199, pp. 1145-1152, 2022.

[82] N. Kannan and D. Vakeesan, "Solar energy for future world: - A review," *Renewable and Sustainable Energy Reviews,* vol. 62, pp. 1092-1105, 2016.

[83] Z. Zakaria, S. K. Kamarudin, K. A. Abd Wahid, and S. H. Abu Hassan, "The progress of fuel cell for malaysian residential consumption: Energy status and prospects to introduction as a renewable power generation system," *Renewable and Sustainable Energy Reviews*, vol. 144, 2021.

[84] M. T. Ross and B. C. Murray, "What is the fuel of the future? Prospects under the Clean Power Plan," *Energy Economics*, vol. 60, pp. 451-459, 2016.

[85] S. Masoudi Soltani, A. Lahiri, H. Bahzad, P. Clough, M. Gorbounov, and Y. Yan, "Sorption-enhanced Steam Methane Reforming for Combined CO2 Capture and Hydrogen Production: A State-of-the-Art Review," *Carbon Capture Science & Technology,* vol. 1, 2021.

[86] S. Wang, S. A. Nabavi, and P. T. Clough, "A review on bi/polymetallic catalysts for steam methane reforming," *International Journal of Hydrogen Energy,* vol. 48, no. 42, pp. 15879-15893, 2023.

[87] S. A. Bhat and J. Sadhukhan, "Process intensification aspects for steam methane reforming: An overview," *AIChE Journal,* vol. 55, no. 2, pp. 408-422, 2009.

[88] H. T. Arat and M. G. SÜRer, "State of art of hydrogen usage as a fuel on aviation," *European Mechanical Science,* vol. 2, no. 1, pp. 20-30, 2017.

[89] F. Safari and I. Dincer, "A review and comparative evaluation of thermochemical water splitting cycles for hydrogen production," *Energy Conversion and Management,* vol. 205, 2020.

[90] M. Mehrpooya and R. Habibi, "A review on hydrogen production thermochemical water-splitting cycles," *Journal of Cleaner Production,* vol. 275, 2020.

[91] C. L. Muhich, B. D. Ehrhart, I. Al-Shankiti, B. J. Ward, C. B. Musgrave, and A. W. Weimer, "A review and perspective of efficient hydrogen generation via solar thermal water splitting," *WIREs Energy and Environment,* vol. 5, no. 3, pp. 261-287, 2015.

[92] A. A. Ahmad, N. A. Zawawi, F. H. Kasim, A. Inayat, and A. Khasri, "Assessing the gasification performance of biomass: A review on biomass gasification process conditions, optimization and economic evaluation," *Renewable and Sustainable Energy Reviews,* vol. 53, pp. 1333-1347, 2016.

[93] S. Singh Siwal, Q. Zhang, C. Sun, S. Thakur, V. Kumar Gupta, and V. Kumar Thakur, "Energy production from steam gasification processes and parameters that contemplate in biomass gasifier - A review," *Bioresour Technol,* vol. 297, p. 122481, Feb 2020.

[94] T. K. Patra and P. N. Sheth, "Biomass gasification models for downdraft gasifier: A state-of-the-art review," *Renewable and Sustainable Energy Reviews,* vol. 50, pp. 583-593, 2015.

[95] S. K. Sansaniwal, K. Pal, M. A. Rosen, and S. K. Tyagi, "Recent advances in the development of biomass gasification technology: A comprehensive review," *Renewable and Sustainable Energy Reviews,* vol. 72, pp. 363-384, 2017.

[96] S. Safarian, R. Unnþórsson, and C. Richter, "A review of biomass gasification modelling," *Renewable and Sustainable Energy Reviews,* vol. 110, pp. 378-391, 2019.

[97] L. Singh and Z. A. Wahid, "Methods for enhancing bio-hydrogen production from biological process: A review," *Journal of Industrial and Engineering Chemistry,* vol. 21, pp. 70-80, 2015.

[98] I. K. Kapdan and F. Kargi, "Bio-hydrogen production from waste materials," *Enzyme and Microbial Technology,* vol. 38, no. 5, pp. 569-582, 2006.

[99] D. D. T. Ferraren-De Cagalitan and M. L. S. Abundo, "A review of biohydrogen production technology for application towards hydrogen fuel cells," *Renewable and Sustainable Energy Reviews,* vol. 151, 2021.

[100] M. Wang, Z. Wang, X. Gong, and Z. Guo, "The intensification technologies to water electrolysis for hydrogen production – A review," *Renewable and Sustainable Energy Reviews,* vol. 29, pp. 573-588, 2014.

[101] J. Chi and H. Yu, "Water electrolysis based on renewable energy for hydrogen production," *Chinese Journal of Catalysis,* vol. 39, no. 3, pp. 390-394, 2018.

[102] W. Han, M. Li, Y. Ma, and J. Yang, "Cobalt-Based Metal-Organic Frameworks and Their Derivatives for Hydrogen Evolution Reaction," *Front Chem,* vol. 8, p. 592915, 2020.

[103] A. Ursua, L. M. Gandia, and P. Sanchis, "Hydrogen Production From Water Electrolysis: Current Status and Future Trends," *Proceedings of the IEEE,* vol. 100, no. 2, pp. 410-426, 2012.

[104] S. Shiva Kumar and V. Himabindu, "Hydrogen production by PEM water electrolysis – A review," *Materials Science for Energy Technologies,* vol. 2, no. 3, pp. 442-454, 2019.

[105] S. Shiva Kumar and H. Lim, "An overview of water electrolysis technologies for green hydrogen production," *Energy Reports,* vol. 8, pp. 13793-13813, 2022.

[106] S. Wang, A. Lu, and C. J. Zhong, "Hydrogen production from water electrolysis: role of catalysts," *Nano Converg,* vol. 8, no. 1, p. 4, Feb 11 2021.

[107] M. Ahmed and I. Dincer, "A review on photoelectrochemical hydrogen production systems: Challenges and future directions," *International Journal of Hydrogen Energy,* vol. 44, no. 5, pp. 2474-2507, 2019.

[108] M. D. Bhatt and J. S. Lee, "Recent theoretical progress in the development of photoanode materials for solar water splitting photoelectrochemical cells," *Journal of Materials Chemistry A,* vol. 3, no. 20, pp. 10632-10659, 2015.

[109] L. Clarizia, M. N. Nadagouda, and D. D. Dionysiou, "Recent advances and challenges of photoelectrochemical cells for hydrogen production," *Current Opinion in Green and Sustainable Chemistry,* vol. 41, 2023.

[110] B. Y. Alfaifi, H. Ullah, S. Alfaifi, A. A. Tahir, and T. K. Mallick, "Photoelectrochemical solar water splitting: From basic principles to advanced devices," *Veruscript Functional Nanomaterials,* vol. 2, 2018.

[111] N. S. Hassan *et al.*, "Recent review and evaluation of green hydrogen production via water electrolysis for a sustainable and clean energy society," *International Journal of Hydrogen Energy,* 2023.

[112] F. Mumtaz *et al.*, "Optimization of z-scheme Bi0.5Na0.5TiO3/RGO-Co3O4 composite catalyst for water splitting reaction through piezo-photocatalysis," *International Journal of Hydrogen Energy,* vol. 78, pp. 1468-1480, 2024/08/12/ 2024.

[113] C. Acar and I. Dincer, "A review and evaluation of photoelectrode coating materials and methods for photoelectrochemical hydrogen production," *International Journal of Hydrogen Energy,* vol. 41, no. 19, pp. 7950-7959, 2016.

[114] J. Ekspong *et al.*, "Solar-Driven Water Splitting at 13.8% Solar-to-Hydrogen Efficiency by an Earth-Abundant Electrolyzer," *ACS Sustainable Chemistry & Engineering,* vol. 9, no. 42, pp. 14070-14078, 2021.

[115] J. M. Yu *et al.*, "High-performance and stable photoelectrochemical water splitting cell with organic-photoactive-layer-based photoanode," *Nat Commun,* vol. 11, no. 1, p. 5509, Nov 2 2020.

[116] M. F. R. Samsudin, "Photovoltaic-Assisted Photo(electro)catalytic Hydrogen Production: A Review," *Energies,* vol. 16, no. 15, 2023.

[117] M. Tayebi and B.-K. Lee, "Recent advances in BiVO4 semiconductor materials for hydrogen production using photoelectrochemical water splitting," *Renewable and Sustainable Energy Reviews,* vol. 111, pp. 332-343, 2019.

[118] P. Varadhan, H. C. Fu, Y. C. Kao, R. H. Horng, and J. H. He, "An efficient and stable photoelectrochemical system with 9% solar-to-hydrogen conversion

efficiency via InGaP/GaAs double junction," *Nat Commun,* vol. 10, no. 1, p. 5282, Nov 21 2019.

[119] J. H. Kim, D. Hansora, P. Sharma, J. W. Jang, and J. S. Lee, "Toward practical solar hydrogen production - an artificial photosynthetic leaf-to-farm challenge," *Chem Soc Rev,* vol. 48, no. 7, pp. 1908-1971, Apr 1 2019.

[120] V. Preethi and S. Kanmani, "Photocatalytic hydrogen production," *Materials Science in Semiconductor Processing,* vol. 16, no. 3, pp. 561-575, 2013.

[121] A. R. Araujo Scharnberg, A. Carvalho de Loreto, and A. Kopp Alves, "Optical and Structural Characterization of Bi2FexNbO7 Nanoparticles for Environmental Applications," *Emerging Science Journal,* vol. 4, no. 1, pp. 11-17, 2020.

[122] H. Idriss, "Hydrogen production from water: past and present," *Current Opinion in Chemical Engineering,* vol. 29, pp. 74-82, 2020.

[123] Y. Lim, D. K. Lee, S. M. Kim, W. Park, S. Y. Cho, and U. Sim, "Low Dimensional Carbon-Based Catalysts for Efficient Photocatalytic and Photo/Electrochemical Water Splitting Reactions," *Materials (Basel),* vol. 13, no. 1, Dec 25 2019.

[124] C. Acar, I. Dincer, and C. Zamfirescu, "A review on selected heterogeneous photocatalysts for hydrogen production," *International Journal of Energy Research,* vol. 38, no. 15, pp. 1903-1920, 2014.

[125] M. Xiao *et al.*, "Addressing the stability challenge of metal halide perovskite based photocatalysts for solar fuel production," *Journal of Physics: Energy,* vol. 4, no. 4, 2022.

[126] S. Cao, J. Low, J. Yu, and M. Jaroniec, "Polymeric photocatalysts based on graphitic carbon nitride," *Adv Mater,* vol. 27, no. 13, pp. 2150-76, Apr 1 2015.

[127] L. Jiang *et al.*, "Doping of graphitic carbon nitride for photocatalysis: A review," *Applied Catalysis B: Environmental,* vol. 217, pp. 388-406, 2017.

[128] G. Liu *et al.*, "Enhancement of the photoelectrochemical water splitting by perovskite BiFeO3 via interfacial engineering," *Solar Energy,* vol. 202, pp. 198-203, 2020.

[129] T. Hisatomi, K. Takanabe, and K. Domen, "Photocatalytic Water-Splitting Reaction from Catalytic and Kinetic Perspectives," *Catalysis Letters*, vol. 145, no. 1, pp. 95-108, 2014.

[130] S. Das *et al.*, "High performance BiFeO(3) ferroelectric nanostructured photocathodes," *J Chem Phys,* vol. 153, no. 8, p. 084705, Aug 28 2020.

[131] Y. Yan, Z. Chen, X. Cheng, and W. Shi, "Research Progress of ZnIn2S4-Based Catalysts for Photocatalytic Overall Water Splitting," *Catalysts,* vol. 13, no. 6, 2023.

[132] A. V. Zhurenok, D. B. Vasilchenko, and E. A. Kozlova, "Comprehensive Review on g-C(3)N(4)-Based Photocatalysts for the Photocatalytic Hydrogen Production under Visible Light," *Int J Mol Sci*, vol. 24, no. 1, Dec 25 2022.

[133] J. Y. Kim and D. H. Youn, "Nanomaterials for Advanced Photocatalytic Plastic Conversion," *Molecules*, vol. 28, no. 18, Sep 7 2023.

[134] K. H. Ng, S. Y. Lai, C. K. Cheng, Y. W. Cheng, and C. C. Chong, "Photocatalytic water splitting for solving energy crisis: Myth, Fact or Busted?," *Chemical Engineering Journal,* vol. 417, 2021.

[135] Z. Yan, H. Wu, A. Han, X. Yu, and P. Du, "Noble metal-free cobalt oxide (CoO) nanoparticles loaded on titanium dioxide/cadmium sulfide composite for enhanced photocatalytic hydrogen production from water," *International Journal of Hydrogen Energy,* vol. 39, no. 25, pp. 13353-13360, 2014.

[136] C. Acar, I. Dincer, and G. F. Naterer, "Review of photocatalytic water-splitting methods for sustainable hydrogen production," *International Journal of Energy Research,* vol. 40, no. 11, pp. 1449-1473, 2016.

[137] V. Dal Santo and A. Naldoni, "Titanium Dioxide Photocatalysis," *Catalysts,* vol. 8, no. 12, 2018.

[138] S. Horikoshi and N. Serpone, "Can the photocatalyst TiO2 be incorporated into a wastewater treatment method? Background and prospects," *Catalysis Today,* vol. 340, pp. 334-346, 2020.

[139] B. A. Bhanvase, T. P. Shende, and S. H. Sonawane, "A review on graphene–TiO2 and doped graphene–TiO2 nanocomposite photocatalyst for water and wastewater treatment," *Environmental Technology Reviews,* vol. 6, no. 1, pp. 1-14, 2016.

[140] D. J. Martin, P. J. Reardon, S. J. Moniz, and J. Tang, "Visible light-driven pure water splitting by a nature-inspired organic semiconductor-based system," *J Am Chem Soc,* vol. 136, no. 36, pp. 12568-71, Sep 10 2014.

[141] Z. Mamiyev and N. O. Balayeva, "Metal Sulfide Photocatalysts for Hydrogen Generation: A Review of Recent Advances," *Catalysts,* vol. 12, no. 11, 2022.

[142] T. F. Qahtan, T. O. Owolabi, O. E. Olubi, and A. Hezam, "State-of-the-art, challenges and prospects of heterogeneous tandem photocatalysis," *Coordination Chemistry Reviews,* vol. 492, 2023.

[143] S. Liu, K. Yin, W. Ren, B. Cheng, and J. Yu, "Tandem photocatalytic oxidation of Rhodamine B over surface fluorinated bismuth vanadate crystals," *Journal of Materials Chemistry,* vol. 22, no. 34, 2012.

[144] T. Li, N. Tsubaki, and Z. Jin, "S-scheme heterojunction in photocatalytic hydrogen production," *Journal of Materials Science & Technology,* vol. 169, pp. 82-104, 2024.

[145] Y. Jing, Z. Zhou, W. Geng, X. Zhu, and T. Heine, "2D Honeycomb-Kagome Polymer Tandem as Effective Metal-Free Photocatalysts for Water Splitting," *Adv Mater,* vol. 33, no. 21, p. e2008645, May 2021.

[146] S. Navalon, A. Dhakshinamoorthy, M. Alvaro, B. Ferrer, and H. Garcia, "Metal-Organic Frameworks as Photocatalysts for Solar-Driven Overall Water Splitting," *Chem Rev,* vol. 123, no. 1, pp. 445-490, Jan 11 2023.

[147] Y. Bai *et al.*, "Photocatalytic Overall Water Splitting Under Visible Light Enabled by a Particulate Conjugated Polymer Loaded with Palladium and Iridium," *Angew Chem Int Ed Engl,* vol. 61, no. 26, p. e202201299, Jun 27 2022.

[148] J. Liu *et al.*, "Enhanced visible-light photocatalytic performances of ZnO through loading AgI and coupling piezo-photocatalysis," *Journal of Alloys and Compounds,* vol. 852, 2021.

[149] G. Cilaveni, K. V. Ashok Kumar, S. S. K. Raavi, C. Subrahmanyam, and S. Asthana, "Control over relaxor, piezo-photocatalytic and energy storage properties in Na0.5Bi0.5TiO3 via processing methodologies," *Journal of Alloys and Compounds,* vol. 798, pp. 540-552, 2019.

[150] X. Xu, X. Lin, F. Yang, S. Huang, and X. Cheng, "Piezo-photocatalytic Activity of Bi0.5Na0.5TiO3@TiO2 Composite Catalyst with Heterojunction for Degradation of Organic Dye Molecule," *The Journal of Physical Chemistry C,* vol. 124, no. 44, pp. 24126-24134, 2020.

[151] W. Qian, K. Zhao, D. Zhang, C. R. Bowen, Y. Wang, and Y. Yang, "Piezoelectric Material-Polymer Composite Porous Foam for Efficient Dye Degradation via the Piezo-Catalytic Effect," *ACS Appl Mater Interfaces,* vol. 11, no. 31, pp. 27862-27869, Aug 7 2019.

[152] S. Li, Z. Zhao, J. Zhao, Z. Zhang, X. Li, and J. Zhang, "Recent Advances of Ferro-, Piezo-, and Pyroelectric Nanomaterials for Catalytic Applications," *ACS Applied Nano Materials,* vol. 3, no. 2, pp. 1063-1079, 2020.

[153] Y. Xia *et al.*, "Pyroelectrically Induced Pyro-Electro-Chemical Catalytic Activity of BaTiO3 Nanofibers under Room-Temperature Cold–Hot Cycle Excitations," *Metals,* vol. 7, no. 4, 2017.

[154] X. Xu *et al.*, "Strong piezo-electro-chemical effect of piezoelectric BaTiO3 nanofibers for vibration-catalysis," *Journal of Alloys and Compounds,* vol. 762, pp. 915-921, 2018.

[155] A. Al Nafiey *et al.*, "Reduced graphene oxide decorated with Co3O4 nanoparticles (rGO-Co3O4) nanocomposite: A reusable catalyst for highly efficient reduction of 4-nitrophenol, and Cr(VI) and dye removal from aqueous solutions," *Chemical Engineering Journal,* vol. 322, pp. 375-384, 2017.

[156] Y. Wang *et al.*, "Piezo-catalysis for nondestructive tooth whitening," *Nat Commun,* vol. 11, no. 1, p. 1328, Mar 12 2020.

[157] R. Su *et al.*, "Nano-Ferroelectric for High Efficiency Overall Water Splitting under Ultrasonic Vibration," *Angew Chem Int Ed Engl,* vol. 58, no. 42, pp. 15076-15081, Oct 14 2019.

[158] D. Masekela, N. C. Hintsho-Mbita, B. Ntsendwana, and N. Mabuba, "Thin Films (FTO/BaTiO(3)/AgNPs) for Enhanced Piezo-Photocatalytic Degradation of Methylene Blue and Ciprofloxacin in Wastewater," *ACS Omega,* vol. 7, no. 28, pp. 24329-24343, Jul 19 2022.

[159] F. Bößl and I. Tudela, "Piezocatalysis: Can catalysts really dance?," *Current Opinion in Green and Sustainable Chemistry,* vol. 32, 2021.

[160] L. Chen *et al.*, "Strong piezocatalysis in barium titanate/carbon hybrid nanocomposites for dye wastewater decomposition," *J Colloid Interface Sci,* vol. 586, pp. 758-765, Mar 15 2021.

[161] S. Tu *et al.*, "Band shifting triggered ·OH evolution and charge separation enhanced H2O2 generation in piezo-photocatalysis of Silleń-Aurivillius-structured Bi4W0.5Ti0.5O8Cl," *Chemical Engineering Journal,* vol. 465, 2023.

[162] P. Wang, Y. Zong, H. Liu, H. Wen, H.-B. Wu, and J.-B. Xia, "Highly efficient photocatalytic water splitting and enhanced piezoelectric properties of 2D Janus group-III chalcogenides," *Journal of Materials Chemistry C,* vol. 9, no. 14, pp. 4989-4999, 2021.

[163] M. K. Mohanta, A. Rawat, Dimple, N. Jena, R. Ahammed, and A. De Sarkar, "Superhigh out-of-plane piezoelectricity, low thermal conductivity and photocatalytic abilities in ultrathin 2D van der Waals heterostructures of boron monophosphide and gallium nitride," *Nanoscale,* vol. 11, no. 45, pp. 21880-21890, Nov 21 2019.

[164] Q. Zhang, S. Zuo, P. Chen, and C. Pan, "Piezotronics in two-dimensional materials," *InfoMat,* vol. 3, no. 9, pp. 987-1007, 2021.

[165] M. Junaid *et al.*, "Structural, microstructural, spectral, and dielectric properties of erbium substituted spinel ferrites," vol. 641, p. 414120, 2022.

[166] X. Huang *et al.*, "Insight into the piezo-photo coupling effect of PbTiO3/CdS composites for piezo-photocatalytic hydrogen production," *Applied Catalysis B: Environmental,* vol. 282, 2021.