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SYED AHMAD RAZA

SU92-MSCHW-F23-010

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**Band Gap Engineering of Binary Metal Complex Doped with Graphene for Carbon
Dioxide Photoreduction**



SUPERIOR UNIVERSITY

Thesis Submitted to

The Superior University Lahore

In Partial Fulfillment of the

Requirement for the Degree of

M.Phil. Chemistry

By

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No part of this thesis has been submitted anywhere else for any other degree. This thesis is submitted to the Faculty of Sciences, The Superior University, Lahore in partial fulfillment of the requirements for the degree of Master of Philosophy in the field of “**Chemistry**” in Faculty of Sciences at The Superior University, Lahore.

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Dedication

This thesis is dedicated with deepest love and gratitude to my beloved parents, whose endless prayers, sacrifices, and unconditional support have been the foundation of all my achievements. Their love is the light that guided me through every difficulty.

I also dedicate this work to my respected supervisor, Dr. Fizza Naseem, whose constant guidance, encouragement, and sincere concern made this journey possible. Her mentorship has not only enriched my research but also inspired me personally, for which I will always remain grateful.

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List of Abbreviations

WO_3	Tungsten Oxide
SnO_2	Tin Oxide
HCOOH	Formic Acid
CO_2RR	Carbon Dioxide Reduction Reaction
Ga_2O_3	Gallium Oxide
ZrO_2	Zirconium Dioxide
Y_2O_3	Yttrium Oxide
MgO	Magnesium Oxide
La_2O_3	Lanthanum Oxide

ABSTRACT

The potential of artificial photosynthesis to efficiently convert carbon dioxide into clean fuels has garnered attention. It is necessary to use photocatalysts that can absorb visible light. To overcome the concern of having carbon dioxide emissions in the atmosphere, CuO/CuFe₂O₄ as a binary composite and CuO/CuFe₂O₄-doped graphene oxide as a ternary composite were found to be good photocatalysts in the transformation of carbon dioxide into methanol and carbon monoxide. Each binary composite only promote the formation of carbon monoxide, but upon the addition of graphene oxide, not only carbon monoxide but also methanol will be formed. Graphene doping mediates new band gap energy levels, which enhanced the photocatalytic activity of the metal complex as compared to individually. The photocatalytic performance of the synthesized photocatalysts has been explained in this thesis. Various spectroscopic, microscopic, and electrochemical methods were employed to characterize the synthesized nanocomposites, including FTIR analysis, UV-visible spectroscopy, SEM, XRD, PL spectroscopy, electrochemical impedance spectroscopy, and XPS. The characterization methods suggest the successful synthesis of the desired photocatalysts. Gas chromatography has been used to measure methanol yield while carbon monoxide detected through portable air quality detector. The reaction is carried out for 3 hours under controlled temperature and pressure, and a sample is taken after every hour for methanol detection, and the detector reading is monitored also for carbon monoxide production. The maximum methanol and carbon monoxide yields achieved were $1.40 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ and 120 PPM, respectively, through the photocatalytic activity of CuO/CuFe₂O₄-doped graphene oxide. While on the other hand, CuO doped CuFe₂O₄ produced a maximum yield of carbon monoxide, which was 75 ppm. Present research focused on engineering the band gap to get maximum output of photocatalysts for carbon dioxide reduction.

CHAPTER 1

INTRODUCTION

A change in the Earth's climate that lasts for decades or even centuries is referred to as climate change. This includes variations in temperature, precipitation, wind patterns, and extreme weather occurrences. Escalating alarm regarding climate change is one of the major problems of our time. Over the past few decades, there has been an extraordinary warming of the Earth's weather. Between 1880 and 2012, there was an increase of 0.85°C in the average worldwide surface temperature. A major contributing factor to the change in our climate is the use of fossil fuels, industrialization, garbage mishandling, agriculture, urbanization, and greenhouse gas emissions. The weather, wildlife, food, water, health, and even human habitation are all impacted by global warming. The effects of global warming may have a substantial effect on the health of living creatures. Excessive heat can worsen heart disease and stress. An excessive amount of heat may cause stress. Global warming-related famines and crop failures may weaken people's resistance to viruses and illness [1-3].

1.1 Effect of Greenhouse Gases on Global Warming

Greenhouse gas emissions are a major contributor to global warming. Atmospheric chemicals known as greenhouse gases trap infrared radiation, preventing heat from escaping into space and causing global warming. The natural greenhouse effects keeps Earth's average surface around 15°C, which is about 33°C warmer than it would be without these gases. At least three atoms make up greenhouse gases. These gases can retain heat in the atmosphere and subsequently transfer it to the surface, further warming the Earth, according to their molecular structure. This continuous cycle of heat trapping is a sign that global temperatures are rising. They consist of fluorinated gases, carbon dioxide, methane, and nitrous oxide [4].

1.2 Carbon Dioxide as a Major Greenhouse Gas

One of the principle greenhouse gas is carbon dioxide increasing CO₂ is arguably the most significant cause of global warming and climate change, and it is widely acknowledged by scientific societies and research organizations worldwide that global warming is real and mostly caused by human activity. In May 2013 atmospheric

carbon dioxide levels passed the record 400 parts per million. On May 2, 2019, the reading at Mauna Loa Observatory was 415 ppm. Why can't we convert CO₂ into useful products like is one question that might come up. The issue with CO₂ is that it is difficult to convert into other compounds. Since it is the most oxidized form of carbon, it has a fairly stable thermodynamic state. Consequently, a substantial amount of energy will be needed for every chemical process containing CO₂. To put it briefly, its Gibbs energy of formation is enormous and negative. One carbon atom is involved, and each side is connected to an oxygen atom. When the carbon dioxide molecule's atoms are thoroughly joined, it can absorb infrared light and begin to vibrate. By the time the vibrating molecule dissipates the radiation, an additional molecule of a different greenhouse gas is most likely to absorb the radiation. This absorption-emission-absorption cycle is an effective means of insulating the surface to the cold temperatures of space because the heat is retained close to the surface [5].

It means that the process of turning carbon dioxide, the main greenhouse gas, into clean fuels is needed to eliminate the climate change and fossil fuel dependence problems. Scientific research in recent years has focused on developing new technologies that efficiently transform, CO₂ as valuable goods. Many novel approaches to CO₂ reduction have been put forth, including bio-electrochemical systems, photocatalysis, electrochemical conversion, artificial photosynthesis, and carbon capture and utilization. In addition to halting climate change, these tactics enable the creation of useful chemicals and fuel [6-8].

1.2.1 Electrochemical Conversion

It uses electrical energy in renewable resources to alter carbon dioxide into products that have more value. Carbon dioxide reduction would be done at the cathode working on an electrochemical cell when an electrocatalyst and electrolyte are added. This approach does have some shortcomings, though, which must be fixed. For instance, low temperature fuel cells and CO₂ electrolysis cells are both frequently constrained by cathode performance; therefore, both aim to increase slow cathode kinetics by creating more active catalysts. Although the catalyst for CO₂ reduction must be active, it must also have high product selectivity in order to suppress undesirable reactions and greatly favor the creation of desired products. Additionally, it is crucial for both

fuel cells and CO₂ electrolysis cells to remove products from the catalyst layer effectively in order to prevent clogging of active sites [9].

1.2.2 Thermochemical Conversion

A very high temperature (>2500K) and pressure are necessary for the thermochemical conversion of carbon dioxide in order to convert it into solar fuels like methanol and others. It achieves a high rate of reaction, which leads to a recombination process and the creation of a hazardous product mixture .requires expensive clean hydrogen; deactivation of the catalyst as a result of carbon deposition or sintering; and intricate heat control [10].

1.2.3 Photocatalytic Conversion

Photocatalysis is therefore highly important in order to complete chemical transformations of synthetic interest with minimum negative impact on the environment. In reality photochemical reactions require milder conditions than the thermal ones. They can also be able to design short yet effective reaction series which will reduce side effects. All light-induced catalytic processes can be broadly characterized as photocatalysis since the term refers to spontaneous events in the appropriate physical domains. For photocatalysis, it makes use of a photocatalyst. A material that uses light energy to accelerate chemical reactions without being consumed is referred to as a photocatalyst. It produces excited carriers of charge that can start a redox reaction after absorbing light [11]. Photocatalysts are often semiconductors, such as titanium dioxide (TiO₂). Zinc oxide (ZnO), carbon nitride graphitic (g-C₃N₄), bismuth vanadate (BiVO₄), CuO material heterojunctions, or boron nitride. This material acts as a semiconductor photocatalyst, whereby, sunlight is absorbed when the energy in the incident photons is greater or equal to the band gap of the semiconductor (E_g). This means that as an electron is pushed out of the valence band (VB) region of the semiconductor into the conduction band a vacancy, a hole is created in the VB region. Photocatalytic reduction, such as that of CO₂, can be carried out using the photoexcited electron by these steps;

1. Charge carrier photoexcitation
2. Charge diffusion and carrier separation to the surface of the photocatalyst
3. The catalyst surface's oxidation and reduction reaction [12]

1.2.3.1 Challenges in Photocatalytic Conversion of CO₂

However, despite its potential, its effectiveness and commercial use are constrained by a number of scientific, technological, and practical issues. A thorough explanation of these difficulties is provided below:

1. Reaction Pathways and Product Selectivity
2. Charge Transfer Mechanism
3. Overestimate of Product Yield
4. Low efficiency and Quantum yield
5. Poor stability of photocatalyst [13]

1.3 Band Gap Engineering

One such method in development of effective photocatalysts is the band-gap engineering since it provides the means of controlling the optical and electrical properties of semiconductors. Core/shell design is an attractive option as charge carrier recombination is virtually eliminated and light harvesting range significantly expanded, both of which are vital to photocatalysis performance enhancement. Despite progress, we still do not have highly effective catalysts that can initiate photocatalytic reactions like CO₂ reduction with adequate effectiveness. Band engineering offers a route to break this limitation by creating catalysts with suitable band gaps that are engineered to suit special reactions. The right photocatalyst should possess an optimal band gap that facilitates the thermodynamically viable electron and hole transfer to start and maintain the target chemical processes. Concurrently, the band gap must be sufficiently small to facilitate absorption of a considerable part of the solar spectrum, particularly visible light. Thus, the ideal balance in band gap energy must be achieved for optimal light absorption and effective photocatalysis [14, 15].

Metal or nonmetal doping, heterojunction formation, defect structuring, and surface coverage with carbon materials all can be forms of engineering a band gap [16, 17].

1.4 Doping

Doping is one of the important areas of research in photocatalysis, making a contribution of approximately 20% of all studies in this field. Doping involves the deliberate inclusion of foreign atoms in the crystal structure of a photocatalyst to

improve its electronic and optical performance. There are several advantages this process has to offer:

1. Increased absorption of the light: Through doping, the band gap between the materials can be reduced so that a greater amount of light, both in visible wavelength as well as infrared can be absorbed.
2. The band level may be adjusted so that the conduction/valence bands resonate with the lower/higher energies needed in processes such as water splitting.
3. Improved charge carrier dynamics: Doping assists with trapping and stabilizing charge carriers (holes and electrons), lessening their recombination and enhancing overall efficiency.
4. Enhanced macrocyclic surface properties: This enhances the number of surface reactive sites and helps in adsorbing reactants as well as charge transfer during the reaction [18].

1.5 Heterojunction

Heterojunction is the term used for the interface that occurs between two semiconductors with dissimilar band structures to result in particular band alignments. Formation of heterojunction is highly practical and a highly efficient technique in the preparation of high performing photocatalysts in the separation of photoinduced electron hole pairs in photocatalysts pronounced by the fact that it facilitates effective spatial separation of charge carriers on the heterojoint in semiconductor based photocatalysts [19]. The role of the heterojunction is enhancing the separation efficiency of electron hole pairs. To prevent the recombination of the photogenerated electrons and holes a well-defined heterojunction can be formed using two semiconductors with a similar electronic band structure. The efficacy of electron-hole interaction separation is better in p-n heterojunctions. The point of contact between two semiconductors one with acceptor (p-type), and other with a donor (n-type) is known as p-n heterojunction. The concentration of positively and negatively ions is high around the junction because of which strong local electric field is created pointing toward n-p. This increases the quantum efficiency of the photocatalytic reactions by better separating the electrons and holes produced by the photosynthesis with the aid of the differential electric potential caused by the electric field [20].

1.6 Defects Engineering

Defects are a common and intrinsic feature in crystal structures, particularly in material science. Their presence is even more common as materials are transformed into the nanoscale. Defects exist in different forms and can be classified according to their spatial nature. Zero-dimensional point defects are the simplest form among them and consist of vacancies and impurity atoms. Vacancies, especially in metal oxides, are some of the best-characterized. Oxygen vacancies occur when oxygen atoms are withdrawn from the lattice, resulting in the presence of coordinatively unsaturated metal sites and an excess electron accumulation. In semiconductors, which are the key materials in photocatalysis, defects directly affect the electronic properties. The fine control and introduction of these structural defects enable the tuning of electrical conductivity, charge carrier density, and band gap energy, which can greatly improve the material's photocatalytic activity [21].

1.7 Selection Criteria for Photocatalytic Materials

The choice of photocatalyst materials is a critical part of the process for CO₂ photoreduction because it determines various essential elements like the reaction pathway, the nature of the light absorbed, the potential end products, and the reaction efficiency and yield. It is one of the fields of study to still explore on selecting the right photocatalyst since this is critical. Researchers have investigated a wide variety of materials showing promise for CO₂ reduction, including metal oxides, sulfides, nitrides, and carbides above them. Metal oxide semiconductors are most widely used because they are highly efficient photocatalysts for CO₂ conversion [22].

1.8 Metal Oxides

An essential class of compounds for photocatalysis and the electronics sector are metal oxide semiconductors, which have a bandgap of 2-4 eV. Since there is a growing need for these materials, particularly in the field of photocatalysis, recent study is focused on creating nanoscale metal oxide particles that lower material prices by increasing the surface-to-volume ratio. The capacity to properly absorb light is a crucial attribute for photocatalysis. However, the absorptions are only found in the ultraviolet spectrum because of the broad bandgap of metal oxide semiconductors. It is convenient to dope these metal oxide nanoparticles to provide a greater variety of wavelengths and physical properties [23, 24].

1.9 Copper Oxide

The semiconducting monoclinic compound is known as copper oxide (CuO). Some of its potentially favorable physical properties are spin dynamics, electron correlation effects, and high-temperature superconductivity. It is the basic member of the family of copper compounds. CuO comprises one of the p-type semiconductors in the transition metal oxides with small band gap of 1.2 eV. CuO is getting much attention due to the possibility of many diverse technological applications. It finds widespread application in solar energy conversion, high-temperature superconductors, batteries, gas sensors, field emission devices, and catalysis. Nanofluids containing CuO nanoparticles can improve fluid viscosity and thermal conductivity, making them suitable for use in heat transfer systems in the energy saving sector. In the structure of the CuO crystal, each copper ion is coordinated by four oxygen ions. This compound combines the elements of the periodic table's d and p-blocks, copper and oxygen, respectively. Super thermal conductivity, photoconductive qualities, and photovoltaic performance are among the high thermal and optical characteristics of CuO that are attributed to its monoclinic crystal structure. CuO is less expensive than other metals like silver and has good chemical and physical stability. It has a high ionic character and can be used to create inexpensive nanoparticles with very large surface areas. Their unique electrical, superconducting, optical, mechanical, and nanoscale composite capabilities have drawn a lot of interest in these nanoparticles [25, 26]. In the structure of the CuO crystal, each copper ion is coordinated by four oxygen ions. This compound combines the elements of the periodic table's d and p-blocks, copper and oxygen, respectively. Super thermal conductivity, photoconductive qualities, and photovoltaic performance are among the high thermal and optical characteristics of CuO that are attributed to its monoclinic crystal structure. CuO is less expensive than other metals like silver and has good chemical and physical stability. It has a high ionic character and can be used to create inexpensive nanoparticles with very large surface areas. Their unique electrical, superconducting, optical, mechanical, and nanoscale composite capabilities have drawn a lot of interest in these nanoparticles. In addition to its widespread use in ceramic preparations, CuO is also utilized in mineral supplements, fireworks, and interactions with mineral acids such as nitric acid and hydrochloric acid. CuO is being sought after for novel applications in electronics, energy storage devices, environmental cleanup, biological research, sensing devices,

and catalysis due to its multifunctionality. The unique magnetic and super-hydrophobic properties of CuO nanostructures differ with other metal oxide nanostructures like TiO₂, ZnO, WO₃ and SnO₂. CuO's properties make it a prime candidate for applications such as super-hydrophobic coating, lithium-ion battery (LIB) anode materials, heterogeneous catalysis, total hydrocarbon conversion to carbon dioxide, improving nanofluid heat transfer, carbon dioxide reduction nanoenergetic materials [27, 28].

1.9.1 Photocatalytic Activity of Copper Oxide

Large surface area, high surface area, and increased oxygen adsorption capacities of CuO-NPs provide evidence that it is a good candidate and exhibit increased photocatalytic activity. The significant tendency of CuO NPs to adsorb molecular oxygen allows regulating the rearrangement of the electron and hole pair at the interface, which is necessary to remove photogenerated electron [29].

1.10 Ferrites

It is common to use the term "ferrite" to describe a class of magnetic oxide compounds where iron oxide is the main component. The earliest magnetic material that the ancient people knew about was magnetite, a real ferrite. Iron, chromium, manganese, and other rapid transition metals, as well as lanthanides, are members of a unique class of materials called ferrites. Ferrite's crystal structure is similar to spinel. Ferrites are a spinel type material that consists of tightly packed cubic oxides and the M cation fills half octahedral apertures and one-8th tetrahedral openings. Spinel ferrites are usually red, blue, green, yellow, and brown in color [30].

1.10.1 Photocatalytic Potential of Ferrites

Photocatalytic characteristics are significant for ferrites. Different metals present in the lattice structure can alter the ferrites' redox characteristics and stability while preserving the spinel structure. The advantageous features of ferrites are its band gap that can absorb visible light and band gap property that has the advantage of increasing efficiency because more catalytic sites are used via crystal lattice component known as spinel crystal structure. The redox characteristics of the ferrites are significantly altered by the substitution of transition metals into the spinel lattice. The usefulness of ferrites is due to their spinel structure of the crystal that serves to increase efficiency

due to increased number of catalytic sites due to employing a lattice crystal structure and their band gap that can absorb visible light. In an attempt to increase photocatalytic activity, ferrites have also been utilized in conjunction with metal oxides and other photocatalysts. The composite photocatalysts that are created when metal oxides and ferrite are mixed exhibit greater photocatalytic efficiency than either metal oxide or ferrite alone [31].

1.11 Copper Ferrite NPS

Recently, spinel ferrites at the NPs size has received much attention owing to its superparamagnetic characteristics. In contrast to other spinel ferrites, these mostly iron and oxygen based ferrites attracted a lot of attention from researchers in the past [32]. One of the significant spinel ferrites is copper ferrite (CuFe_2O_4). It is known that CuFe_2O_4 can form both cubic and tetragonal forms. Copper ferrite may be crystallized out in a gradual manner, as a tetragonal crystal whose lattice parameter ratio approaches 1.06. The tetragonal phase of copper ferrite has the inverted spinel structure in which nearly all the Cu^{2+} ions reside on the octahedral sub lattice. In contrast, the distribution of the Fe^{3+} ions is equitable between octahedral and the tetrahedral sub lattice [33].

The topic of using CuFe_2O_4 nanomaterials as photocatalysts in degrading contaminants is still being researched. However, nanoparticles CuFe_2O_4 cluster together to form large particles because they are ferromagnetic. In addition, the photocatalytic activity of the material dropped rapidly because of the fast recombination of the created electrons and holes related to the narrow band-gap. Such a combination with the suitable material can give it a further boost in terms of its photocatalytic activity [34].

1.12 Graphene

A carbon-based substance called graphene came into existence in 1985 by Robert Curl. But four years later, Krätschmer verified that C_{60} -fullerene had a cage structure. The carbon material family was extended and carbon nanotubes were first reported by Nippon Electric Company Ltd. in 1991. Using a microcomputer peeling technique, effectively removed graphene from the monolithic state in 2004. There has been many research on it in the past years. The 2010 Nobel Prize in Physics was awarded to Andre Geim and Konstantin Novoselov who pioneered the study on graphene. Graphene

consists of a layer of carbon atoms that are hybridized in sp^2 . It is a graphical 2D carbonaceous crystal structure that consists of hexagonal honeycombed structure. Graphene is the strongest and thinnest nanomaterial available in the market with 0.34 nm as the thickness of a sheet. Since a single layer of graphene consists of two carbon atoms per unit cell, each carbon atom is connected to three of its neighbours by a 3 centre 2 electron sigma bond. The other p electrons would most likely desire to form a 1 bond with the adjacent atoms as they cannot bond, the direction of the bond being perpendicular to the plane of graphene. The C-C bond is short (0.142 nm), and the structure is very stable. All carbon atoms are tightly connected to all others in graphene. The atomic surface located inside the graphene is deformed and bent as a force is applied exteriorly, to oppose the force. Because of this, the carbon atoms are neither misaligned nor rearranged, preserving the structure's stability. The intrinsic orbit of graphene electrons prevents any scattering caused by lattice imperfections or interference from other atoms. Graphene's exceptional qualities are attributed to its distinct lattice structure. Strengths of graphene oxide (GO) compared to graphene (G) were affordability of production and processing, ease of scale up production. Their disadvantages by far outweigh its strength since little electrochemical activity, easy agglomeration, and complex processing of the single component graphene based material greatly add on to their limitation in use [35, 36].

1.13 Graphene Oxide

Millions of graphene layers organize and construct the three-dimensional substance known as graphite. Graphite is converted to graphite oxide by attaching functional groups containing oxygen on its surface in an oxidation procedure. On sonication of graphite oxide, a single or multiple layer graphene, graphene oxide (GO), is produced. Additionally, it adds several types of oxygenated functional moieties to the graphene surface to functionalize it [37]. The hydrophilicity and segmental layer partitioning of graphene layers are made possible by these various functional moieties on their surface. Due to the hydrophilic nature of graphene oxide (GO), an ultrasonic process forms only 1 or a few layers of graphene, which have great stability in deionized water and other solvents. One should keep in mind that there is a contrast between the graphene oxide and graphite oxide. Graphite oxide is multilayered, but graphene oxide is few or single layered. Separation between the interlayers of graphite oxide is 6.35 Å. It, however, expands to 11.6 and 6.35 Å in liquid. Through functionalization, it is

possible to modify the properties of graphene oxide, based on the required purpose. The free radical oxygen species as well as the electron rich graphene backbone are useful in applications spanning materials chemistry to quantum physics. Because of its low electrical conductivity, GO has a wide range of applications [38].

The differences between GO and graphene are significant. Because graphene excels in both mechanical strength and electric conductivity, GO is both chemically flexible and processable. GO's conductivity is decreased but its chemical reactivity is increased by the addition of oxygen-based functional groups, which may be advantageous in some applications that call for functionalization. GO has several advantages over pristine graphene, particularly in terms of material processing and chemical manipulation. It facilitates the creation of composite parts, coatings, and films due to its ability to generate stable aqueous dispersions. Because GO is hydrophilic, it interacts efficiently with contaminants, making these synthetic materials suitable for a range of applications, including water filtering [39].

Moreover, the functional groups on GO can be used to bind other chemicals, small particles, or polymers to create hybrid materials with improved properties for use in drug delivery, sensing, and catalytic applications [40].

1.13.1 Photocatalytic Role of Graphene Oxide

In the photocatalytic system, GO can act as a cocatalyst as well as a photocatalyst. GO has two domains, the sp^2 domain, which contains carbon atoms, and the sp^3 domain, which is made up of several functional groups that contain oxygen. Later research has demonstrated that altering the C/O ratio, adjusting the ratio of hydroxyl and epoxy groups, and adding other functional groups can all modify the band gap of graphene oxide. The photocatalytic reduction capability of GO for organic matter reduction and water splitting has been validated by recent experimental investigations. Few studies have looked at the idea that GO itself could be able to photocatalytically reduce CO_2 , despite the results suggesting that it might. Reduction of CO_2 to methanol could be catalyzed by GO and using copper can enhance the catalytic activity of the GO, which would increase its applicability in photocatalytic reduction of CO_2 . The inherent potential of GO to serve as an inexpensive and sustainable material for photocatalyzing the reduction of CO_2 requires more research, though [41].

1.14 Characterization Methods

Techniques of characterization play an important role and the knowledge that is gained using characterization techniques is important in understanding the physical, chemical, structural and optical properties of materials such as composites and nanoparticles [42].

1.14.1 Fourier Transform Infrared Spectroscopy

One of the most common methods to the determination of many functional groups that comprise a molecule is Fourier Transform Infrared Spectroscopy. FTIR is a non-destructive and fast technique to ascertain qualitative and quantitative aspects of biomass in mid IR band. FTIR spectroscopy can be used to give more information on the structure of the fibres, their molecular fragments, and presence or absence of certain functional groups [43].

1.14.2 UV-Vis Spectrophotometry

The ultraviolet (UV) spectroscopy is a physical method of optical spectroscopy with light in the visible, ultraviolet and near infrared regions. It relies on the Beer Lambert law that states that the concentration of the species being absorbed in a solution, and the path length are highly related to the absorbance of that solution. Thus, it can be employed in calculation of the concentration of an absorber in a solution at a given length of a route. The process of analysis determines the extent of monochromatic light within the 200-400 nucleotide of the near ultraviolet spectrum being absorbed by colorless matters [44].

1.14.3 X-ray Photoelectron Spectroscopy

This most often is characterized through surface nanostructures by X-ray photoelectron spectroscopy. There are two types of information that XPS extracts. The intensity of the peak gives information on the concentration of the respective atoms in the surface area to determine the atomic composition. Secondly, the exact energy of a photon excited core electron depends on the chemical state of the corresponding atom which is often exploited information of the chemical state of the atoms in the surface region [45].

1.14.4 Photoluminescence Spectroscopy

It is an analytical tool that is non-destructive and helps in the understanding of flaws, electrical, structural, and atomic configuration deviation. It involves illuminating a substance with light, typically from a laser, and recording the luminescence that results as a plot of the intensity of the light emitted against wavelength [46].

1.14.5 Scanning Electron Microscopy

Using scanning electron microscopy, we can learn more about the topography, dopant's shape and structural configuration on the graphene oxide surface. This approach typically uses high energy electrons to scan the sample's surface and identify signals [47].

1.14.6 Electrochemical Impedance Spectroscopy

It offers useful and accessible information about charge transfer and recombination, making it an appropriate method for characterizing photocatalysts [48].

AIMS AND OBJECTIVES

Objectives of this study are:

- To synthesize graphene doped copper ferrite and copper oxide nanoparticles.
- To characterize graphene doped copper ferrite and copper oxide nanoparticles.
- To determine efficiency of synthesized catalyst for carbon dioxide reduction.

CHAPTER 2

LITERATURE REVIEW

Thamaraiselvi & Sivakumar, order to increase photocatalytic activity, the bandgap of TiO_2 was changed using a significant proportion of copper oxide. The by-products of photocatalytic reduction of carbon dioxide were formaldehyde, formic acid and methanol with methanol being predominant. The photocatalyst produced methanol at $4120 \mu\text{mol/g cat}$. Reuse of the optimized catalyst, led to 3080 micromole of methanol/gram of catalyst production. The minimal decrease in catalytic activity is caused by problematic catalyst recovery [49].

Rambabu et al., graphene oxide coated TiO_2 nanotubes are synthesized to be used in photocatalytic reduction of CO_2 . The electrochemically anodized TiO_2 nanotubes are scored by graphene oxide/reduced graphene oxide (GO/rGO) films and act as the bridging zone between neighboring nanotubes. To reduce the adsorbed CO_2 molecules, this novel nanostructure facilitated easy separation of the photogenerated electron-hole pairs and had an increased charge transfer. These rGO/ TiO_2 multi-leg nanotubes showed the highest production of photocatalytic CO_2 , $1348 \mu\text{mol g}^{-1}$ after 2 hours of UV-A irradiation [50].

Torres-Arellano et al., deliver renewable solar fuels and supply viable solutions to the global warming, this contribution suggests the earth-abundant materials to be used in CO_2 photoreduction. The material selected in this case is cuprous oxide (Cu_2O) which is among the most promising photocatalysts to be used in photoreduction of CO_2 due to its high affinity with solar energy and electric properties. Cu_2O nanoparticles (NPs) were synthesized using *Psidium guajava* residues in the photocatalytic reduction of CO_2 . As stabilizing and reducing agent, the aqueous residue of *Psidium guajava* was suitable in the synthesis of Cu_2O NPs. The formation of the cubic structure of Cu_2O was confirmed by the XRD analysis. The direct band gap of nanoparticle is approximately 1.8 eV and is absorbent to light of 430 nm wavelength. The efficiency of the CO_2 photoreduction activity exhibited by Cu_2O NPs, albeit, limited in number, was maximized by an orthogonal Taguchi L9 design. The following variables were investigated: temperature, air flow and catalyst loading. CO_2 photoreduction with Cu_2O NPs reported HCOOH as the initial product with a maximum production of 103.4 3 m^{-1} over visual light [51].

Multiple component semiconductor hybrid structures have been seen as the best photocatalyst design for producing long lived charge separated states. Especially for reactions that need large activation energies, like a CO₂ reduction process, an engine component and shape have an important influence on the reaction activity. Cu₂O and g-C₃N₄ had been selected for the purpose of this research as photocatalytic components with bandgaps appropriate for CO₂RR. By directly growing Cu on g-C₃N₄ by a polyol method, we were able to create substantial electric relations between these domains. As photocatalysts in an aqueous solution devoid of hole acceptors, the resultant g-C₃N₄/Cu₂O hybrid was utilized. The catalyst remained stable more than 6 h and showed a good activity to produce CO (94 $\mu\text{mol gcat}^{-1} \text{ h}^{-1}$), and CH₄ (218 $\mu\text{mol gcat}^{-1} \text{ h}^{-1}$). Proper electron transport to facilitate CO₂RR was because of the natural compatibility between g-C₃N₄ and Cu₂O since conductive contacts were formed. These findings confirmed significance of junctions and interfaces in hybrid catalyst design to support optimum photocatalytic CO₂RR performance [51].

Karawek et al., have prepared TiO₂ nanosheets using a hydrothermal technique involving soft template of hydrofluoric acid. Copper TiO₂ nanosheets/ graphene oxide were made by doping the nanosheets with copper oxide during hydrothermal process and compositing them with graphene oxide. A great photoactivity has been demonstrated in the course of converting CO₂ gas to acetone and methane via the CTNSG. The carbon ($n = 71.70 \mu\text{mol gcat}^{-1}$) consumed at relative humidity was 100%. Relative humidity acetone and methane were produced at a rate of 0.75 and 12.09 $\mu\text{mol gcat}^{-1}$, respectively. It was explained that this photoactivity of CTNSG was attributed to internal heterostructure of the two-dimensional nanostructures, i.e. copper-TiO₂ nanosheets and graphene oxide. The n-p heterojunctions between the graphene oxide and the nanosheets were characterized by the connections that kept the energetic radicals to be engaged in further reactions [52].

Wang et al., approach in which a metal-organic layer of fixed thickness (three metal coordination layers, approximately 1.5 nm) is generated with graphene oxide applied as both the template and an electron mediator. The hybrid product catalyst shows greater improvement (approximately 34-fold) over the bulky Co-based metal-organic framework achieving total yield CO $\text{mmol g}^{-1} \text{ MOL}$ (CO selectivity of 95%) in CO₂ photoreduction. Due to a well-exposed active site in the metal organic layers as well

as a simple electron shuttle between heterogeneous and homogeneous constituents, systematic studies revealed that the high activity of graphene oxide is mainly attributed to efficient electron transfer between heterogeneous and homogeneous components by simple electron hopping between well active sites in metal-organic layers. Here, charge transfer pathway at the interface between a conductive template and catalyst has been disclosed and it has been shown that a simple method can be employed to form very thin metal organic layers to enhance photocatalysis [53].

Karawek, Kitjanukit, et al., photoactivity of alkanolamine-grafted TNS and alkanolamine-grafted as well as copper-doped TNS/GO were investigated. In the initial experiment, triethanolamine-grafted TNS (TEA-TNS) was more effective in the CO₂ photoreduction process as compared to monoethanolamine- and diethanolamine-grafted TNS (MEA-TNS and DEA-TNS) due to the base catalyzed CO₂-TEA hydration relation. The four composites whose photoactivity we tested in the second experiment are as follows: TNS/GO, TEA-[Cu-TNS/GO] (grafting TEA on Cu-TNS/GO), Cu-[TEA-TNS]/GO (doping the Cu on TEA-TNS/GO), and TEA-Cu-TNS/GO (one-step hydrothermal synthesis TEA, a Cu precursor, and GO). The addition sequence of TEA-[Cu-TNS/GO] being the last heterostructure allowed it to ensure TEA exposure to CO₂ and prevent side chelation reactions between TEA and Cu ions, which provided the highest photoactivity [54].

Gong et al., covalently grafted COF-366-Co on the graphene oxides (GO) to form a stable COF-based composites (GO-COF -366-Co) that were used in the photocatalytic reduction of CO₂. In 100% of acetonitrile (CH₃CN), GO-COF-366-Co astonishingly demonstrated a high selectivity of 94.4% with a formate yield of 15.8 mmol/g which is about four times more than COF-366-Co. The primary product formed by the photocatalytic CO reduction reaction on GO-COF-366-Co is CO (96.1%) with a CO yield of up to 52.2 mmol/g, which is four-fold higher than the corresponding product when the pure COF-366-Co is used, indicating a strong synergistic effect between Co and GO. The enhanced catalytic performance can be attributed to Photoelectrochemical experiments that indicate that the semi-covalent bonding between COF-366-Co and GO to form a GO-COF-366-Co composite ensures significant enhancement in charge separation and transfer [55].

L. Wang et al., photogenerated charge carriers have to be transferred and separated at close interfacial contact between semiconductor photocatalysts and cocatalysts. In this case, highly efficient cocatalyst such as few-layer graphene was in-situ deposited on ZnO. The combination of ZnO-graphene can also give a better photocatalytic CO₂ reduction as a result of the close interfacial contact, and the Schott key junction between ZnO and graphene. Its photothermal effect, as well as, interaction between graphene and CO₂ molecules known as π - π conjugation, also helped improve satisfying performance in the interim. In this work, the authors have designed an effective photocatalyst in reducing CO₂ and a viable method to in-situ production of graphene [56].

Zhang et al., photoreduction of CO₂ is a good option towards environmental problems. In the present work, we synthesized titanium particulate doped with hydrogen, by vaporizing NaBH₄ in the presence of TiO₂. They coated the reduced Titania with platinum nanoparticles by using the Pt solution passivated in Poly PVP. The standby sample was blended with copper precursor with the purpose of depositing Cu-Pt bi-metal co-catalysts over the reduced TiO₂ surface. Graphene-wrapped Cu-Pt / rTiO₂ is covered by sheet-shaped graphene oxide (GO) to make core-shell photocatalysts of three dimensions. The CO₂ photoreduction capacity of the Graphene-wrapped Cu-Pt/rTiO₂ was evaluated in detail by the means of the online GC with the SiO₂ fiber as an electrode. Graphene-wrapped Cu-Pt/rTiO₂@SiO₂ demonstrated both high selectivity (99%) and a carbon monoxide yield (394.84 $\mu\text{mol g}^{-1}\text{cat h}^{-1}$) that was above average. Elemental mapping and images of the transmission electron microscope proved the presence of Cu-Pt bi-metal nanoparticles on the TiO₂ nanoparticles surface. The experiment of inert gas control group has proved that the supplier of carbon monoxide products is CO₂ [57].

Yang et al., solutions to the current energy/environment problems that will be found to be attractive is one that involves applying nonmetal catalysts in order to reduce carbon dioxide (CO₂) in the process of using solar electricity. We hereby resulted to a photochemical synthesis of nitrogen rich nanocarbons. The NCNs structure has been identified to serve as a catalyst in trying to promote conversion of CO₂ to CO. The CO evolution activity on the NCNs was 34.5 $\mu\text{mol}/30\text{ min}$, and the selectivity was 80.4%. The quantum efficiency of the reduction of 450 nm irradiation was 2.3% at its

overlying NCNs, a value that approaches the metal catalyst with CO₂ under exposure to visible light. CO₂ reduction activities were studied under adsorption, CO₂ temperature-programmed desorption, and in situ diffuse reflectance Fourier transform infrared spectroscopy. Their results indicated that NCNs pyridinic nitrogen sites were the primary active sites of CO₂ reduction catalysis. Further, we found that the CO₂ reduction reaction can also be driven by nanocarbons modified with oxygen. However, compared to the oxygen alteration, the nitrogen modification had a greater promotion effect on CO₂ decrease. Furthermore, by altering the carbon precursors, we were able to create various nanocarbons using this photochemical method, illustrating the method's versatility [58].

Sahoo et al., g-C₃N₄ is a two-dimensional material that has a number of benefits over other photocatalysts, including being biocompatible, metal-free, and chemically and thermally stable. Low electrical conductivity, high recombination rate, low charge carrier mobility, and most significantly low absorption in the visible spectrum are its regular drawbacks. In order to overcome the many drawbacks, g-C₃N₄ was created using an efficient and economical copolymerization technique. The bandgap also was made smaller (as low as 2.40 eV with the right precursors and optimized synthesis conditions) compared to the precursors used. Reduced graphene oxide (rGO) and g-C₃N₄-based composites were designed to enhance once again the conductivity and the charge separation. The consequent composite catalysts were investigated on photocatalytic reduction of CO₂. g-C₃N₄/rGO composites displayed excellent performance of selective photoreduction of CO₂ to methanol with no scavengers present under ambient conditions. Such composites demonstrated very good stability and evolution rates of 114 $\mu\text{mol g}^{-1} \text{h}^{-1}$ and H₂ (68 $\mu\text{mol g}^{-1} \text{h}^{-1}$) [59].

Olivo et al., use of TiO₂ photocatalyst as green reductant (water) and the low level of operating conditions (the normal temperature and pressure) has been particularly attentive regarding the sustainability of the process. The catalysis and the process parameters were found to greatly influence carbon dioxide photoreduction efficiency. TiO₂ was mixed with oxide or metal species to make it versatile and effective catalyst. Copper (as the oxide CuO) or gold in the nano particle form were used as the promoting metals. In the evaluation of CuO-TiO₂ and Au-TiO₂ and their suitability in terms of selectivity and photocatalytic activity, the type of promoter altered the selectivity of the process toward two valuable products namely CH₄ or H₂. The

catalytic activity was discussed in detail and correlate with the physicochemical properties of the photocatalysts [60].

Kato et al., photocatalytic activity of a few metal oxides in reduction of CO₂ with the use of water was determined after the impregnation with Ag loaded as cocatalyst. Out of all the metal oxides loaded with Ag in which UV produced the reaction products that were synthesized, Ga₂O₃, ZrO₂, Y₂O₃, MgO, and La₂O₃ exhibited an ability to form CO and H₂. In this way, CO₂ might be decreased in metal oxides composed of metal cations having closed-shell electronic configurations, e.g., d⁰, d¹⁰, and s⁰. In situ Fourier transform infrared measurement indicates that the photocatalytic activity and selectivity toward CO production is controlled by the amount and chemical states of CO₂ adsorbed on the catalyst surface, and the basicity of the catalyst surface. This can be summarized as follows: Ag/ZrO₂ increased the generation of H₂ compared to CO production because of the less adsorbed CO₂. Ag/Ga₂O₃ achieved the best CO production activity, given that low surface basicity of adsorbed monodentate bicarbonate allowed its successful transformation to bidentate formate, the chemical precursor of CO production. Both weak and strong basic sites on Ag/MgO, Ag/La₂O₃ and Ag/Y₂O₃ reduced H₂ production and promoted carbonate species adsorption and ascorbifying ion. Nonetheless the adsorbed carbonate species did not often reduce to the bidentate formate [61].

Yin et al., reaction of the evaporated zinc and copper film or nanoparticles-copper film or nanoparticles under vacuum sealing, a copper-and-zinc alloy material was obtained. This introduced a homogenized CuZn alloy. The alloy has been tested as an electrocatalyst and/or cocatalyst on photocatalytic reactions to convert selectively carbon dioxide to formic acid. According to improved composition of alloys, Cu₅Zn₈ catalyst exhibited good electrochemical CO₂ reduction. In addition, we developed a three-electrode photoelectrochemical (PEC) cell in which Cu₅Zn₈ film was used as the cathode in the dark to reduce CO₂ and strontium titanate (SrTiO₃) as a photoanode to oxidize water. Moreover, PEC system and its faradaic efficiency in selective conversion of CO₂ to formic acid was 79.11% and 100.00%, respectively, under UV and without bias potential. CO₂ was photocatalytically converted to formic acid by SrTiO₃ particles coated with Cu-Zn alloy nanoparticles when exposed to UV light. Isotope trace analysis showed that, like photosynthesis in plants, water acted as an

electron donor to create oxygen and organic compounds when exposed to UV radiation [62].

Getahun et al., procedure that converts atmospheric carbon dioxide to other biofuels was described. Copper oxide (CuO) nanoclusters were deposited on ethandiol-made zinc oxide (ZnO) nanoparticle surfaces by femtosecond pulsed-laser irradiation. ZnO-deposited CuO was chemically bonded to amine functionality chelated poly (amidoamine) dendrimer-3-glycidylpropyltrimethoxysilan. This was then combined with TEMPO-oxidized cellulose nanofibril and cast into a film (CuO/ZnO-Den-TOCNF film). In addition, CuO/ZnO was patterned and cast into a film via chitosan (CS) matrix. The adsorption and conversion of gaseous carbon dioxide were realized in both films. The amine groups on the dendrimer composited on TOCNF and the COP on the CS adsorb carbon dioxide, and CuO/ZnO catalyzes it as a photocatalyst. Following six-hour UV-light treatment, a composite film reduced both the formation of acetaldehyde (0.030 and 0.037 mmol/g(catalyst) and conversion of gaseous carbon dioxide to methanol (maximum 2.42 and 2.16 mmol/g(catalyst) on CuO/ZnO-Den-TOCNF and CuO/ZnO-CS films, respectively). According to the results, besides requiring the catalyst (CuO/ZnO) in carbon dioxide conversion, the carbon dioxide adsorption also requires an amine group [63].

Omadoko et al., development of methods for converting carbon dioxide into valuable compounds such methanol, formaldehyde, formic acid, and hydrocarbons is necessary. These compounds can be produced by photochemical, electrochemical, thermochemical, or bacterial hydrogenation processes from carbon dioxide. Because it can be utilized as a precursor for biological fuels, as an additive in pyrolysis vapors, and in liquid fuel cells, formate is of interest. In this work, titanium dioxide, metal phthalocyanines, and cheap incandescent sources were used in a photoreduction setup to convert carbon dioxide to formate under basic or neutral settings and to formic acid under acidic conditions. According to anion chromatography, the formic acid yield was 1.54%. Using chemical actinometry, a genuine quantum yield of about 2.0% is also discussed and presented in this paper. The amount of formate produced is influenced by the pH, light intensity, and sensitizer amount, according to thorough investigations of the photoreduction process [64].

Kumar et al., sacrificial electron donor, triethylamine was added to a hybrid photocatalyst, consisting of the molecular complex cobalt phthalocyanine tetracarboxylic acid (CoPc-COOH) immobilized to the organic semiconductor graphitic carbon nitride (g-C₃N₄) produced a significantly higher methanol yield than using the bare g-C₃N₄ film when carbon dioxide was reduced under visible light. Various methods including FTIR, UV-Vis, Raman, XPS, TGA, BET, etc. were used in characterizing the structural and morphological qualities of the hybrid photocatalyst. At the 24 hours of light irradiation, the yield of methanol was measured to be 646.5 $\mu\text{mol/g}^{-1}\text{cat}$ or 12.9 $\text{mmol/g}^{-1}\text{cat}$ using g-C₃N₄/ CoPc-COOH as the photocatalyst (50 mg), and the conversion rate was 538.75 $\mu\text{mol/h}^{-1}\text{g}^{-1}\text{cat}$. Homogeneous CoPc-COOH (6.5 μmol Co, corresponding to g-C₃N₄/CoPc-COOH) and g-C₃N₄ (50 mg) gave a yield of 88.5 μmol (1770 $\mu\text{mol g}^{-1}\text{cat}$) and 59.2 μmol (1184 $\mu\text{mol g}^{-1}\text{cat}$) under identical conditions. This was attributed to the increased concentration of CO₂ on the support of the hybrid which was influenced by the ability of CoPc-COOH to bind with CO₂ resulting in the improved photocatalytic characteristics of the hybrid. At the conclusion of the reduction process, the semiconductor support also offered improved charge separation and electron mobility, along with the added advantage of easy material recovery and recycling [65].

Shoji et al., photocatalysis using H₂O as an electron donor, amorphous mixture of copper oxide (Cu_xO) nanoclusters coated on a strontium titanate (SrTiO₃: STO) nanorods thin film could convert carbon dioxide (CO₂) into carbon monoxide (CO). When Cu_xO-cocatalysts were deposited on STO nanorods, there was an appreciable enhancement in the photocatalytic activity as compared to the same when STO nanorods were left bare. The Cu_xO-cocatalysts can be loaded using a straightforward and cost-effective technique and are made up of several, non-toxic components. According to our research, Cu_xO nanoclusters can be employed as a general cocatalyst in conjunction with a variety of semiconductors to create effective and reasonably priced photocatalytic CO₂ reduction systems [66].

Zhu et al., Ag/Cu₂O triangular composites with various Ag loadings (TAgNPT/Cu₂O) under visible-light illumination will be applied to evaluate their potentiality in photocatalytic CO₂ reduction. Various characterization methods were used to characterize the microstructures, compositions and properties of as-prepared samples of the photocatalyst. In the presence of green light-emitting diodes (427-622 nm),

cumulative weekly yields of CO₂-to-CO and CO₂-to-CH₄ were 31.02 and 30.9 $\mu\text{mol g}^{-1}$ nanoseconds (quantum yield of 0.32%), respectively, whereas under blue light-emitting diodes (412-505 nm), cumulative weekly yields of CO₂-to-CH₄ were 19.56 $\mu\text{mol g}^{-1}$ Calculated quantum yields of 0.21%. We lastly offered a potential reason of the higher catalytic activity of TAgNPT/Cu₂O in CO₂ photoreduction processes [67].

Gong et al., Cu₂O layer in situ was hydrothermally grown using oil bath method on the C₃N₄ (CN) photocatalysts to form C₃N₄/Cu₂O (CN/Cu₂O) composites photocatalysts. Heterojunction with CN and Cu₂O has the potential to increase the photocatalytic activity of carbon nitride because light absorption could be enhanced, internal resistance to the charge transport reduced, and the efficiency of the charge generated in the electron-hole separations could be improved. Photocatalytic activity of the CN/Cu₂O composite photocatalysts produced was also evaluated. The test data indicated that the highest photocatalytic ability of CN/Cu₂O-60 was 2.27 $\mu\text{mol g}^{-1}\text{h}^{-1}$ at 3 hours xenon lamp irradiation. This was 8.5 and 5.7 times higher than that of the pure CN and pure Cu₂O, respectively [68].

Geovo et al., composites were created by two different processes: coprecipitation and salt impregnation, and they were characterized using a variety of methodologies. In the visible electromagnetic range, composites with large surface area and band gap energy were produced using both techniques. The MCM-41/CuO composites and pure MCM-41 were proven to have a potential in CO₂ photoreduction, with the composition, and a diverse coverage of the active sites of the photocatalysts exerting a significant influence on the activity and selectivity of the products. In comparison to MCM-41, composites with 1% CuO produced using both techniques produced more ethylene; however, materials produced using the impregnation method showed less photocatalytic activity than MCM-41 and the coprecipitation method composites. The aforementioned findings demonstrate the adaptability of MCM-41 in creating composites with semiconductors and the significance of comprehending the critical elements that impact CO₂ photoreduction and composite selectivity, such as their electrical, structural, and surface properties [69].

Ramos-Huerta et al., studied the activity of the GO-based catalysts comprising commercially available GO, All Kemie Sus-method-synthesized GO, and GO/TiO₂ combinations, in the reduction of CO₂ in visible and UV light. Several XRD, SEM,

FTIR, EDS, UV, and XPS techniques characterizations were conducted to explain structural and chemical features of the catalysts. These components can serve to manufacture numerous value-added products such as methanol, formaldehyde, ethane, and methane, which proves their unbelievable diversity. Commercial GO had the greatest score at $2.25 \times 10^2 \mu\text{mol}$ and initial reaction rate of $2.7 \times 10^4 \mu\text{mol g cat hour}$ to both ethane and GO/TiO_2 $4.16 \mu\text{mol}$ and an initial reaction rate of $4.99 \times 10^2 \mu\text{mol g cat hour}$ respectively. Interestingly, the GO/TiO_2 composite was only investigated because of its potential to improve charge separation and catalytic ability, it is still advisable to conduct additional research [70].

Kumar et al., many peculiarities were found comparing with TiO_2 nanotube arrays grown in the standard ethylene glycol-based electrolyte (TNTA-EG) and those generated by electrochemical anodization in formamide-based electrolyte (TNTA-FA). In addition to such a unique adsorbate structure consisting of linearly adsorbed CO_2 chemisorbed and physisorbed CO, and a variety of monodentate and bidentate carbonate species, TNTA-FA was also demonstrated as possessing a lower work function, shorter phonon lifetimes, less lattice strain and increased visible light absorption. CO is highly unlikely to adsorb in the dark, showing that spontaneous deoxygenation of CO_2 occurs on the TNTA-FA surface. Similar to other TiO_2 surfaces, the bottleneck of CO_2 reduction on TNTA-FA surfaces is no longer the formation of $\text{CO}_2^{\cdot-}$. It is a significant observation. In contrast to the morphology of TNTA-EG composed of a honeycomb-like structure arranged in an approximate triangular lattice, TNTA-FA samples demonstrate rounded, vertically oriented hollow cylinders of the bright color, and neon green as well. The photocatalytic activity was determined by the aid of CO_2 photoreduction and dyes degradation testing. Nanotubes formed with formamide performed better than EG-based nanotubes by nearly 1.7 times during CO_2 reduction and twice in the degradation of dyes methylene blue, brilliant green, and rhodamine B. The obtained outcomes are attributed to the increased surface band bending in TNTA-FA that allows dividing more effectively the photogenerated electron-hole pairs [71].

Jantarasorn et al., nanocrystalline Cu/TiO_2 catalysts have been prepared based on their sputtering of Cu targets into an Ar atmosphere on P25- TiO_2 support under pulsed direct current (DC) reactive magnetron sputtering. The uniform coating on the substrate was attained in the oscillating bowl. The filling level of Cu was adjusted with

a variation of coating time. The resultant catalysts were characterized by energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), UV-Vis spectroscopy and X-ray diffraction (XRD). The photocatalytic capabilities of all catalysts were studied and compared to those of pure TiO_2 support as well as Cu/TiO_2 manufactured through conventional impregnation and tested as photocatalysts to convert CO_2 and H_2O to CH_4 under UV light. The findings indicated that the photocatalytic advantages of the sputtergenerated Cu/TiO_2 catalyst were dramatically improved compared to this of the pure TiO_2 support [72].

Faria et al., show that Niobium oxide (Nb_2O_5) material has better photocatalytic activity when a little amount of Cu nano-particle is deposited through DC-magnetron sputtering over its surface. The carbon dioxide (CO_2) is reduced to isopropanol ($\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$), formate (HCOO^-), methanol (CH_3OH), acetone (CH_3COCH_3), acetic acid (CH_3COOH), and methane (CH_4). The photoluminescence results indicate that high dispersion of Cu, high specific surface area of material even after the deposition of Cu, and the reduction in the recombination rate of the photogenerated electron-hole pairs due to the electron trapping effect by the Cu species can be considered as the key factors that lead to the enhancement in the CO_2 photoreduction of the $\text{Nb}_2\text{O}_5/\text{Cu}$ [73].

He et al., photoreduce hexavalent chromium (Cr(VI)) using visible light, a variety of rGO/CuOx composites with varying doping levels by the alkaline hydrothermal process was also synthesized. XRD, BET, FTIR, Raman, SEM, TEM, XPS and PL characterization were applied to the morphology, crystal structure and surface of the composites. The result exhibited that a hetero junction between rGO and CuO nanoparticle had been formed and the CuO had successfully been synthesized in-situ on the surface of rGO . The $\text{rGO/CuO}_{0.3}$ composite proved to be exceptional under visible light with remarkable results in terms of Cr(VI) reducing percentile difference of 97.03% and 100% adsorption occurred in 10 minutes. Its high stability and reusability could also be evidenced by its removing efficiency that remained above 83% after five times. The interfacial migration and valence changes of Cr(VI) and Cr(III) in the direct adsorption and photocatalysis reduction system were evaluated by measuring their concentrations in the solid phase and liquid phase and conducted desorption-dissolution tests. The findings of the inhibitor test and characterize of the applied $\text{rGO/CuO}_{0.3}$ composite would explain the photo-reduction mechanisms of

Cr(VI) in Vis/rGO/CuO system. The results indicated that the transformation of Cr(VI) was a reaction involving numerous processes, and catalytic activity of synthesized composites was markedly enhanced with the synergistic effect of CuO and rGO. The rGO/CuO_{0.3} composite showed good potential in the removal of Cr(VI) and hence raising the possibility of the creation of advanced water purification systems [74].

Urbanek et al., CoO_x/g-C₃N₄ heterojunction photocatalysts the authors developed have a high selectivity to C²⁺ (58%) under visible light and demonstrate superior CO₂RR performance to form CH₃COOH (up to 383 μmol·gcatalyst⁻¹) and CH₃OH (up to 371 μmol·gcatalyst⁻¹). Nevertheless, since the same method increases the content of cobalt oxide and produces high H₂ evolution (HER), the selectivity and preference of CO₂RR or HER appears to depend on oxide ornamentation. The comparative evolution of HER and CO₂RR in the same system gives excellent insights into the catalytic mechanism, and the formation of the CoO_x/g-C₃N₄ heterojunction is required to achieve high visible light photoactivity [75].

da Cruz et al., process of converting cheap, easily available and abundant molecules of a single carbon (C1) to significantly valuable and more carbon (C²⁺) multiple compounds has become a highly focused but difficult area of concern. Herein, a magnetic photocatalyst to CO₂ C-C coupling processes was designed and prepared, benignly in potassium ferrate/ sulfur-doped patterned carbon nitride (K₂Fe₂O₄/ SC₃N₄, or KFO/SCN) without the need resort to any sacrificial chemicals. This new catalyst strongly enhances the possibility of converting CO₂ via photocatalytic reactions to multi-carbon molecules, especially hydrocarbons, which have become important resources in both the chemical and energy sectors. The catalyst possessed 100% CH₄ (64% and 36% C²⁺) hydrocarbon selectivity and maximized the low conversion rate of CO₂ to CH₄, producing C²⁺ hydrocarbons effectively. The optimized KFO/5%-SCN displayed the greatest rate of CO₂ conversion to CH₄ at 57.78 μmolg⁻¹h⁻¹ (283.1 ppm), and 3.49 times the rates of KFO and 8.85 times that of SCN, respectively. A potential reaction mechanism was postulated on the basis of an analysis of the end products. This results in increased CO₂ activation of use in the photocatalytic reduction reaction and in increasing selectivity to drive hydrocarbon production via C-C coupling processes [76].

Chen et al., difficult to photoreduce CO₂ because there are no photocatalysts endowed with dynamic active charge separation, wide-spectrum absorption, and CO₂ adsorption. The mesoporous Pt/ZnO nanocomposites prepared using sol-gel route at different percentages of Pt (0.5-2%) in this case served as a template towards the CO₂ photoreduction when exposed to visible light. Under this condition, when Pt nanoparticles (NPs) are deposited on a large-surface mesoporous ZnO, charge mobility can be effectively enhanced. The mesoporous 1.5% Pt/ZnO nanocomposite follows an optimum CH₃OH yield (668 $\mu\text{mol g}^{-1}$), which is 18.5 times more than the mesoporous ZnO (36 $\mu\text{mol g}^{-1}$) [77].

Albukhari & Ismail, photoactive nanozyme design and synthesis used to carry out CO₂ reduction is a major challenge. An efficient nanozyme of hierarchically constructed ZFs-tpyNi heterojunction using an interfacial engineering method has been designed in order to reduce CO₂ with the help of visible light by means of using a terpyridine-based Ni complex supported by ZrO₂ nanoframes. ZFs-tpyNi can provide greater photocatalytic CO₂ to CO conversion than its analogue, ZFs and tpyNi because of its specific structural and composition benefits, delivering an output of 18.2 μmol , a high apparent quantum efficiency of 0.96%, and a selectivity of 92.4% in 3 hours. Such innovative catalysts exhibit exceptional heat and mechanical stability to at least eight turns without activity loss, and their impressive maintenance of structure fails to collapse their structure and shape slightly. Systematic experiments have revealed that ZFs-tpyNi heterostructures possess an exceptional high specific surface area, which is beneficial to the considerable loading and exposure of tpyNi. The strong ZFs structure with extensive porosity actively facilitates transfer and inhibits agglomeration of nanoparticles in the course of catalysis. Also, precise control of the band alignment and bandgap variation in nanozymes also facilitates light absorption, as well as the production and dissociation of photolysis-generated charge carriers using the spatiotemporally heterogeneous interface. Hence, the higher catalytic activity of the nanozyme to selectively form products is the result of its accelerated binding and activation of CO₂. This paper endeavours to explain how nanozyme catalysts are helping to achieve sustainable energy [78].

Liang et al., CO₂ is one of the primary contributors to the greenhouse effect, and the widespread use of fossil fuels, primarily in electric power plants and vehicle engines, is causing its concentration in the atmosphere to rise quickly. CO₂ emissions are also

a result of resource extraction and forest burning. As a result, the strict emission regulations for a sustainable global environment are making the separation of carbon dioxide a difficult study problem. Methods such as using metal oxides as the sorbent are becoming more and more relevant for CO₂ separation because of their economic feasibility. The creation of high surface area adsorbents with micropores greatly improves the process' efficacy. In their interaction with CO₂, metal oxides often yield carbonates of metal, which break down at high temperatures to produce pure CO₂, regenerating the metal oxide. Iron oxide is one of the several metal oxides that exhibits the ability to absorb CO₂, which can be carbonated and regenerated multiple times. Applications of iron oxides and ferrites for CO₂ capture are covered in this chapter [79].

Agarwal et al., Cu/Ti(air) and Cu/Ti(H₂) denote the copper species of different valences which were loaded on TiO₂ during the CO₂ photoreduction due to oxidative and reducing atmospheres treatment. Amount of methanol produced by Cu/Ti(H₂) was 17 times larger than Cu/Ti(air) with low-valence copper species. The production of oxygen vacancies and Ti³⁺ species in the reducing environment led to richer surface hydroxyl protons adsorbed on the surface and accessible photo-electrons in the Cu/Ti(H₂). In-situ low valence copper species of Cu/Ti(H₂), a highly CO₂ adsorption-DRIFTS, exhibited enhanced CO₂ activating and CO*, HOCO⁻ and HCOOH active intermediates adsorption potentials, according to CO₂ adsorption-DRIFTS. These intermediates were then further hydrogenated and converted to CH₃OH with the assistance of protons and photo electrons which enhanced conversion and selectivity to CO₂ conversion due to the combined synergistic effect of low valence copper species (Cu/Ti(H₂)) and surface hydroxyl species [80].

Xi et al., solar light photocatalytic performance of MoO₃ to convert CO₂ to CH₄ and CO was enhanced by dielectric barrier discharge (DBD) plasma sulfurized CuS and MoS₂ co-modified h-MoO₃ (MoO₃@MoS₂-CuS) composites. The better photocatalytic activity of MoO₃@MoS₂ and MoO₃@MoS₂-CuS than h-MoO₃ to use solar light to drive CO₂ to breakthrough to CH₄ was due to the higher CH₄ yield produced by MoO₃@MoS₂-CuS and the decreasing CO yield. It is attributed to the effective isolation and transfer of charge in addition to the enhanced light sensitivity to visible light. Moreover, the CO₂ and H₂O molecules were held and photoreduced at the bare edges-rich parts of CuS-MoO₃-MoS₂ interfacial junction. Setting the CuS

concentration at 2.27 weight percent, the optimum $\text{MoO}_3@\text{MoS}_2\text{-CuS-3}$ reached a CH_4 yield of $44.64 \mu\text{mol g}^{-1} \text{h}^{-1}$ and a CO yield of $7.59 \mu\text{mol g}^{-1} \text{h}^{-1}$ but the durability then decreased a little following three cycles [81].

Zheng et al., discussed how the stability of the catalyst is influenced by the $\text{Cu}_0\text{-TiO}_2$ interaction where the semiconductor acts as support and separator of charge of Cu_0 . To add Cu_0 nanoparticles: copper nitrate was reduced on the surface of TiO_2 by use of a solution made of sodium borohydride. Although metallic copper exhibits greater selectivity towards producing CO (82.32 %), pure TiO_2 exhibits selectivity towards producing CH_4 (62.44%). The activity of the photocatalysts however elevates with the development of the heterostructure and the selectivity varies depending on the copper content in relation to TiO_2 . Besides the typical C1 products (CH_4 , CO , and CH_3OH), molecules with 2 or more carbons (C^{2+}) were also obtained, e.g. acetone ($\text{C}_3\text{H}_6\text{O}$), acetic acid ($\text{C}_2\text{H}_4\text{O}_2$), and isopropanol ($\text{C}_3\text{H}_8\text{O}$). H_2 was formed despite the fact that the selectivity of the formed molecules based on the photoreduction of CO_2 significantly improved. The marked permanence of the tendentious TiO_2/Cu 30% furnished the significance that a fitting heterojunction can have on the catalytic activities. These findings indicate that certain copper species are working in combination with TiO_2 to embrace the development of the catalytic reaction employing both substances [82].

Torres et al., full arc and visible light ($>420 \text{ nm}$) irradiation showed that the photocatalytic conversion of water to H_2 and CO_2 to CO occurred simultaneously over a Cu_2O photocatalyst. Controllable exposed facets of Cu_2O were shown to alter the reduction preference of photocatalytic water splitting (preferentially splitting H_2) to photocatalytic CO_2 reduction (preferentially splitting CO). More surprisingly, the low index facets of Cu_2O are more active than high index ones, contrary to the common wisdom that one would expect more photoactive facets to be those with high Miller indices. The CO conversion yield could be increased further through coupling the Cu_2O with RuOx to create heterojunction that prevents the high recombination of charges and relatively stabilizes Cu_2O photocatalyst. Moreover, RuOx film was varied in order to maximize the photoactivity of the junction [83].

Handoko & Tang, developing a highly efficient composite material to reduce CO_2 by photoreduction is the key initial step towards achieving carbon neutrality, a complete picture regarding the factors governing CO_2 reduction activity is yet to be understood.

Here, Cu in situ coupled to Cu₂O series (Cu/Cu₂O -1, -2, -3) was synthesized by controlling the processing time and using an acid disproportionation method. The best photocatalyst (Cu/Cu₂O⁻²) yields a CO rate of 10.43 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ that is more than four-fold greater than that of pristine Cu₂O. X-ray absorption spectroscopy (XAS), and X-ray photoelectron spectroscopy (XPS) were used in determining the electron transport in the samples. Strangely enough, the best photoreduction performance was obtained with the sample giving the most modest electron transfer (Cu/Cu₂O⁻²). The calculated results in density functional theory (DFT) simulations showed that the adsorption energy of CO₂ reduction intermediates linearly increased with the difference in Bader charges (Δq) of various active sites. CO₂ photoreduction activity has a significant advantage because suitable adsorption energy correlates with a modest charge transfer. In this research, I provide suggestions of designing composite catalysts that can effectively catalyze CO₂ photoreduction based on the aspect of electron transfer quantity [84].

Chen et al., transformation of CO to value added high single carbon (C₁) or multi carbon (C²⁺) chemicals is the desired phenomenon, although challenging. Photocatalysis could deactivate and regulate the C-C coupling of CO₂ under mild, nontoxic conditions. We have synthesized a photocatalyst of CO₂ photocatalytic reduction using K₂Fe₂O₄/rGO, magnetic ferrite. A conversion rate value of CO₂ to methane of 23.35 $\mu\text{mol g}^{-1} \text{h}^{-1}$ was displayed by the predicted K₂Fe₂O₄/5%rGO, which is 3.24 and 2.49 times that of photocatalytic catalysts K₂Fe₂O₄ and rGO. K₂Fe₂O₄/rGO provides a superior way to generate multi carbon hydrocarbons, including 43% CH₄ and 57% C²⁺, at one-hundred percent selectivity. The time dependent hydrocarbon profile concentrations to perform photocatalytic reduction of CO₂ are of great strength in serving the purpose of gaining insight to photoreduction mechanics. K₂Fe₂O₄/rGO enables the CO₂ photoreduction process in an alkaline environment, and when simultaneous deoxygenation and C-C coupling occurs [85].

Spilarewicz et al., investigate the gas phase CO₂ to CO photocatalytic reduction reaction at room temperature, ZnFe₂O₄ (ZFO) composites were synthesized with TiO₂ (anatase, rutile). ZFO was synthesized through hydrothermal processing and precipitation of precursors zinc and iron nitrates (V), and the physicochemical characteristics were investigated by XRD, FT-IR, XPS, SEM-EDS, and XRF instruments. ZFO was merely mechanically blended with one of the TiO₂ polymorphs

in an agate mortar to result ZFO/anatase and ZFO/rutile. The fate of the photogenerated electrons and holes was studied by diffuse reflectance UV vis (DRS), transient photocurrent, surface photovoltaic (SPV) and spectroelectrochemical (SE-DRS) spectroscopies. The findings indicate that all the ZFO/TiO₂ systems form a type-I heterojunction. The composites' increased photoactivity as compared to their constituent parts is the result of this kind of band alignment. According to the data, choosing anatase over rutile favors achieving higher CO production yields. This is because anatase has superior electron mobility than rutile, which is explained by the rutile's conduction band's preferential, reducing characteristics [86].

Karim et al., composite PANI@CuFe₂O₄ photocathode was synthesized, characterized, and successfully applied as a photocathode in the photoelectrocatalytic reduction of CO in aqueous medium at an applied potential of -0.4 V and exposed to visible light. Surface chemisorption capacity of CO₂ toward the photocathode was considerably higher upon addition of both PANI and CuFe₂O₄ and further contributed to a significant increase in PEC CO₂ reduction to methanol. This also facilitated the ease of separation of the photogenerated electron hole (e⁻/h⁺) pairs. In PEC CO₂ reduction, IPCE and QE values could be obtained as 7.1 and 24.0%, respectively. The rate of methanol synthesis was 49.3 μmol g⁻¹h⁻¹ and 73 Faradaic efficiency. In comparing to photocatalytic reaction, the results indicated the potential that was applied could successfully dissociate the photogenerated e⁻/h⁺ pairs, enhancing the PEC CO₂ reduction activity of the hybrid photocatalyst [87].

Khan et al., research is devoted to pay attention to the photocatalytic reduction of carbon dioxide (CO₂) to methanol under the impact of visible light (500 W xenon lamp) on a TiO₂ loaded copper ferrite (CuFe₂O₄) photocatalyst. CuFe₂O₄ and CuFe₂O₄/TiO₂ were prepared using the sol gel process with iron(III) nitrate, Fe(NO₃)₃·9H₂O (99%) and copper (II) nitrate, Cu (NO₃)₂·3H₂O (99%) powders as the precursors. The crystal structure and dimensions of the crystallites of the photocatalysts were analyzed with electron hole (e⁻/h⁺) recombination process on a photoluminescence spectrophotometer, morphology on a scanning electron microscope (SEM), absorption characteristics on a UV-Vis and elemental composition on energy dispersive X-ray spectroscopy (EDX) device. The increased photoactivity of the CuFe₂O₄/TiO₂ semiconductor catalyst is attributed to the transfer of photogenerated charges at the interfacial region that effectively separated the charges

and prevented the recombination of the photogenerated electronholes (e^-/h^+) pairs. The key product of $\text{CuFe}_2\text{O}_4/\text{TiO}_2$ was found to be methanol, and it also exhibited nearly three times higher photocatalytic activity to reduce CO_2 than CuFe_2O_4 photocatalyst ($651 \mu\text{mol/gcat L}$). This may be owing to the fact that, the addition of TiO_2 changes the band gap [88].

Batool et al., solar water splitting is a really creative way to produce energy, particularly hydrogen energy. It is necessary to overcome a number of challenges in order to replace the generation of energy resources from fossil fuels. The main component of solar energy harvesting is light absorbers, which transform solar photons into charge carriers for CO_2 reduction and water splitting. Since iron based metal ferrites are abundant, stable, and harmless in water, they have been seen as prospective light absorbers. Additionally, the correct band location of metal ferrites is encouraging for redox reactions (CO_2 reduction, water splitting). To get further advantages in the future, more research is needed in this area. Metal ferrites are also being explored as photocathode and photoanode. Ferrite materials should be thoroughly studied for their fundamental characteristics, creative synthetic procedures should be developed, and their performance should be enhanced through various modification strategies in order to make them effective as photoelectrodes [89].

Liu et al., straightforward hydrothermal process was adopted to synthesize bismuth oxybromide/bismuth oxyiodide coupled with graphitic carbon nitride heterojunctions to suppress the rapid recombination of photogenerated charge carriers of the pure BiOX . The end-product, $\text{BiO}_x\text{Br}_y/\text{BiOI}_n/\text{GCN}$ was stable and strongly promoted the Visible-light-driven catalytic performance in crystal violet and 2-hydroxybenzoic acid. The BB2I1-200-7-10%GCN heterojunction was also observed to have a yield of $0.018 \mu\text{mol/g.h}$ under UV-vis irradiation, indicating a selective conversion of carbon dioxide to figure out methane [90].

Lu et al., use of graphene-based semi-conductor materials is rampant in the experiments conducted to reduce the occurrence of carbon dioxide that offers stability against energy crises as well as climate change. Bad contacts, inadequate active area and charge separation are the defects in the poor semiconducting materials. In order to solve the problems, a ternary nanomaterial structure has been used to design a quaternary chalcogenide nanocomposite that manages the bandgap energy. The

quaternary chalcogenides have been prepared by the use of alpha-hydroxide carboxylic acids. It has as its main aim the induction of interactions between transition metals with the aim of creating a chain. The AgFeNi₂S₄-Graphene-ZnO ternary nanocomposite was synthesized through a modified solvothermal method and applied in CO₂ photoreduction. CO₂ photoreduction was conducted with two types of electron donors and various light sources ($\lambda = 254$ and 565 nm) in order to promote the further diffusion of the CO₂ vapor and extend the lifetime of the oxygen adsorbed electrons. The hybrid AgFeNi₂S₄-Graphene-ZnO photocatalyst exhibited high amounts of CO₂ reduction to methanol due to the excellent connection of the graphene, ZnO and quaternary chalcogenide nanocomposites. The recyclability and stability of the photocatalysts was ensured by carrying out six recycling experiments. This paper has outlined a viable plan of minimising CO₂ and developed a high capacity catalyst in production of hydrocarbon fuels [91].

Otgonbayar & Oh, photocatalytic reductions of CO₂ involving a Cu₂Se graphene nanocatalyst have been studied. A modification of hydrothermal method enabled the successful synthesis of their nanocomposite. X-ray diffraction, transmission electron microscopy, scanning electron microscopy with energy dispersive X-ray microscopy, Raman spectroscopy and X-ray photoelectron spectroscopy were carried out to outline the structure and properties of the synthesized composite. The couple of Cu₂Se and graphene together contributed in providing CO₂ with an effective photocatalytic reduction potential. The photocatalytic activity of the samples were measured by means of photoreduction of CO, to alcohol under visible light irradiation. The results indicated that graphene-based semiconductor hybrid materials have large potentials in terms of use as a photocatalyst in reduction of CO₂ [92].

Li et al., demonstrate a simple impregnation-calcination method to prepare the WO/CN heterojunction photocatalyst with high photocatalytic CO₂ reduction performance. TEM analysis suggests that WO₃ NPs have attached successfully to the g-C₃N₄ nanosheets (CN). Photoluminescence spectrum (PL), UV-vis reflectance spectrum (UV-vis DRS), and photoelectrochemical (PEC) data indicate that photocarrier separation and transfer mechanisms on the photocatalysts are enhanced by the formation of WO/CN heterojunction. Effectiveness of the photocatalytic reduction of CO₂ in the UV and visible light region reflects the photoreduction ability of the formed samples. Like compared with other acquired photocatalysts, these

studies demonstrate that 10-WO/CN photocatalyst is more superior in the realm of photoreduction. With the 10-WO/CN photocatalyst, CO yield is increased by 8.9-fold and CH₄ yield by 47.7-fold under the UV irradiation. The CO and CH₄ yield rates over 10-WO/CN are 8.6 and 7.5 times, respectively, larger than the CN yield rates under visible light irradiation. These photocatalytic and ESR studies have led to the possible direct Z-scheme electron transfer reaction mechanism of 10-WO/CN with the enhanced photoreduction activity of CO₂ [93].

CHAPTER 3

METHODOLOGY

The approach used in this study is a systematic one for synthesis. All experiments were carried out using analytical-grade chemicals to provide purity and accuracy. The synthesis pathway was chosen meticulously on the basis of its applicability towards the structural and functional characteristics of the target materials.

3.1 Chemicals Required

Graphite powder, sulfuric acid (H_2SO_4), sodium nitrate (NaNO_3), potassium permanganate (KMnO_4), hydrochloric acid (HCl), iron chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), sodium hydroxide (NaOH), ethanol, distilled water, and deionized water.

3.2 Synthesis of Graphene Oxide

Two grams of graphite and two grams of NaNO_3 were dissolved in 150 milliliters of H_2SO_4 and stirred for two hours on an ice bath. Six grams of KMnO_4 were then added, pinch by pinch, and stirred for twenty to twenty-four hours. Next, 100 milliliters of DI water and 20 mL of H_2O_2 were added, drop by drop, to halt the reaction. The product was washed with 200 milliliters of 10% HCl and then with DI water, and the nanoparticles were left for three days at 60 degrees Celsius in a dry oven until the GO nanoparticles were collected [94].



Figure 3.1 Synthesis of graphene oxide (GO).

3.3 Copper Ferrite Synthesis

Copper ferrite was prepared by hydrothermal synthesis by first dissolving 0.1M of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and CuCl_2 dihydrate into deionized water (50 ml), and stirring magnetically in 30 minutes. Then NaOH was added to the mixture dropwise until the pH approaches to 11. After that the precursors immediately transfer into a Teflon lined stainless steel autoclave reactor with 150 ml capacity. After that placed the autoclave in heating oven at 140 centigrade for 18 hours. The precipitate of magnetic properties was then separated, cleaned with ethanol and deionized water several times, air-dried to 80 degrees Celsius, and then by using oven treatment, finally calcined for four hours at 500 degrees Celsius [95].



Figure 3.2 Synthesis of copper ferrite (CuFe_2O_4) nanoparticles.

3.4 Copper Oxide Synthesis

Co-precipitation was used to synthesize copper oxide nanoparticles. Initially, 200 mL of distilled water was used to dissolve 0.1 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ while being continuously stirred by magnetic means for 30 minutes. Then NaOH (0.1M) added to the solution dropwise until the pH reached 12. Then the mixture was kept under magnetic stirring at 80 centigrade for two hours. Washing with distilled water several times to remove impurities and transfer the nanoparticles in oven at 80 centigrade for drying. After drying calcined them at 450 °C in a furnace [96].



Figure 3.3 Synthesis of copper oxide (CuO) nanoparticles.

3.5 Synthesis of Binary and Ternary Composite

Binary and ternary composite synthesized by Sonication method.

3.5.1 Binary Composite Synthesis(CuO/CF)

Separately dissolved 3 gram copper oxide and 1 gram copper ferrite in 70 ml deionized water and sonicate them 1 hours .After that mix the both solution and sonicate for 1 hours. Centrifuged it several time with distilled water and ethanol, and transfer them into the oven at 80 centigrade for 2 days [97].



Figure 3.4 Synthesis of copper oxide doped copper ferrite (CuO/CF) binary composite.

3.5.2 Ternary Composite Synthesis(CuO/CF/GO)

To synthesize ternary photocatalyst 3 gram copper oxide, 0.5 gram copper ferrite and 0.5 gram Graphene oxide separately dissolved in ethanol in beakers and sonicate for 1 hour. After that firstly transfer Graphene oxide into 250 ml round bottom flask then dropwise add copper oxide and copper ferrite and sonicate them 1 hour. After one hour centrifugation with ethanol and distilled water was done and transfer to the oven at 80 centigrade for drying [98].



Figure 3.5 Synthesis of copper oxide doped copper ferrite doped graphene oxide (CuO/CF/GO) ternary composite.

3.6 Carbon Dioxide Photoreduction Procedure

A series of preliminary tests were performed under UV and visible light irradiation for three hours in the absence of CO₂ and H₂O before commencing the actual CO₂ photoreduction trials. No detectable reaction products were obtained in these control experiments, confirming that the photoreduction products originated solely from CO₂ sources [99]. For the reduction process, 0.5 g of photocatalyst was dispersed in 80 mL of water, serving as a reducing medium capable of donating electrons. The photocatalytic reactor was purged with CO₂ gas at a pressure of 15 Psi. Illumination, with an intensity of approximately 3.5729 W/cm², was uniformly distributed around the reactor walls and positioned 5 cm from the catalyst surface to ensure effective irradiation. The reaction was carried out for four hours, with liquid samples collected at one-hour intervals. An Agilent 6890N equipped with a Head-space Sampler G1888 (USA) and fitted with a DB-Wax Column containing a polyethylene glycol stationary phase was employed for GC-FID analysis. High-purity nitrogen (99.995%) was used as the carrier gas. Calibration curves were prepared using standards of potential photoreduction products, such as methanol, at different concentrations to determine unknown product content and verify the detector's linear response [100]. Additionally, a carbon monoxide (CO) detector was integrated into the setup to monitor any CO formation during the reaction, ensuring accurate product identification and safety during the photocatalytic reduction process [101].

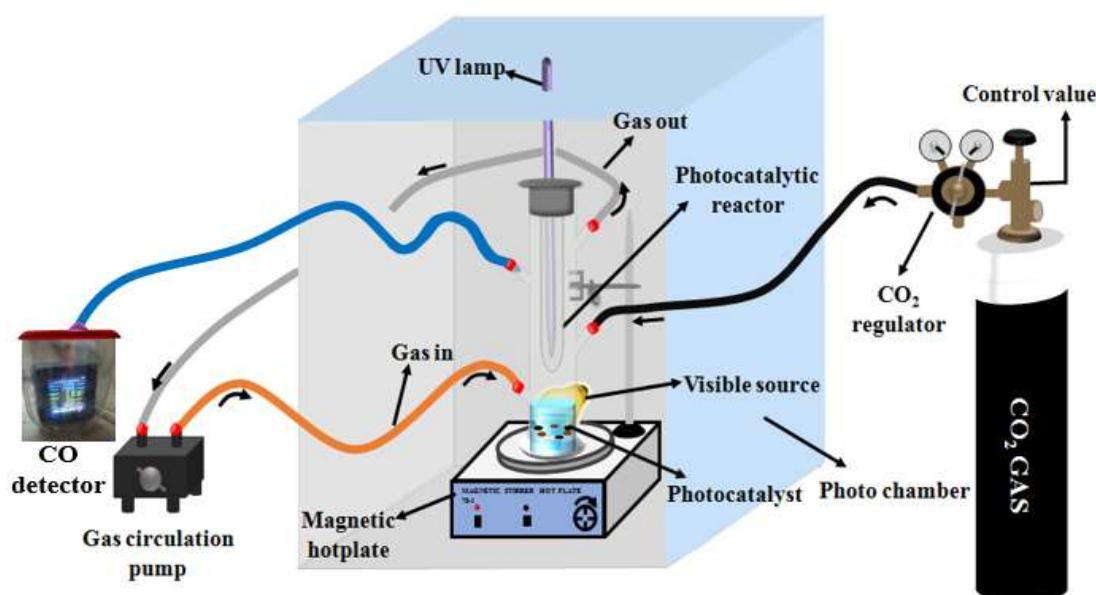


Figure 3.6 Experimental setup with UV-Vis lamp as a radiation source for photocatalytic conversion of CO₂ to carbon monoxide and methan

CHAPTER 4

RESULTS

In this chapter of the synthesized materials the real outcomes of this material as well as the comprehensive characterization of the materials using different analytical tools discussed. The main goals of this section will be to confirm an efficient synthesis and study structural, morphological, optical, and chemical properties of obtained samples, as well as the assessment of their photocatalytic activity (or other properties). Many methods were used like photoluminescence (PL) and Fourier-Transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS), X-ray diffraction (XRD) and electrical examination.

4.1 Optical Analysis

4.1.1 Ultraviolet-Visible Spectroscopy (UV-Vis)

Optical absorption spectra of the suspended GO were obtained. The UV-visible spectrum of the suspended GO showed a characteristic peak at 224 nm (Figure 4.1). This peak was attributed to the π - π^* transitions of the C=C aromatic bond. The 300 nm shoulder is attributed to the n - π^* transitions of C=O bond [102-104]. The CuO doped copper ferrite (CuO/CF) binary composite exhibited a high rate of light absorption in the visible region and UV region with maximum range around 410 nm (Figure 4.1). The CuO and CF nanoparticles collaborate to enhance sustained light collecting properties, hence the enhancement of the absorption spectrum in CuO/CF. The enhancement offers better photocatalytic capability to reduce CO₂ when it is irradiated by UV-Vis [105]. Moreover, the band edge of copper-based ternary composites in comparison with binary composites covers a wide spectrum of the UV-Vis absorption spectrum (Figure 4.1) [106]. Also, the incorporation of GO in the binary composite of CuO/CF provides a surface that inhibits the recombination of electrons and holes, which may otherwise cause an increase in the product yield and a photocatalytic reduction reaction [107]. According to Ahmed et al., the optimal range

of UV-Vis spectrum in which photocatalytic CO₂ reduction can take place is between 300 and 430 nm [88].

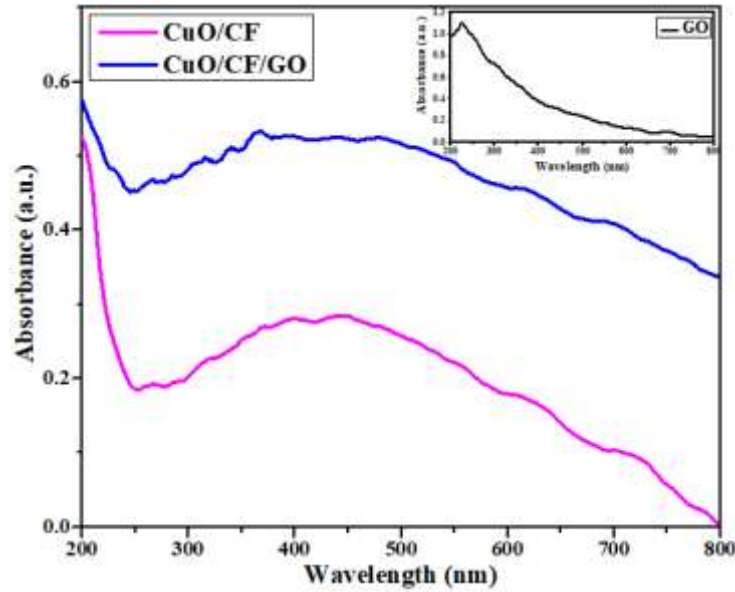


Figure 4.1 UV-Vis spectrum analysis of graphene oxide (GO), copper oxide doped copper ferrite (CuO/CF) binary composite, copper oxide doped copper ferrite doped graphene (CuO/CF/GO) ternary composite.

Band Gap Estimation:

The band gap explains the change of $\bar{e}$ of VB to CB of photo-composite material due to the band gap energy of 1.23 to 3.26 eV is the best energy in CO₂ reduction photocatalytic activity [108-110]. A Tauc plot is used to compute band gap energy; the formula is as follows:

$$\alpha (h\nu)^2 = A (h\nu - E_g) \quad (1)$$

In the above equation (1), α signifies the absorption co-efficient and is determined by using below expression mentioned in equation 2.

The absorption coefficient, α denoted in equation (1) is computed by the following calculation, which appears in equation 2.

$$\alpha = \pi k / \lambda \quad (2)$$

Where k is absorbance and λ is the wavelength.

Figure 4.2 tauc plot using linear extrapolation suggests that the band gap energy of GO is 2.10 eV, which agrees with the one in the literature [111], and that GO cannot perform photocatalysis or absorb light under visible light sources. Marotti et al. explain that smaller crystallites sizes lead to smaller band gaps. The ability of the CuO/CF binary composite to absorb the UV and the visible light is justified by the 1.70 eV band gap (Figure 4.2). The binary system is superior to its individual components due to the interaction between CuO/CF that improves interfacial charge separation, reduces electron-hole recombination, and improves charge mobility [108]. It was also found that the ternary composite (CuO/CF/GO) exhibited a band gap energy of 1.40 eV (Figure 4.2), which suggested the low energy barrier required to facilitate $\bar{e}$ and hole transfer. Hence, the lower band gap semiconductor materials consumed less energy to generate $\bar{e}/h^+$ pairs at UV/Vis light [112]. Semiconducting materials that have lower energy band gap are highly efficient in the reduction of CO_2 by photocatalysis and are highly sensitive to visible light.

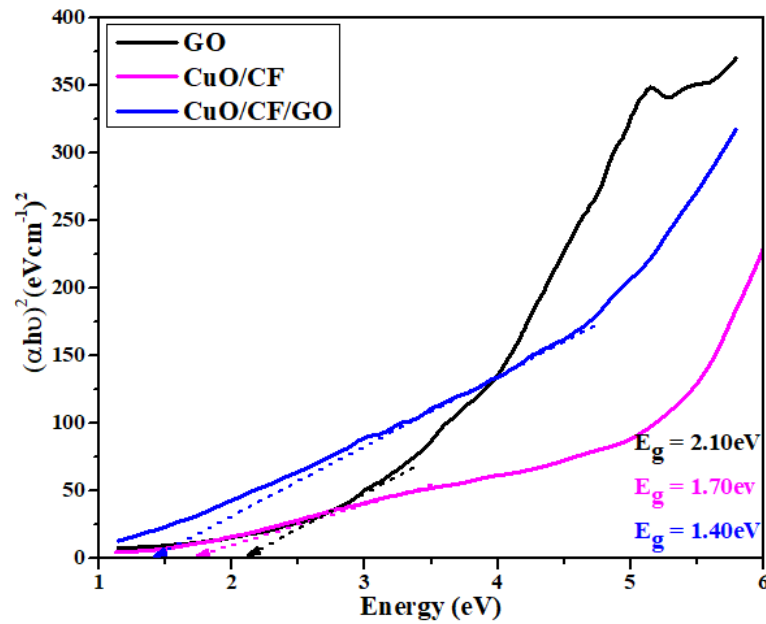


Figure 4.2 Tauc's plot to estimate comparative band gap energies (E_g) of synthesized graphene oxide (GO), copper oxide doped copper ferrite (CuO/CF) binary composite, and copper oxide doped copper ferrite doped graphene (CuO/CF/GO) ternary composite.

4.1.2 Photoluminescence Emission Spectroscopy (PL)

PL (Agilent Cary Eclipse Fluorescence Spectrometer, USA) emission spectra were used to investigate the trapping efficiency, migration, and electron-hole ($\bar{e}/h^+$) pair recombination in a photocatalytic material, reduced PL emissions intensity indicates reduced rate of $\bar{e}/h^+$ pair recombination [113]. The qualitative examination of all the required samples intensities was carried out utilizing the same experimental set-up. Also, the PL spectra of the CuO/CF binary and CuO/CF/GO ternary composite were compared (Figure 4.3).

Ternary composite exhibits reduced PL intensity than the CuO/CF binary composite because the photogenerated electrons of CF are segregated to the CuO nanoparticles through loading of GO sheets as electron mediator. This implies that ternary composite can be successful in inhibiting recombination of $\bar{e}/h^+$ pair, increasing the lifetime of the charge carrier and yielding greater photocatalytic reduction activity. It shows that doping over CF and CuO NPs might lead to a stronger electron-sink property of GO and promote charge carrier separation in a photo-composite [87, 113, 114].

In fact, the two defects normally attributed to the PL peaks include OV's and shallow defects. Peaks indicate that the $\bar{e}$ is transferred in the CF valence band by trapped $\bar{e}$ of OV's. It is also these OV's that make the photogenerated $\bar{e}$ at CB go to the empty spaces, and recombine with holes created at VB to give a fluorescent emission at a specific wavelength [115]. Moreover, the surface hydroxyl groups of MO_x (H_2O-OH) play an important role in $\bar{e}$ trapping. With a decrease in PL intensity, $\bar{e}/h^+$ couple density increases and the recombination rate decreases. Thus, the CuO/CF/GO ternary composite contains more vacancies and defects than the CuO/CF binary, improving the separation of $\bar{e}/h^+$ pairs. Also, individual nanomaterials enhance the rate at which CO_2 is reduced by a composite [116].

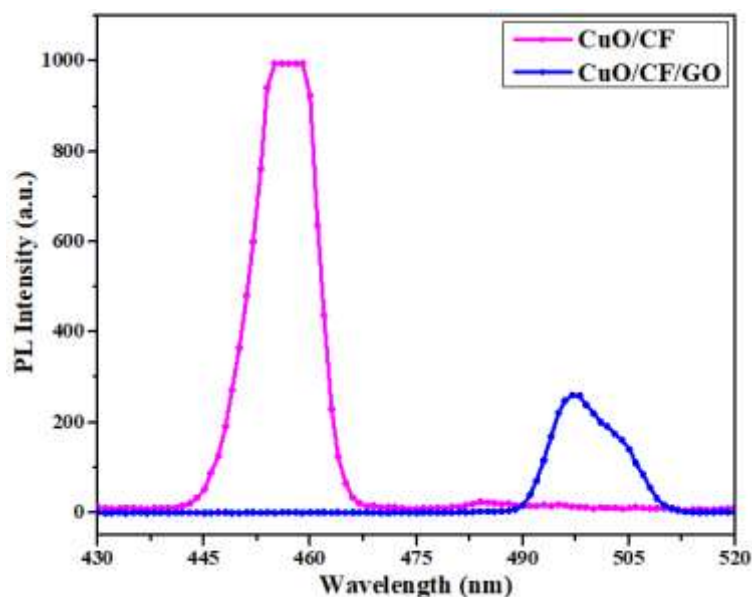


Figure 4.3 PL emission spectra/spectral analysis of copper oxide doped copper ferrite (CuO/CF) binary composite, and copper oxide doped copper ferrite doped graphene (CuO/CF/GO) ternary composite.

4.2 Electrochemical Analysis

4.2.1 Electrochemical Impedance Spectroscopy (EIS)

Besides PL analysis, electrochemical impedance spectroscopy (EIS) Nyquist plot in visible lighting as observed in Figure 4.4 may be employed to further elaborate the charge carrier mobility of the CuO/CF binary and CuO/CF/GO ternary composites. These characteristic graphs indicate that the charge transfer process can be denoted by a semicircle of diameter: charge transfer resistance (R_{ct}), and the semicircle and the warburg at high frequencies. Based on the EIS plot (Figure 4.4), the arc radius of the ternary composite of CuO/CF/GO seems to be smaller, which means that the ternary composite can transfer interfacial charges better and consequently, the photocatalytic activity of CuO/CF/GO is higher. This may be attributed to the fact that the superior conductivity of graphene or its incorporation, which decreased the charge transfer resistance (R_{ct}), could be the probable cause. In addition, the high-level of agreement between NPs leads to higher graphene conductivity, therefore, reducing resistance and charge recombination due to $\bar{e}$ transfer involving CF to CuO through $\bar{e}$ mediator GO.

In addition, the ternary composite has a slimmer semicircle than the binary composite could be because UV-visible light can be more strongly absorbed, generating photo-induced charge. This further substantiates the Schottky heterojunction between the CuO/CF and GO that promotes the movement of the photogenerated charge carriers. All these results revealed that the binary composite (CuO/CF), owing to its relatively higher impedance, mainly facilitated the generation of carbon monoxide as the reduction product. In contrast, the ternary composite (CuO/CF/GO), with its lower impedance value, exhibited superior charge transfer and enhanced reaction kinetics, enabling the photoreduction of CO₂ into both carbon monoxide and methanol, with methanol being produced at the maximum yield.

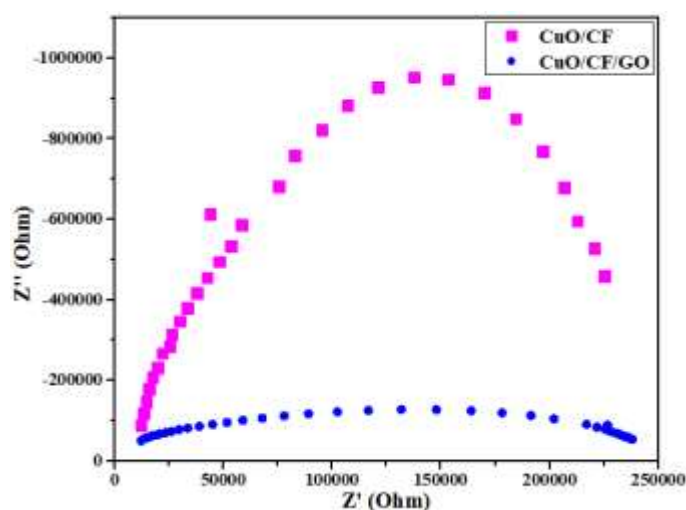


Figure 4.4 EIS Nyquist plots of copper oxide doped copper ferrite (CuO/CF) binary composite, and copper oxide doped copper ferrite doped graphene (CuO/CF/GO) ternary composite.

4.3 Morphological Analysis

4.3.1 Scanning Electron Microscopy (SEM)

The morphology and topography of the surface of the produced GO, and ternary composite were studied by scanning electron microscopy (SEM) apparatus (Zeiss EVO LS10 system, Germany). The morphological features of graphene oxide (GO) are ultrathin, wrinkled and layered sheet-like structures composed of sharply edged graphitic carbon flakes as indicated in SEM micrograph of GO (Figure 4.5a). Besides

giving the material a large specific surface area and offering many anchoring sites, the folded and wrinkled geometry confirms the nature of graphene oxide. Such a two-dimensional layered structure with an efficient platform can create a uniform and stable composite structure in which CuO and CF nanoparticles can be deposited [117]. Conversely, a uniform mosaic distribution of CuO and CF nanoparticles attached to the wrinkled GO sheets is evident on the SEM image of the ternary composite of CuO/CF/GO (Figure 4.5b). CuO and Fe-based nanoparticles have a high surface energy and magnetic dipolar interactions; hence the particles are evenly distributed across the surface with minimal aggregation observed in some regions [118]. The GO framework is used to efficiently prevent extreme aggregation and ensure that dispersion remains constant regardless of this gathering. Monolithic distribution of nanoparticles across the GO substrate is beneficial to enhanced sonocatalytic performance [119]. The observed weak aggregation is also explained by Van der Waals, whereby high surface energy nanoparticles seek to reduce their energy state by sticking to each other [120]. Nevertheless, the overall morphology indicates that, the CuO nanoparticles enlarge the surface area, as well as the pore diameters and this significantly augments the transport and adsorption of CO₂ molecules on the photocatalyst surface [121]. This structural benefit has the direct effect of increasing CO₂ reduction rate, which raises the methanol production.

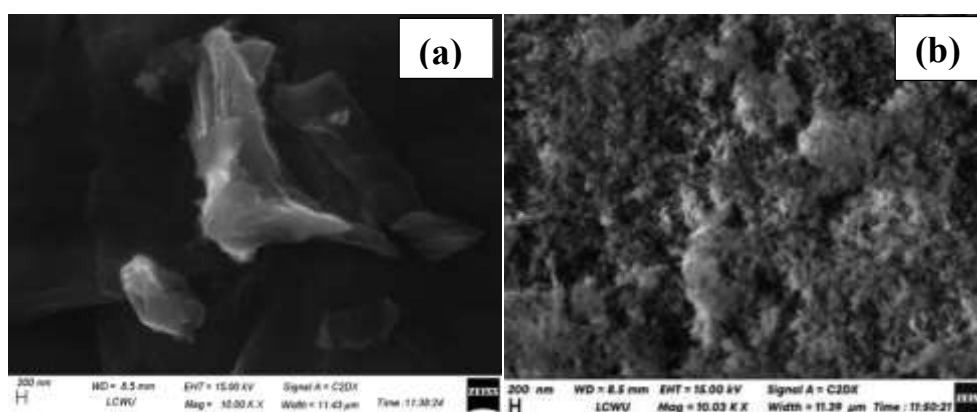


Figure 4.5 SEM micrographs of (a) graphene oxide (GO), and (b) Copper oxide doped copper ferrite doped graphene oxide (CuO/CF/GO) ternary composite.

4.4 Structural Analysis

4.4.1 Fourier Transform Infrared Spectroscopy (FTIR)

In order to clarify the functional groups and prove the effective synthesis of the materials, Figure 4.6 presents the FTIR spectra of GO, CuO/CF binary, and CuO/CF/GO ternary composites. The instance of GO had a few unique vibrational modes (Figure 4.6a). When the sample contained surface hydroxyl functionalities, the wide absorption band at 3348 cm^{-1} was attributed to the OH stretching vibrations of phenolic or alcoholic groups [122, 123]. The C=C band at 1634 cm^{-1} indicated the retention of unoxidized graphitic domains in the GO structure [124], and the extra bands in 1404 cm^{-1} were correlated with O-H deformation vibrations [125]. The asymmetric C-O-C stretching and C-O stretching of alkoxy groups at 1188 cm^{-1} and 1050 cm^{-1} , respectively, were attributed to the absorption features [126, 127]. The connection of the components was established as the vibrational characteristics increased significantly upon the CuO doped CF in the binary composite (Figure 4.6b). The presence of the O-H stretching vibration band at 3341 cm^{-1} was a sign of retained hydroxyl functionalities [128, 129]. Bands at 1544 cm^{-1} and 783 cm^{-1} were found to have O-H and C-H vibrational modes, respectively [130, 131]. Importantly, the generation of metal-oxygen bonds was confirmed with high absorption peaks under low frequency range. This peak at 510 cm^{-1} was attributed to Cu-O vibrations [132] whereas the one at 471 cm^{-1} was attributed to Fe-O stretching modes [133]. The ternary composite of CuO/CF/GO (Figure 4.6c) spectrum reflected some properties that indicated effective incorporation of the GO sheets. Strong O-H stretch vibrations were observed at 3570 cm^{-1} and 3485 cm^{-1} , indicating that there were adsorbed water molecules and surface hydroxyl groups [134]. Though the band at 1640 cm^{-1} was ascribed to C = C stretching [135] the peak at 1110 cm^{-1} was correlated with C-O-C stretching vibrations, which is a characteristic of graphitic domains of GO [136]. Also, C-H out-of-plane bending vibrations were observed at 987 , 895 and 847 cm^{-1} [137]. Cu-GO and Fe-O stretching vibrations were found to be the reason behind the new prominent bands that emerged at 806 and 750 cm^{-1} , respectively [138, 139]. Moreover,

the presence of a high absorption feature at 580 cm^{-1} was congruent with the Cu-O vibrations, which is closely comparable with published observations [96, 140, 141].

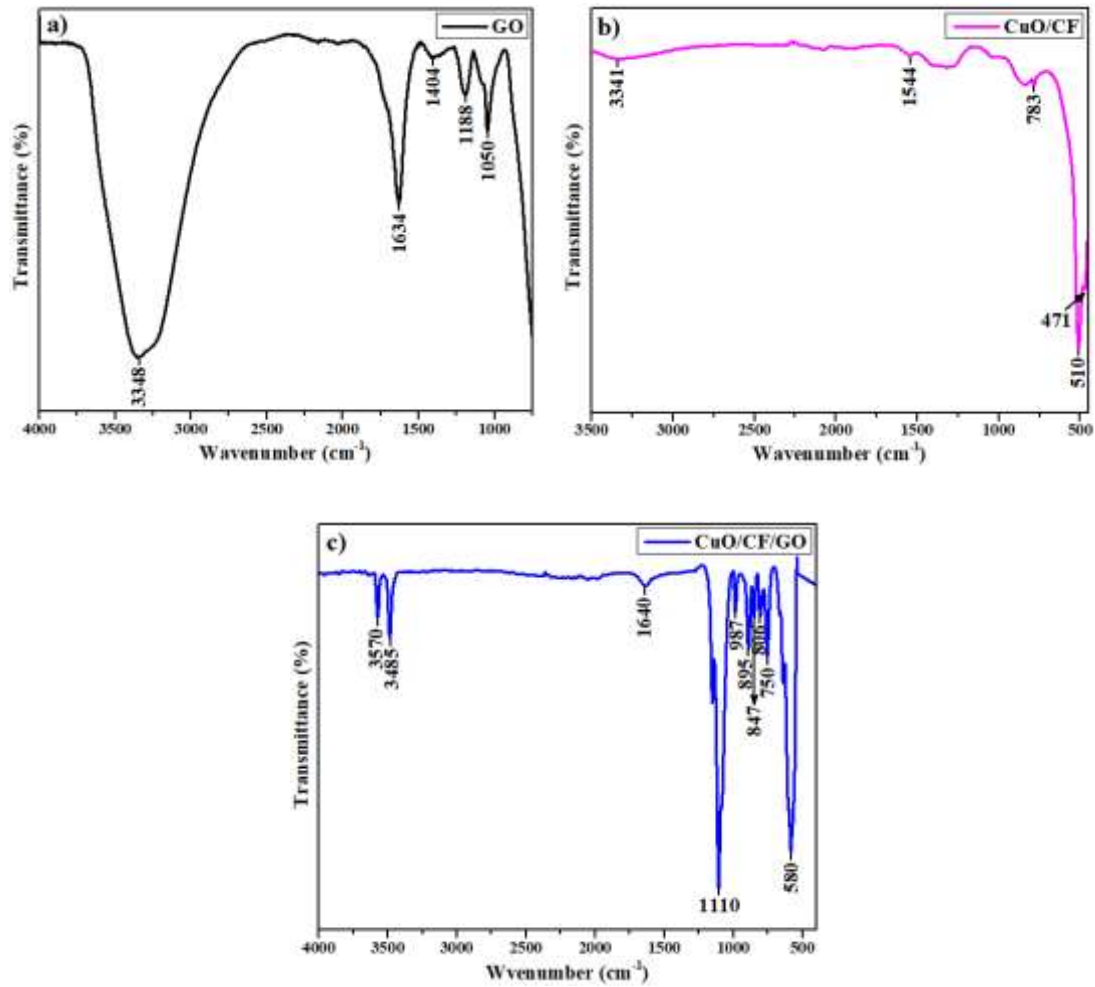


Figure 4.6 FT-IR spectra of (a) graphene oxide (GO), (b) copper oxide doped copper ferrite (CuO/CF) binary composite, and (c) copper oxide doped copper ferrite doped graphene oxide (CuO/CF/GO) ternary composite.

4.4.2 X-Ray Diffraction Analysis (XRD)

The crystallite size and structure composition of CuO/CF binary and CuO/CF/GO ternary composite were analyzed with XRD and are presented in Figure 4.7 (a, b). CuO/CF binary composite exhibited distinct peaks (Figure 4.7a) of diffraction at 2θ values of 39.22° , 49.06° , 58.66° , 68.50° , and 75.69° , all corresponded to the crystal planes hkl (200), (-202), (202), (220), and (-222) of CuO nanoparticles JCPDS card no (96-101-1149) [108, 142]. CF shows several diffraction 2θ angles observed at

30.80°, 36.09°, 37.19°, 54.20°, 62.05°, 64.17°, 66.54° attributed to planes (200), (211), (202), (312), (224), (400) and (314) respectively that has a good agreement with the results reported in the JCPDS card no (96-901-1013). The diffraction peaks of prepared CuO/CF/GO ternary composite observed (Figure 4.7b) at 2θ (35.73°, 39.22°, 49.61°, 53.71°, 58.66°, 61.86°, 66.31°, 68.27° and 72.93°) consistent to hkl values (-111), (200), (-202), (020), (202), (-113), (022), (113), (311) respectively shows the planes of monoclinic copper oxide JCPDS card no (96-900-8962) [143]. While other peaks observed at 30.17° (022), 37.18° (222), and 75.24° (262) confirm the presence cubic spinel copper ferrite JCPDS card no (96-156-5337). Surprisingly, the ternary composite did not evidently show the characteristic diffraction peak of GO. This absence can be attributed to the relative dilution of GO, to the disordered and exfoliated nature of its nanosheets, or to overlap of the broad background signals by the metal oxides. In addition, the diffraction strength in GO can be lowered further to nondetectable extents because of its highly scattered or amorphous character of the composite matrix [113, 144]. The crystallite sizes of the composites using the Debye-Scherrer equation were found to be approximately 10.46 nm and 11.89 nm in the CuO/CF binary and CuO/CF/GO ternary composite, respectively [142-144]. The slight enhancement in the crystallite size with the addition of GO sheets is implied to indicate an interaction between CuO and CF phases and GO sheets. This reaction may result in higher crystallinity and higher stability of the ternary composite.

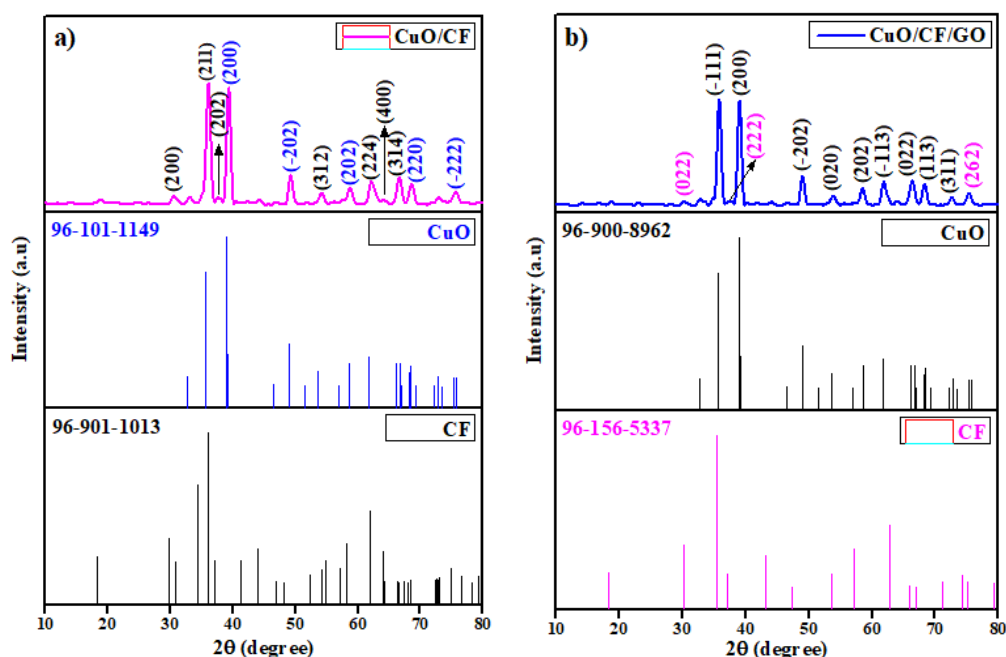


Figure 4.7 XRD profile of the synthesized (a) copper oxide doped copper ferrite (CuO/CF) binary composite, and (b) copper oxide doped copper ferrite doped graphene oxide (CuO/CF/GO) ternary composite with reference pattern of CuO and CF NPs.

4.4.3 X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was used to analyze the electrical structure of the CuO/CF binary and CuO/CF/GO ternary composite systems as well as the surface chemical states. The wide survey spectra confirmed the presence of Cu, Fe, and O in the binary and ternary composites without any evidence of extraneous contaminants. Also, the C signal was detected in the ternary composite. The O 1s, Fe 2p and Cu 2p states are attributed to the observable binding energy peaks identified at 529.7, 711.8, and 933.9 eV, respectively. Also, a second binding energy peak at 286.6 eV corresponding to C 1s was observed in the ternary composite, indicating that GO was indeed integrated into the photocatalyst system. As depicted in Figures 4.8(a) and 4.9(a) these findings confirm the successful synthesis of the binary and ternary composites in high phase purity [145].

The high-resolution Cu 2p spectra analysis provided more insight into the oxidation state of copper in the binary and ternary composites. The existence of the Cu^{2+} species

was ascertained by the fact that two distinct peaks were observed in the CuO/CF binary composite at 934.37 eV and 954.06 eV, respectively. These peaks are due to the spin orbit doublet of Cu 2p^{3/2} and Cu 2p^{1/2}. Three shakeup satellite peaks (942.11, 944.55, and 962.90 eV) were discovered, too. The peaks of 942.11 and 944.55 eV are associated with the Cu 2p^{3/2} state and the Cu 2p^{1/2} state with the higher binding energy at 962.90 eV. All these peaks are a pointer to the presence of Cu²⁺ ions in a tetrahedral coordination environment (Figure 4.8(b)). The experimentally determined satellite characteristics were 933.95 eV (Cu 2p^{3/2}) and 953.76 eV (Cu 2p^{1/2}). Cu 2p spectra further confirmed that the species was Cu 2p. The peak at 962.60 eV corresponds to the tetrahedral coordinated Cu 2p^{1/2} which is consistent with the tetrahedral coordinated Cu²⁺ state (Figure 4.9(b)). The Cu 2p^{3/2} is here located at 941.70 and 944.21 eV. Final-state effects and ligand-to-metal charge transfer interactions make these shake-up satellite peaks characteristic fingerprints of Cu²⁺ and so their appearance is a strong illustration of the divalent copper [143, 146-148].

High-resolution Fe 2p spectra are presented in figures 4.8(c) and 4.9(c) and were utilized to further investigate the oxidation state of iron in binary and ternary composites. In the deconvoluted spectra, four distinct peaks could be seen. Fe 2p^{3/2} state of Fe³⁺ were determined by the binding energy values of 712.3 and 715.7 eV, but Fe 2p^{1/2} of Fe³⁺ was determined by the peak of 722.8 eV. Moreover, we have also observed a satellite peak at 719.3 eV, again relatable to Fe 2p^{1/2} of Fe³⁺. The presence of these characteristic properties justifies the trivalent state of the iron in the composites as values reported near these before in the literature [143, 148, 149]. It is interesting that in XPS spectra Fe 2p^{1/2} is larger, and this is consistent with effects of spin-orbit splitting, despite its lower angular momentum than Fe 2p^{3/2} [143, 148].

The O 1s high-resolution spectra gave further evidence of the CF and CuO phase formation. The spectrum of the CuO/CF binary composite (Figure 4.8(d)) was decomposed into three compositions: lattice oxygen (O_{Lo}) of CF and CuO was attributed to the peak at 529.66 eV, surface-adsorbed oxygen (O_{So}) was attributed to the peak at 530.11 eV, and chemisorbed oxygen species existing on the composite surface were attributed to the shoulder at 531.64 eV. O 1s spectrum of the ternary

e4composite of CuO/CF/GO (Figure 4.9(d)) was as well decomposed into 3 peaks. The binding energy of the lattice oxygen ($O_1 = 529.51$ eV) of CF and CuO, the surface-adsorbed oxygen ($O_2 = 530.0$ eV), and the chemisorbed hydroxyl groups and adsorbed H_2O molecules were attributed to the shoulder at 531.39 eV [106, 165]. Lattice oxygen (O_1) species critically mediate the redox reaction of metal oxides by facilitating the oxidation of water (O_2) and the restocking of nearby oxygen vacancies (OVs) at active metal sites through the incorporation of molecular O_2 . These OVs form superoxide radicals ($O_2^{\bullet-}$) by acting as the active sites of the O_2 molecules, and enhance the reoxidation potential of the photocatalyst by exchanging with oxygen species on the surface (O_{So}) [150]. The binary composite (CuO/CF) displayed surface oxygen vacancies at a CuO loading of 70%, whereas the ternary composite (CuO/CF/GO) exhibited these vacancies at a CuO loading of 100%. These defects facilitate the CO_2 adsorption process by donating a few OV-forming electrons to the neighboring CuO metal ions partly reducing the oxidation state of the latter [146, 151-153]. Moreover, redox cycling of Cu(I) and Cu(II) species and consequently the electron delocalization stimulates the OV production [154]. By effectively inhibiting the recombination of electrons and holes as well as promoting the transportation of electrons, these defect sites improve photocatalytic functionality [151, 155, 156]. Previous studies by Rodriguez and Pipornpong et al. have shown that higher electron density stored in OVs leads to CO_x adsorbing selectively at defect sites and is then transferred to the adsorbed CO_x molecules [157, 158]. Moreover, OVs play a crucial role by adsorbing and dissociating H_2O and O_2 gas molecules on the catalytic surface. They also play a similarly significant part in improving visible light absorption and accelerating the production of methanol during photocatalysis [159].

Figure 4.9(e) also shows that C 1s XPS spectrum was employed to further examine the incorporation of GO sheets within ternary composite. A strong C 1s signal at 284.38 eV was also observed indicating a presence of graphitic sp^2 hybridized carbon in graphene. The peaks associated with oxygenated functional groups e.g. C-O (286.20 eV), C=O (287.87 eV) and COOH (approximately 288 eV), on the contrary, exhibited significantly reduced strength. This finding confirms the partial deoxygenation of GO during synthesis of the CuO/CF/GO ternary composite which clearly shows the

deoxygenation process [145, 160]. The close C-C bonding of the reduced GO network increases electronic conductivity, thus enabling more effective charge transportation in the composite and boosting photocatalytic CO₂ reduction to methanol [143]. In addition, the high-resolution Cu 2p and Fe 2p spectra confirmed the presence of both Cu and Fe species in the ternary compound. The strong interfacial contact between CuO and CF promotes the formation of the oxygen vacancies, which are common active sites in redox reactions. The strong interfacial contact between CF and CuO facilitates the formation of oxygen vacancies which are highly recognized as redox active sites. The concentration of such vacancies under photocatalytic conditions plays a vital role in the activation of CO₂ and the subsequent re-oxidation process. In the binary composite (CuO/CF), this primarily promotes the formation of carbon monoxide as the major reduction product. However, in the ternary composite (CuO/CF/GO), the presence of these vacancies further enhances the charge transfer process, which not only supports the generation of carbon monoxide but also enables the effective production of methanol with higher efficiency.

4.4.3.1 Oxygen Vacancies Quantitative Analysis (OVs)

Quantitative analysis of the oxygen vacancies in the binary and ternary composite was performed using the deconvoluted O 1s XPS spectra as shown in Figure 4.8(d) and 4.9(d). To do this, the areas of peaks of different oxygen species were numerically added. The fractional distribution of lattice oxygen, adsorbed oxygen on the surface, and oxygen species associated with vacancies was determined by the application of the Trapezoidal rule, a popular computational method of approximating the area under discrete spectral data samples. Trapezoidal rule as used in this analysis can be expressed mathematically as shown in equation (3). This technique allowed the concentration of the oxygen vacancies within the ternary composite to be accurately determined and further details on the chemistry of the defects as well as the relationship between the defects and photocatalytic activity were obtained.

$$\int_a^b f(x) = d_x \approx \sum_{i=1}^n \left(\frac{(x_i - x_{i-1})(f(x_i) + f(x_{i-1})))}{2} \right) \quad (3)$$

Relative Content Calculation %:

Relative contribution of each peak in O 1s spectra was also calculated using relative percentage formula as represented below in equation 4.

$$Peak\ \%age = \left(\frac{Peak\ Area}{Peak\ Area\ (Total)} \right) \times 100 \quad (4)$$

By using this formula, % age calculations of each peak was calculated.

Integration of Peaks:

Quantitative deconvolution of O 1s spectra was used to determine the relative contributions of lattice oxygen, oxygen vacancies and surface hydroxyl/adsorbed water species in binary and ternary composites. CuO/CF lattice oxygen (529.66 eV), oxygen vacancies (530.11 eV) and surface OH/H₂O (531.64 eV) oxygen species contributions occurred at 49.37% and 34.35% and 16.28% of total O 1s, respectively, in the binary CuO/CF system (Figure 4.8(d)). The 45.95% of the CuO/CF/GO ternary composite consisted of lattice oxygen (529.51 eV), oxygen vacancy (530.00 eV), and surface hydroxyl/ adsorbed water species (531.39 eV) (Figure 4.9d)). These results indicate that the addition of GO preserves a high density of oxygen vacancies and the proportion of surface hydroxyl/adsorbed water species. Although lattice oxygen assists in preserving the redox cycling processes at the active sites, the relatively higher proportion of OVs in both binary and ternary composites are necessary in CO₂ activation by offering electrons to adsorbed molecules. An optimal ratio between OVs and lattice oxygen in the ternary system facilitates superior reduction of CO₂ to methanol by catalysts, and further leads to better charge separation and transfer as compared to the binary composite.

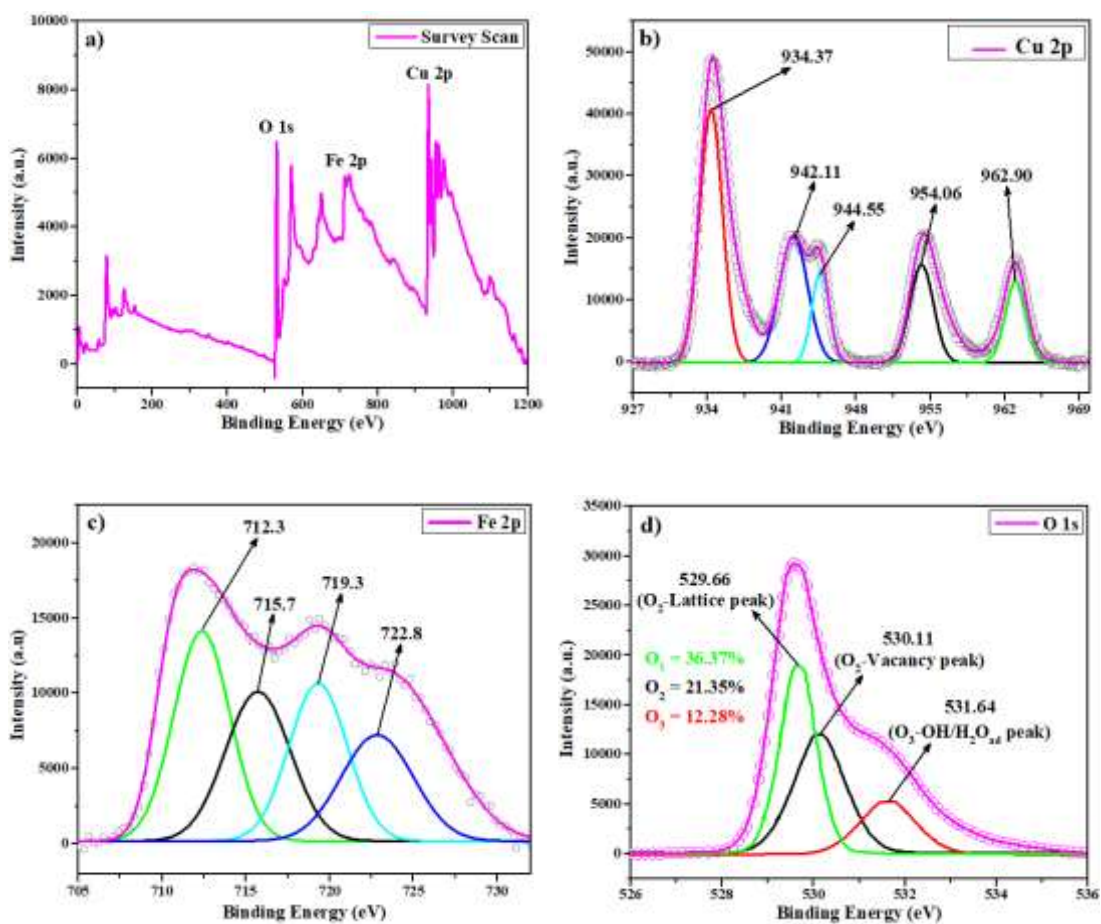
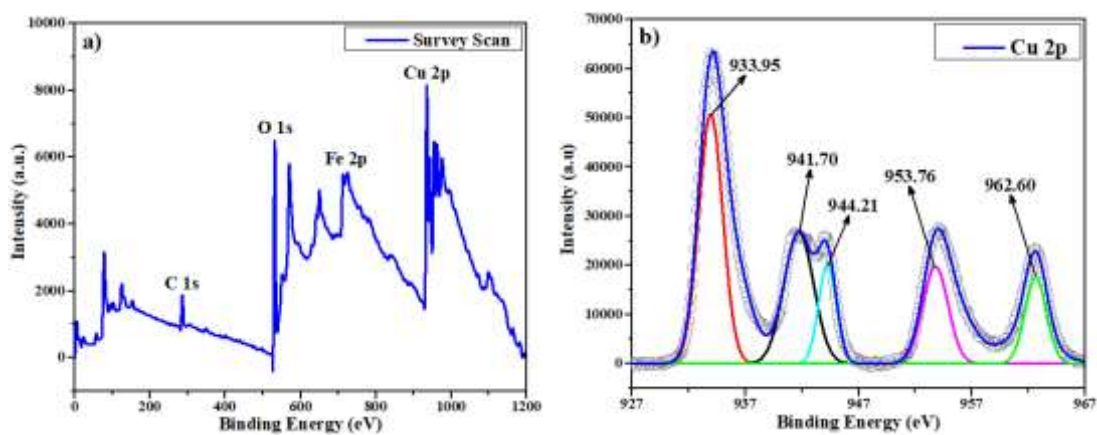


Figure 4.8 XPS spectra of S-scheme copper oxide doped copper ferrite (CuO/CF) binary composite heterostructure: (a) Survey scan, (b) Cu 2p, (c) Fe 2p, and (d) O 1s.



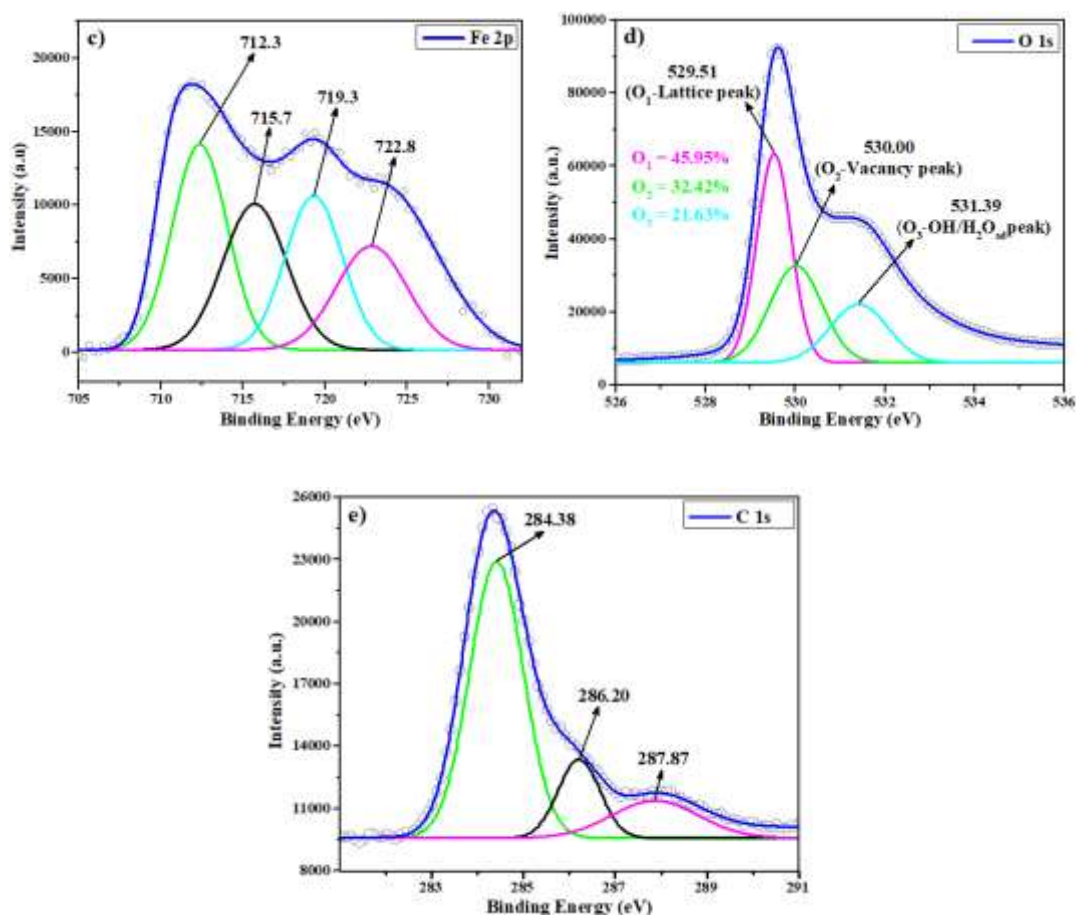


Figure 4.9 XPS spectra of S-scheme copper oxide doped copper ferrite doped graphene oxide (CuO/CF/GO) ternary composite heterostructure: (a) Survey scan, (b) Cu 2p, (c) Fe 2p, (d) O 1s, and (e) C 1s.

4.5 Gas Chromatography-Mass Spectrometry (GC-MS)

The GC-MS chromatogram presents the separation profile of the injected sample, where the x-axis represents the retention time (minutes) and the y-axis corresponds to detector response (pA). A distinct peak is observed at approximately 2.0 minutes, which is identified as methanol (Figure 4.10). This indicates that methanol eluted quickly from the column due to its low molecular weight, high volatility, and weak interaction with the stationary phase. The sharp nature of the peak reflects good resolution, confirming the presence of methanol in the tested sample. Beyond this point, the chromatogram shows a gradual baseline decline without significant additional peaks, suggesting that methanol is the primary detectable component under

the given analytical conditions. The result demonstrates that GC-MS effectively separated and detected methanol in the sample with high sensitivity.

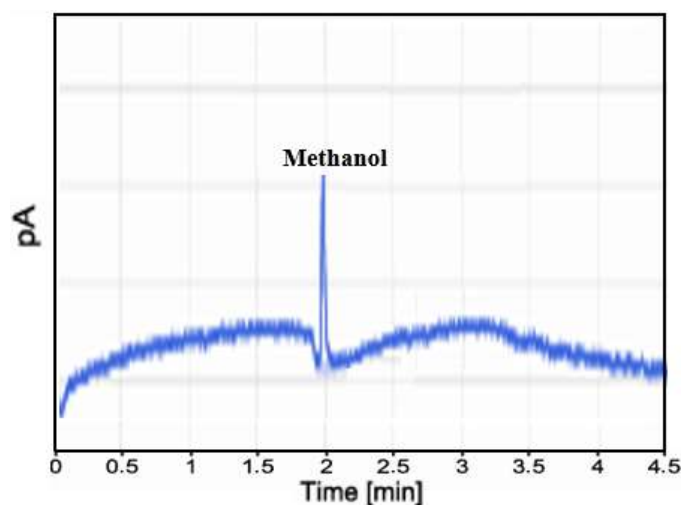


Figure 4.10 Chromatographic Profile of Methanol Detected by GC-MS.

4.6 Photoreduction of CuO/CF/GO Composite

To verify that the detected products, such as methanol and carbon monoxide, are genuinely generated through the photocatalytic reduction of CO_2 and not from external contaminants, a series of control experiments were conducted, as summarized in Table 4.1. These controls included:

1. Operating the reactor without introducing CO_2
2. Carrying out the reaction in the absence of any light source (both UV and visible)
3. Performing the reaction without adding the photocatalyst to the reactor

In all these blank experiments, no formation of methanol or carbon monoxide was observed, confirming that these products originate exclusively from CO_2 reduction under photocatalytic conditions [161]. If, however, any trace products are detected in such control runs, their amounts must be subtracted from the experimental values obtained under real CO_2 reduction conditions to avoid overestimating the catalytic performance [162].

Table 4.1 Elucidates sundry control experiment to affirm the source of carbon based compounds, X= Without particular substance, ☒ = Sign shows availability of particular reactants.

Experiment Number	Reaction Conditions				
	CO ₂	Light Intensity	Photocatalyst	Reducing Agent	MeOH Formation
1	X	☒	☒	☒	X
2	☒	X	☒	☒	X
3	☒	☒	X	☒	X
4	☒	☒	☒	X	X
5	☒	☒	☒	☒	☒

4.6.1 Photocatalytic CO₂ Reduction Performances

The photocatalytic performance of the binary CuO/CF composite confirmed that this system is selective exclusively toward carbon monoxide (CO) formation, as presented in Figure 4.11(a) and Table 4.2. The CO yield increased progressively with reaction time, recording 58 ppm, 70 ppm, and 75 ppm after the first, second, and third hours, respectively, while no methanol formation was observed throughout the experiment. This selective CO generation is mainly linked to the limited charge separation capability of the binary catalyst and the absence of efficient electron transport channels. Although CuFe₂O₄ (CF) contributes visible-light absorption owing to its narrow band gap (1.64 eV), the lack of a strong mediator for electron transfer results in rapid recombination of charge carriers. Consequently, only a single-electron reduction of CO₂ occurs, favoring CO evolution rather than the multi-electron reduction steps necessary for methanol production.

In contrast, the ternary CuO/CF/GO composite exhibited a distinct behavior, as shown in Table 4.2. The incorporation of graphene oxide (GO) not only enhanced CO production but also facilitated methanol generation. CO yields increased to 63, 104, and 120 ppm after one, two, and three hours, respectively (Figure 4.11(a)), surpassing those achieved with the binary system. Simultaneously, methanol production was

recorded with yields of 1.40, 0.0086, and 0.00914 $\mu\text{mol g}^{-1} \text{h}^{-1}$ (Figure 4.11(b)), along with quantum efficiencies of 0.0001215%, 0.00002%, and 0.000034%, at the respective time intervals (Figure 4.11(c)).

The improved activity of the ternary system arises from the synergistic contribution of GO. Its two-dimensional conductive network accelerates electron transport and suppresses recombination losses, while its sp^2 -hybridized domains and oxygen functionalities provide effective adsorption and activation sites for CO_2 molecules. In conjunction with the catalytic sites of CuO and CF, these features establish favorable charge transfer pathways and enable multi-electron reduction processes. As a result, the ternary composite successfully drives the simultaneous formation of CO and methanol.

Thus, while the binary CuO/CF catalyst is restricted to CO evolution via single-electron transfer, the introduction of GO transforms the system into an efficient ternary photocatalyst (CuO/CF/GO) capable of yielding both CO and methanol under photocatalytic conditions, as clearly demonstrated in Figures 4.11(a-c) [163].

Table 4.2 Photoreduction of CO_2 into methanol under certain controlled experimental conditions.

Sample	Reaction Precursor	Reducing Agent	UV/Vis Light (nm)	Time (h)	CO Yield (ppm)	MeOH Yield ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	QE (%)
CuO/CF	CO_2	H_2O	400/265	1	58	-	-
				2	70	-	-
				3	75	-	-
CuO/CF/GO	CO_2	H_2O	400/265	1	63	1.40	0.0001215
				2	104	0.0086	0.00002
				3	120	0.00914	0.000034

The rate of methanol and carbon monoxide yield was calculated by using the given below formula in Equation (5) [164];

$$\text{Yield} = \frac{\text{Product concentration } (\mu\text{mol}) \times \text{Solution volume (L)}}{\text{Photocatalyst mass (g)} \times \text{Reaction time (h)}} \quad (5)$$

The quantum efficiency estimated from the given expression in Eq. (6 & 7) [165]

$$QE (\%) = \frac{\text{Product no.of moles} \times \text{no.of } e^-}{\text{No.of photon absorbed}} \times 100 \quad (6)$$

$$QE (\%) = \frac{\text{No.of moles (mol.L}^{-1}) \times 6 \times NA}{IE \times A \times \lambda \times T \times h \times C} \times 100 \quad (7)$$

Where IE is the light intensity (3.5729 W/cm²), A is the irradiated area of photocatalyst (0.00321 m²), λ is bombarded wavelength of light (>400nm in case of Visible Light), h is plank's constant (6.634 × 10⁻³⁴ J.s), C is speed of light (3 × 10⁸ m.s⁻¹), T is the time of reaction in seconds (3600 s), NA is the Avogadro's number (6.02 × 10²³).

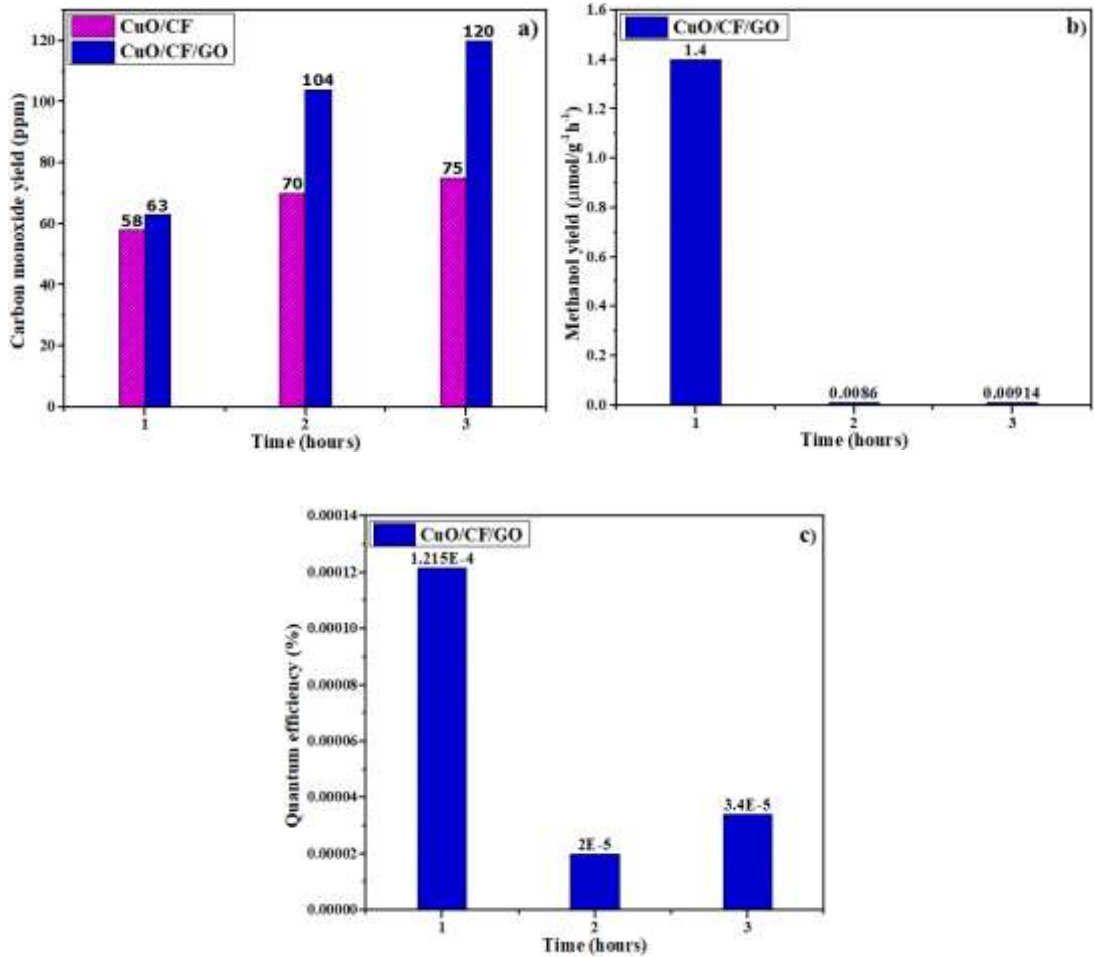


Figure 4.11 Copper oxide doped copper ferrite (CuO/CF) binary and copper oxide doped copper ferrite doped graphene oxide (CuO/CF/GO) ternary composite to produce (a) carbon monoxide yield (b) MeOH yield, and (c) Quantum efficiency.

4.7 Mechanism for Photocatalytic Reduction of CO₂

The mechanism of charge carrier transfer for photoreduction of CO₂ can be visualized from different dimensions;

4.7.1 Multi-Interface Electron Transfer Mechanism Analysis

For the ternary composite (CuO/CF/GO), the optical band gap energy was determined to be 1.40 eV, which allows efficient absorption in the visible-light region (Figure 4.2). The band edge positions were calculated using the Mulliken electronegativity approach as given in Equation (8) and (9):

$$E_{CB}=X - E_C - 0.5E_g \quad (8)$$

$$E_{VB}=E_{CB} + E_g \quad (9)$$

On this basis, the conduction band (CB) of the ternary composite is positioned at approximately -0.62 eV, while the valence band (VB) lies at around +0.78 eV, consistent with its band gap energy of 1.40 eV (Figure 4.2). These band positions provide sufficient reduction potential at the CB for CO₂ conversion and oxidation potential at the VB for water oxidation [166, 167].

The Fermi level of the ternary composite is located between the CB and VB, approximately 0.3-0.4 eV below the CB, indicating strong CuO being p-type semiconductor and CF as n-type semiconductor [168] come into contact with one another, there is mismatching of their fermi level and work functions. This positioning leads to efficient electron transfer from CF to CuO while GO, due to its high conductivity, acts as an electron mediator. The charge redistribution at the CuO/CF and CF/GO interfaces results in the formation of an internal electric field (IEF), which assists in band bending.

The resultant S-scheme mechanism enhances charge carrier separation: the photoexcited electrons in the CB of CuO are preserved with high reducing ability, while the holes in the VB of CF are maintained with strong oxidizing potential [169, 170]. Meanwhile, GO facilitates rapid electron transfer, reduces recombination losses,

and stabilizes the charge flow (Figure 4.12). Altogether, this band alignment and Fermi level distribution in the ternary CuO/CF/GO composite contribute to its superior photocatalytic CO₂ reduction efficiency.

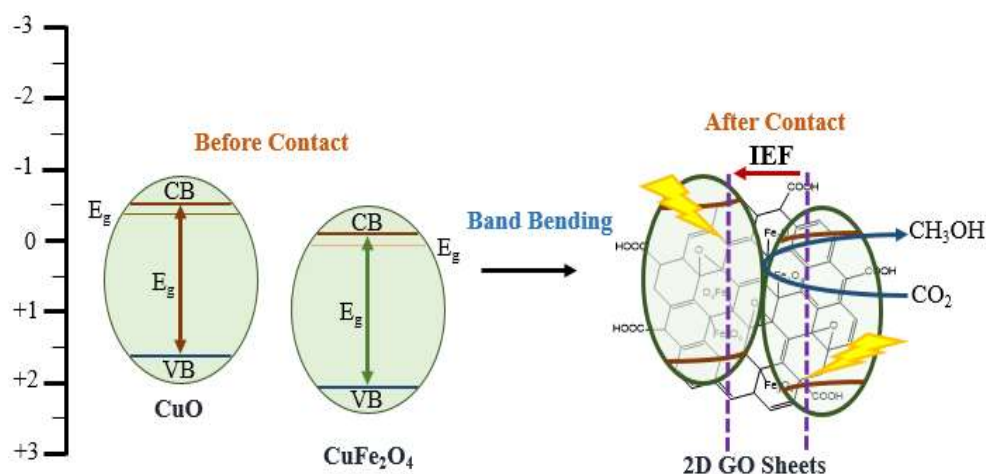


Figure 4.12 Schematic illustration of charge carrier transfer process in CuO/CF/GO.

4.7.2 Photo-Electric Performance Analysis

The separation efficiency of photogenerated charge carrier in photocatalyst is driving force for efficient photocatalytic reduction of CO₂ [171]. The higher charge separation promised us great photocatalyst performance. The electronic conductivity and photocatalytic conversion efficiency was evaluated by Electrochemical Impedance Spectroscopy (EIS) and room-temperature Photoluminescence (PL) spectroscopy. The EIS Nyquist diagram of photocatalysts illustrated that arc radius of CuO/CF/GO, being the smallest arc as compared to pure GO, CF/GO as already described in Figure 4.4. Generally, the smaller arc radius of EIS Nyquist diagram indicates the higher transfer efficiency of electrons. The arc radius of CuO/CF/GO photocatalyst was significantly smallest, indicating that photogenerated electrons and holes were effectively separated through multi-interfacial carriers transfer process [172]. The separation efficiency of photocatalysts was measured using room-temperature PL with particular results presented in Figure 4.3, where the results demonstrated that the low PL intensity of CuO/CF/GO (TC) can be attributed to heterojunction interface between CuO and CF NPs and surface defects of GO which implies that the photogenerated

carrier transfer efficiency at the 1D-2D-1D interface is much higher than the other obtained samples as shown below in Fig.4.13 [173]. CuO/CF/GO outstanding CO₂ photoreduction performance is attributed to its good photoelectric characterizations.

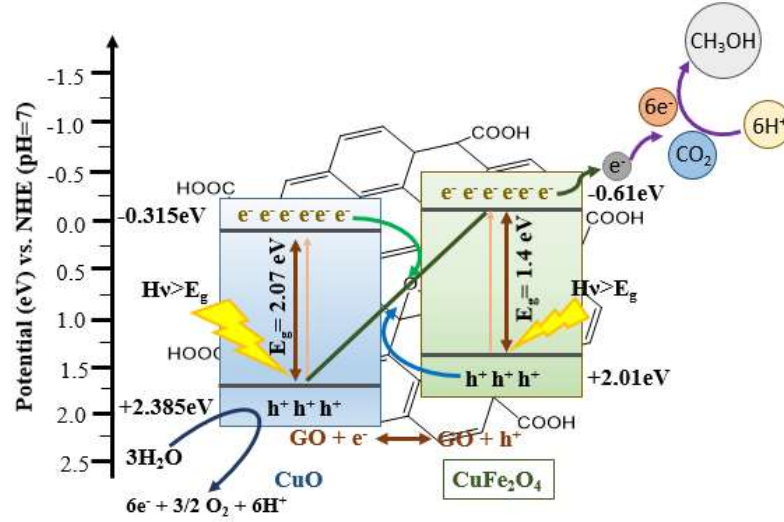


Figure 4.13 S-Scheme mechanism study of CO₂ photoreduction to MeOH via ternary CuO/CF/GO composite under UV-Visible light irradiation.

4.6.3 Band Structure Analysis

The work functions of the constituents, which can be computed from X-ray Photoelectron Spectroscopy (XPS) using the expression below, can be used to visualize the band structure of the photocatalyst (10).

$$\Phi = E_{\text{photon}} - E_{\text{binding}} - E_{\text{kinetic}} \quad (10)$$

E_{Fermi} is typically set at 0 eV for metals, E_{kinetic} is the secondary electron cutoff energy, which is obtained by charting the lower energy graph between kinetic energy and intensity, and E_{photon} is the energy of incident photons (1486.6 eV for alkaline radiation). The total work function was computed at 5.10 eV using XPS data. It was found that the work functions of CuO and CF NPs were 5.24 and 5.02 eV, respectively [174]. By aligning the fermi level for the creation of Schottky's barrier and internal electric field, this confirms the charge migration from CF (lower work function) to CuO (higher work function) [175].

CHAPTER 5

DISCUSSION

The comparative analysis of binary and ternary photocatalytic systems demonstrates that the ternary composites are significantly more efficient in reducing CO₂ into value-added fuels. In the binary CuO/CF catalyst, photocatalytic activity was restricted exclusively to carbon monoxide (CO) formation, with yields of 58 ppm, 70 ppm, and 75 ppm after 1, 2, and 3 hours, respectively (Figure 4.10, Table 4.2). No methanol was detected in this system, which can be attributed to its limited charge separation ability and absence of efficient electron transport pathways. Although CuO/CF binary composite provides visible-light absorption due to its narrow band gap (1.70 eV), the absence of a mediator for electron transfer promotes rapid recombination of electron-hole pairs, thereby favoring only single-electron reduction of CO₂ to CO [146, 176].

In contrast, the CuO/CF/GO ternary heterostructure displayed improved photocatalytic activity and product selectivity, with simultaneous CO and methanol production (Figure 4.11, Table 4.2). The CO yields were 63 ppm, 104 ppm, and 120 ppm at 1, 2, and 3 hours, respectively, while methanol was formed at 1.40 $\mu\text{mol g}^{-1} \text{h}^{-1}$, 0.0086 $\mu\text{mol g}^{-1} \text{h}^{-1}$, and 0.00914 $\mu\text{mol g}^{-1} \text{h}^{-1}$, with quantum efficiencies of 0.0001215%, 0.00002%, and 0.000034%. The incorporation of graphene oxide (GO) provided a conductive two-dimensional channel that enhanced electron mobility and minimized recombination. Its sp²-hybridized domains facilitated π - π^* interactions, while oxygen-containing functional groups promoted CO₂ adsorption and activation [114, 177]. As a result, multi-electron transfer pathways were activated, enabling methanol generation in addition to CO [178, 179].

The superior performance of the ternary system can also be rationalized by band gap engineering and oxygen vacancy (OV) stabilization. CuO, owing to its dual oxidation state (Cu²⁺/Cu⁺), promotes the creation of OVs and metal vacancies (V_m), which play a vital role in band gap tuning, charge carrier separation, and photocatalytic activity enhancement [146, 176]. The band gap energy of CuO/CF/GO composites varied between 1.40 eV, depending on the CuO concentration [112]. Moreover, incorporation

of CuO in CF/GO increased the density of OV_s and prevented them from being occupied, further improving charge transfer [180].

The role of GO as an auxiliary photocatalyst is further evident from its ability to act as an electron acceptor, photosensitizer, and stabilizer. Its extended π -conjugation provides electron storage and transfer capacity, while its large surface area ensures efficient anchoring of CuO and CF nanoparticles. This synergistic configuration suppresses backward reactions, enhances photostability, and improves selectivity towards methanol [181].

Despite the remarkable improvement, challenges such as limited separation efficiency and energy barriers for CO₂ reduction remain. Defect engineering strategies, particularly the creation of OV_s, have been proposed as a promising approach to overcome these barriers by introducing mid-gap states, enhancing light absorption, and suppressing recombination [182]. Furthermore, the formation of Schottky heterojunctions and the integration of low-cost co-catalysts have been explored to further enhance charge transfer and photocatalytic performance [183-185].

Overall, the present study confirms that binary systems are restricted to CO generation due to single-electron transfer, whereas ternary heterostructures such as CuO/CF/GO exhibit superior photocatalytic efficiency and selectivity, simultaneously producing CO and methanol under UV-visible irradiation. The improvement can be attributed to the combined effects of band gap tuning, OV stabilization, and graphene-mediated charge separation. These results highlight the potential of ternary composites as promising candidates for sustainable CO₂ conversion into solar fuels [108, 186-188].

CHAPTER 6

CONCLUSION

This work comprehensively investigated binary (CuO/CF) and ternary (CuO/CF/GO) nanocomposites as photocatalysts for CO₂ reduction, combining structural, surface, and mechanistic analyses to explain their performance. X-ray photoelectron spectroscopy (XPS) confirmed the presence of mixed oxidation states (Cu²⁺/Cu⁺) in CuO and the incorporation of oxygen vacancies (OVs), both of which play a vital role in charge transfer and CO₂ activation. The introduction of GO into the ternary system further increased defect stabilization and provided anchoring sites that improved electronic conductivity and surface reactivity. These surface-level findings aligned well with optical studies that revealed systematic band gap tuning, 1.40 eV of CuO/CF/GO for the optimized ternary composite, enabling enhanced visible-light absorption.

Photocatalytic performance tests highlighted a clear difference between binary and ternary systems. The binary CuO/CF composite selectively produced carbon monoxide (CO) with yields gradually increasing over time but showed no methanol formation. This behavior was attributed to its limited electron mobility and recombination-prone charge carriers, restricting the reduction process to single-electron pathways. In contrast, the ternary CuO/CF/GO composite demonstrated superior activity, producing both CO and methanol. The synergistic role of GO as an electron mediator enabled efficient charge transfer, suppressed recombination, and enhanced CO₂ adsorption. The ternary system thus promoted multielectron reduction reactions, achieving significantly higher methanol yields than previously reported Cu-based photocatalysts.

Mechanistic analysis of the band structure confirmed that the ternary system operates via an S-scheme heterojunction. CuO, as a p-type semiconductor, and CF, as an n-type semiconductor, formed a strong internal electric field upon contact, which promoted spatial charge separation. Electrons accumulated in the conduction band of CuO, while holes remained in the valence band of CF, preserving their strong redox potentials. GO, with its high conductivity and extended π -network, acted as a solid-state electron

channel, further accelerating charge migration across the interface. This cooperative mechanism effectively suppressed electron-hole recombination and maximized the redox ability required for CO₂ conversion.

Overall, this study demonstrated that while the binary system was limited to CO evolution, the ternary CuO/CF/GO heterostructure successfully enabled simultaneous CO and methanol production through synergistic band gap tuning, defect engineering, and graphene-mediated charge transfer. The integration of experimental findings from XPS, UV-Vis, electrochemical impedance, and photocatalytic performance provided consistent evidence for the superiority of the ternary system. The results confirm that constructing S-scheme heterojunctions between p-type and n-type semiconductors with conductive carbon-based mediators offers a powerful strategy to design next-generation photocatalysts for CO₂ reduction.

The CuO/CF/GO ternary composite represents a promising platform for sustainable solar fuel generation, combining structural stability, enhanced selectivity, and efficient utilization of solar energy.

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