

**Eco-benign Synthesis, Characterization, and Application of Metal-oxide Nanoparticles in
Solar Cells and Photodegradation of Neomycin**

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Faculty of Natural and Applied Sciences, Lead City University, Ibadan, Oyo State, Nigeria**

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in Industrial Chemistry**

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Certification

This is to certify that **Oluwole Elijah OGUNBIYI** with matriculation number **LCU/PG/005467** carried out this research work titled “Eco-benign Synthesis, Characterization, and Application of Metal-oxide Nanoparticles in Solar Cells and Photodegradation of Neomycin” in the Department of Chemical Science, Faculty of Natural and Applied Sciences, Lead City University, Ibadan, Oyo State, for the award of Master Degree (MSc) in Industrial Chemistry and that this has not been previously submitted.

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Dedication

This entire thesis is dedicated to Almighty God and also my parents; Mr. & Mrs. Ogunbiyi for their immeasurable support and kindness throughout my academic years.

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Acknowledgement

Without the research facilities offered by the Faculty of Natural and Applied Sciences at Lead City University in Ibadan, my research work could not have been completed.

I want to express my gratitude to the Department's head, Professor O. M. Ighodaro. I also want to express my sincere gratitude to my supervisor, Dr. A. O. Bamisaye, for introducing me to the fascinating field of material science, for giving me all the necessary instructions for my experiments in great detail, and for his insightful comments on the outcomes. I must convey my sincere gratitude to the lecturers and laboratory staff of the Faculty of Natural and Applied Sciences .

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Even though the above-mentioned institution and persons have assisted in the process of this research work, I alone stand responsible for the errors, if any found in the work.

Abstract

The quest for renewable energy and cost-effective degradation of antibiotics has led to the synthesis of Metal-Oxide (MO) nano-photocatalysts via eco-benign approach. The metal oxides were synthesized biogenically using *Syzygium malaccense* leaf extract (as capping and stabilizing agents) and Aluminum sulphate octadecahydrate, Copper sulphate heptahydrate and Zinc sulphate heptahydrate salts as precursors. The synthesized aluminum oxide (Al_2O_3), Copper II oxide (CuO) and Zinc Oxide (ZnO) nanoparticles (NPs) were characterized using Fourier-transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), Energy dispersive x-ray (EDX), X-ray diffraction (XRD), and ultraviolet (UV) spectroscopy. The materials were used for the photodegradation of Neomycin (NEO) and as photoanode, counter electrode and insulating spacer respectively in Dye Sensitized Solar Cells (DSSCs). The FTIR showed absorbance with range value between $400\text{--}800\text{ cm}^{-1}$ which corresponds to Al-O Cu-O and Zn-O vibrational stretch of the MOs. The optical properties of Al_2O_3 , CuO and ZnO NPs were determined using Tauc's plot with band gap energy values of 2.09, 2.05 and 3.23 eV and maximum UV-Vis absorbance values of 371.61, 370 and 371 nm. The SEM micrographs of Al_2O_3 , CuO, and ZnO NPs showed a consistent spherical shape, with average particle sizes of 27.50 nm, 11.01 nm, and 21.98 nm, respectively. The EDX confirmed the elemental composition of the nanoparticles. DSSCs utilizing Al_2O_3 , CuO and ZnO NPs demonstrated a 1.79, 3.44 and 6.4% power conversion efficiency in an increasing order of $\text{ZnO} > \text{CuO} > \text{Al}_2\text{O}_3 > \text{Control}$ (Without NPs). After 120 min of UV irradiation, 75 and 95% of NEO were degraded with CuO and ZnO nanoparticles respectively. ZnO photocatalyst proved more effective than CuO photocatalyst at degrading the antibiotic. The kinetic studies shows that K values of CuO and ZnO photocatalysts had the values of 0.0072 and 0.0179 min^{-1} while $R^2 = 0.83$ and 0.82, respectively. The stability of the photocatalyst showed that the produced material (ZnO biosynthesized nanoparticles) had a major impact on both photocatalytic performance and power conversion efficiency. The findings of this study present the biogenically synthesized MONPs as low-cost, and eco-friendly material for energy conversion and photocatalyst for environmental remediation purposes.

Keywords: Metal-Oxide nanoparticles, Photocatalysis, DSSCs, Neomycin, Semiconductors

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List of Acronyms

Abbreviation	Meaning
Al ₂ O ₃	Aluminum-oxide
CB	Conduction Band
CE	Counter Electrode
CuO	Copper Oxides
DSSCs	Dye-Sensitized Solar Cells
EPD	Electrophoretic Deposition
FeO	Iron Oxides
SEM	Scanning Electron Microscopy
FT-IR	Fourier Transform Infrared
FTO	Fluorine doped with Tin Oxides
ITO	Indium doped with Tin oxides
MIP	Molecular Imprinted Polymers
MOF	Metal Organic Framework
nm	Nano Meter
NEO	Neomycin
PEDOT:PSS	Poly(3,4 Ethylenedioxythiophene):poly(Styrene Sulfonate)
PAHs	Polycyclic Aromatic Hydrocarbons
PV	Photovoltaic Cell

List of Acronyms

Abbreviation	Meaning
VB	Valence Band
UV-Vis	Ultraviolet-visible
XRD	X-ray Diffraction
ZnO	Zinc-oxide

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Chapter One

Introduction

1.1 Background to the Study

The escalating global demand for energy, coupled with the deleterious environmental consequences stemming from the extensive extraction of fossil fuels over recent decades, has catalyzed the quest for alternative energy sources¹. Contemporary efforts are increasingly directed towards the advancement of innovative technologies that facilitate the utilization of what are termed green energy sources. Such green energy is sourced from natural processes that are perpetually replenished. Engaging with these energy sources is advantageous from both economic and ecological perspectives^{1,2}.

Currently, renewable energy represents the most rapidly expanding category of electricity generation, primarily attributed to significant contributions from wind power and hydroelectric. Additionally, solar power generation has witnessed a pronounced acceleration in growth over the past decade. Projections indicate that the proportion of global electricity generation derived from renewable sources is anticipated to rise from 18 percent in 2007 to 23 percent by 2035². Consequently, the optimization of existing power generation processes and the innovation of new technologies have emerged as areas of paramount scientific, technological, economic, and public interest^{1,2}.

Humanity has harnessed solar energy since antiquity; however, it was not until the 19th century that the initial attempts at photovoltaic applications of solar energy were undertaken³. Since that pivotal period, the concept of utilizing the abundant and clean solar energy to generate electricity has remained a persistent theme within the scientific community and society at large. Nonetheless, it was only at the dawn of the 21st century that grid-connected photovoltaic

systems began to substantially contribute to electrical power generation. The photovoltaic sector has experienced exponential growth over the last decade. In addition to the increasing public consciousness regarding the imminent depletion of the Earth's oil reserves, the advancement of photovoltaic technology is also driven by societal environmental concerns³. In this context, solar power generation represents a promising technology for electric power production, characterized by relatively low life cycle emissions of greenhouse gases³.

Solar energy has been recognized as a superior alternative to fossil fuels due to its renewable characteristics and environmentally friendly nature. Solar cells serve as the foundational elements of solar energy technology³. Currently, the solar energy market is predominantly characterized by the utilization of silicon-based solar cells. While these solar cells demonstrate efficacy, they possess inherent limitations that obstruct their comprehensive deployment in developing and economically disadvantaged regions⁴. Silicon-based solar cells function as single band gap devices. A notable limitation is the generation of heat, which tends to diminish their operational efficiency. This phenomenon occurs because solar radiation with energy levels lower than the silicon band gap directly transmits through the material. Moreover, these solar cells are incapable of harnessing the additional energy from radiation that possesses higher energy levels than that of silicon. Another significant limitation is the high cost associated with the manufacturing process, which necessitates the use of energy-intensive equipment such as furnaces, vacuum pumps, and other apparatus. Additionally, the production process involves the utilization of chemicals that pose environmental hazards. Consequently, there exists a pressing necessity to explore alternative methodologies for photovoltaic (PV) cells that are economically viable, sustainable, and environmentally benign while also achieving substantial efficiency. Over the past decade, various innovative strategies have emerged to rival conventional silicon-based

PV devices by incorporating p-n junctions, with a focus on low-cost materials and manufacturing practices⁶.

The photovoltaic sector is poised to exert a profound impact on the energy market contingent upon the enhancement of energy conversion efficiency in solar cells. A majority of PV cell types employ efficient thin film technologies. The performance of solar cells can be augmented by altering the characteristics of these films⁷. Principal challenges associated with solar cells include enhancing photon absorption, diminishing electron-hole recombination, and improving charge transport mechanisms^{2,8}. Metal oxide semiconductors have emerged as promising candidates for PV applications⁹. The environmentally abundant, benign, and stable properties of metal oxides facilitate their deposition even under ambient conditions⁴. Metal oxides are integrated as both active and passive components in a diverse array of commercial applications. Specifically, metal oxides are utilized as transport layers or transparent conducting electrodes within solar cells⁹. Presently, there is significant interest in heterojunction metal oxide solar cells, attributed to their potential for low-cost solutions due to the manufacturing methodologies and inexpensive materials involved. Metal oxide nanoparticles possess the capacity to address the energy challenges associated with emerging sustainable and renewable energy resources. Their infinitely varied structural architectures and morphological characteristics offer new opportunities and prospects for energy harvesting, conversion, and storage devices^{9,10}.

Metal oxide nanoparticles manifest distinctive electronic properties, optical, physical, and chemical when compared to their bulk counterparts, attributable to quantum confinement effects and the increased availability of surface atoms relative to interior atoms for engagement in reactions. The applications of metal oxide nanoparticles (MONPs) are contingent upon various attributes including surface area, morphology, dimensions, stability, crystallinity, anti-corrosive

properties, conductivity, and photocatalytic activity. It is of paramount importance for the commercialization of MONPs to achieve desirable and controllable characteristics during their synthesis¹¹.

Due to pollution from many industries, there has been a significant increase in concern recently over wastewater treatment. Drug contamination in water has negative repercussions that have made people focus on treating it. Wastewater is particularly a typical place for detecting antibiotics¹². Naturally occurring waters may contain these materials since many of them are resistant to the standard primary and secondary treatments used in municipal wastewater treatment facilities. Microbial resistance and bacterial selection are brought on by antibiotic pollution in the biosphere¹³. Humans can become infected with germs that are resistant to antibiotics, which raises the risk of disease and makes treatment more difficult.

Among the most widely used medications in the world, antibiotics have the ability to either kill or stop the growth of germs, helping to treat bacterial infections. Because of the potential harm that antibiotics may cause to individuals and ecosystems, the emergence of antibiotics in the environment has garnered significant attention in recent years¹⁴. Chemicals that come from natural, synthetic, and semi-synthetic sources are known as antibiotics. The earliest antibiotics were naturally occurring substances made by microorganisms, such as penicillin, which was taken from a culture of *Penicillium notatum*¹⁵. Antibiotics can be categorized in three ways. First off, the chemical structure of antibiotics may be used to classify them into various groups, including fluoroquinolones (FQs), tetracyclines (TCs), macrolides (MAs), sulfonamides (SAs) and β -lactams. In addition, the spectrum of activity of antibiotics can be used to classify them into three groups: narrow-spectrum, broad-spectrum, and extended-spectrum antibiotics¹⁶.

In the aquaculture and live-stock industries, antibiotics are widely utilized to cure and prevent human infections as well as to safeguard animal health and foster animal growth⁴. Antibiotic consumption has increased dramatically in recent times due to the growing global human population and the increased need for animal feed. Human use of antibiotics increased by 65% between 2000 and 2015, and by 2030, it was expected to reach 200%¹⁷. According to earlier studies, 63,151 tons of antibiotics were reportedly consumed worldwide by livestock in 2010. Moreover, rising consumer demand for livestock products was expected to cause the share of veterinary antibiotics to rise by 67% (to 105,596 tons) in 2030¹⁸. Due to its vast population and rising need for animal protein, China, the world's largest producer, exporter, and user of antibiotics, consumes a lot of antibiotics. China used 92,700 tons of 36 different antibiotics in total in 2013. Of those, 54,000 tons were thought to be excreted by humans and animals, with 53,800 tons being released into the environment¹⁸.

Neomycin is an aminoglycoside antibiotic. It is used to treat skin infections caused by bacteria. It is active against staphylococci and gram-negative bacilli, in combination with other anti-biotics, anti-fungal and corticosteroids¹⁹. The molecular formula of neomycin is $C_{23}H_{46}N_6O_{13}$ with a molecular weight of 614.644 g/mol. The photodegradation of neomycin, like that of other antibiotics, involves its breakdown due to exposure to light, particularly UV light. Neomycin, being a complex molecule, has certain functional groups that can absorb UV light. This absorption can lead to the excitation of electrons in the antibiotic molecule. Upon excitation, the molecule can undergo various photochemical reactions¹⁹. These reactions may include; Cleavage of Chemical Bonds whereby UV light can break specific bonds within the neomycin molecule, leading to smaller fragments and also the absorption of UV light can generate reactive oxygen species (ROS) like hydroxyl radicals, which can further react with the antibiotic molecule,

causing degradation. The breakdown of neomycin can lead to a variety of degradation products. The exact nature of these products can depend on the specific conditions of the exposure, including light intensity and wavelength²⁰. Photodegradation of neomycin antibiotic using metal oxide nanoparticles involves leveraging the enhanced photocatalytic properties of nanoparticles to accelerate the breakdown of neomycin under light exposure. Metal oxide nanoparticles, such as titanium dioxide (TiO₂) and zinc oxide (ZnO), are particularly effective due to their large surface area-to-volume ratio, which increases their photocatalytic activity. Metal oxide nanoparticles offer an advanced method for the photodegradation of neomycin, providing a powerful tool for environmental cleanup and wastewater treatment. Their high efficiency and effectiveness make them a promising option for addressing antibiotic contamination in various settings²⁰.

As photocatalysts, metal oxide-based semiconductors are essential because they provide a flexible solution for a range of environmental and energy-related problems¹⁹. But these materials' inherent qualities, namely their broad bandgap, had historically restricted their use to the ultraviolet (UV) spectrum, decreasing their ability to effectively use visible light. In order to close this gap, a variety of techniques have been developed to maximize the photo-stability, environmental friendliness, and overall photo-response efficiency of metal oxide photocatalysts in the visible wavelength range¹⁸. Adding nanoscale metal oxide particles is one of the most promising methods in this endeavor since they greatly increase the surface-to-volume ratio, which increases the amount of active sites that are available for catalytic reactions. Of these tactics, purposeful doping of photocatalysts with nanoparticles stands out as a particularly successful way to increase photoresponse efficiency²⁰. When we talk about doping, we mean intentionally adding impurities, either cationic or anionic, to a material in order to cause certain

changes in its characteristics. By altering the electronic structure of photocatalysts, this approach has shown to have great potential for lowering their bandgap and increasing their photoactivity into the visible spectrum²¹.

1.2 Statement of the Problem

As the global demand for energy increasingly surpasses the available supply, the financial implications of electricity provision escalate correspondingly. Moreover, there is a rising apprehension that the phenomena of global warming (greenhouse effect) and climate change are significantly attributable to the consumption of fossil fuels such as coal, oil, and natural gas. These fossil fuels constitute the primary source for approximately 66% of the global electricity supply and are responsible for 95% of the total energy requirements on Earth¹². Thus, it is imperative to identify a source of renewable energy that is both efficient and clean while also being sustainable.

Among the diverse renewable energy sources including biomass, wind, solar, mini hydro solar and geothermal energy is particularly distinguished due to its inexhaustible nature and universal accessibility. Solar energy proves advantageous for electricity generation at both small and large scales. Nevertheless, issues related to cost and energy storage present significant obstacles that impede its widespread adoption globally¹². Consequently, there is an ongoing pursuit to diminish the expenses associated with solar cells and solar panels to render them competitive with traditional electricity generation methods. Therefore, the present study developed a solar cell system based on ZnO, CuO, and Al₂O₃ nanoparticles for dye-sensitized solar cells (DSSCs). Given that traditional wastewater treatment methodologies entail considerable initial expenditures, chemical and energy requirements, and the generation of hazardous wastes necessitating proper disposal, they are perceived as prohibitively costly, especially for small-

scale enterprises in developing countries¹⁶. Thus, there is a pressing need for alternative, cost-effective, and environmentally benign photocatalyst materials endowed with robust sorbent properties. Current literature is replete with prospective studies on the photodegradation of antibiotics in wastewater utilizing nanoporous metal-organic frameworks (MOFs), single-phase nanoporous compounds, superhydrophobic magnetic carboxyl-functional materials, similar substances and multi-walled carbon nanotubes²¹. Conversely, investigations into the bimetallic photocatalysts for wastewater contaminated with antibiotics represent an emergent technique that is witnessing substantial development in the current decade. Consequently, relatively limited research has been conducted in this domain. Therefore, the effective utilization of metal-oxide photocatalysts for the remediation of wastewater contaminated with neomycin (NEO) has the potential to enhance the applicability of photocatalysts and facilitate their practical deployment in addressing environmental challenges²⁰.

1.3 Justification of the Study

Traditional nanoparticle synthesis methods often involve toxic reductants (e.g., NaOH, KOH) and high-energy processes, generating hazardous waste²². In contrast, this study adopts a green synthesis approach using *Syzygium malaccense* leaf extract as a reducing and capping agent. This method is eco-friendly, cost-effective, and aligns with the principles of green chemistry, reducing environmental harm and promoting sustainable practices. The escalating global demand for energy and the environmental degradation caused by fossil fuel consumption necessitate the development of efficient renewable energy technologies. Solar energy, particularly dye-sensitized solar cells (DSSCs), offers a promising alternative. This study explores the use of biosynthesized metal-oxide nanoparticles to enhance the efficiency of DSSCs, addressing the limitations of conventional silicon-based solar cells, such as high production costs and energy-

intensive manufacturing processes. The presence of antibiotics like neomycin in water bodies poses significant public health risks, including antibiotic resistance. Current wastewater treatment methods are often costly and inefficient for antibiotic removal. This study investigates the photocatalytic degradation of neomycin using biosynthesized metal-oxide nanoparticles (CuO and ZnO), offering a low-cost, eco-friendly solution for environmental remediation.

Metal-oxide nanoparticles exhibit unique electronic, optical, and photocatalytic properties due to their high surface-to-volume ratio and quantum confinement effects. By characterizing and optimizing these nanoparticles, the study contributes to advancements in both solar energy conversion and photocatalytic degradation technologies. The study combines energy generation (solar cells) and environmental remediation (antibiotic degradation) using the same eco-friendly materials, demonstrating a circular economy approach. This dual application underscores the versatility and potential of biosynthesized nanoparticles in addressing global sustainability challenges. The research is justified by its innovative use of green synthesis for nanoparticle production, its potential to improve renewable energy technologies, and its contribution to solving the critical issue of antibiotic pollution in water systems. The findings could pave the way for scalable, sustainable solutions in energy and environmental management.

1.4 Aim and Objectives of the Study

The aim of this study is to synthesize and characterize ZnO, CuO, and Al₂O₃ nanoparticles via green synthesis approach. This is used as counter electrode in the fabrication of Dye-sensitized solar cells (DSSCs) and photocatalytic degradation of neomycin (NEO)-polluted wastewater.

The objectives of this study were to:

- i. Synthesize ZnO, CuO, and Al₂O₃ nanoparticles using *Syzygium malaccense* (Malay apple) plant extract as a reducing agent.

- ii. characterize the ZnO, CuO, and Al₂O₃ nanoparticles using Ultraviolet visible spectroscopy, Fourier-transform infrared, X-ray diffractometer, and the scanning electron microscopy for possible areas of application in fabricating solar cells.
- iii. Fabricate a ZnO, CuO, and Al₂O₃ nanoparticles thin film solar cell.
- iv. Determine the solar cell parameters such as series resistance (Is), short circuit current (Isc), fill factor (FF), maximum power output (Pm), open circuit voltage (Voc), current (Io), and conversion efficiency (η) from the I-V measurement.
- v. Investigation photodegradation efficiency of ZnO, CuO, and Al₂O₃ photocatalysts in NEO-polluted wastewater
- vi. Kinetics study of the antibiotics photodegradation

1.5 Scope of the Study

The scope of this work is the synthesis of metal oxide (ZnO, CuO, and Al₂O₃ nanoparticles) using *Syzygium malaccense* (Malay apple) plant extract as a reducing agent, characterization and applications of the Mos for solar cell fabrication and prompt degradation of NEO polluted wastewater.

Endnotes

1. G. Mutezo, & J. Mulopo. *A review of Africa's transition from fossil fuels to renewable energy using circular economy principles*. **Renewable and Sustainable Energy Reviews**. 137, 2021, 110609.
2. M. Memari, & N. Memarian. *Designed structure of bilayer $\text{TiO}_2\text{-Nb}_2\text{O}_5$ photoanode for increasing the performance of dye-sensitized solar cells*. **Journal of Materials Science: Materials in Electronics**. 31, 2020, 2298-2307.
3. J. Meng, X. Hu, P. Chen, D.M. Coffman, & M. Han. *The unequal contribution to global energy consumption Al_2O_3 in the supply chain*. **Journal of Environmental Management**. 268, 2020, 110701.
4. A.K. Irazzaq, G. Boggar, & B. Plesz. *Evaluation of different methods for solar cells/modules parameters extraction*. **Solar Energy**. 196, 2020, 183-195.
5. A.F. Kamil, H. Abdullah, A.M. Rheima, & S.H. Mohammed. *Photochemical synthesized NiO nanoparticles based dye-sensitized solar cells: a comparative study on the counter electrodes and dye-sensitized concentrations*. **Journal of Ovonic Research**. 17, 3, 2021, 299-305.
6. S. Kanimozhi, K.M. Prabu, S. Thambidurai, & S. Suresh. *Dye-sensitized solar cell performance and photocatalytic activity enhancement using binary zinc oxide-copper oxide nanocomposites prepared via co-precipitation route*. **Ceramics International**, 47, 21, 2021, 30234-30246.
7. A.F. Kamil, H.I. Abdullah, A. M. Rheima, & S.H. Mohammed. *Impact of Fe_2NiO_4 nanoparticles to increase efficiency of dye-sensitized solar cells*. *Materials Today: Proceedings*, 49, 2022, 2727-2732.
8. A.F. Kamil, H.I. Abdullah, A.M. Rheima, S.H. Mohammed, S.J. Tumaa, & R.M. Abed. *Fabrication of Fe_2CuO_4 nanoparticles via photolysis technique for improved performance in dye-sensitized solar cells*. **Digest Journal of Nanomaterials & Biostructures (DJNB)**. 16, 4, 2021.
9. K. Pattarith K., & Areerob, Y. *Fabrication of Ag nanoparticles adhered on rGO based on both electrodes in dye-sensitized solar cells (DSSCs)*. **Renewables: Wind, Water, and Solar**, 2020, 7, 2020, 1-10.
10. H.A. Kadhum, W.M. Salih, & A.M. Rheima. *Improved PSi/c-Si and Ga/PSi/c-Si nanostructures dependent solar cell efficiency*. **Applied Physics A**, 126, 10, 2020, 1-5.

11. H.I. Abdulah, A.M. Rheima, D.H. Hussain, & H.J. Abed. *Synthesis of Fe₂O₃ nanoparticles by photolysis method for novel dye-sensitized solar cell.* **Journal of Advanced Sciences and Nanotechnology**, 1, 1, 2022, 292022, 1–8.
12. Q.S. Huang, W. Wu, W. Wei, L. Song, J. Sun, & B.J. Ni. *Highly-efficient Pb²⁺ removal from water by novel K₂WO₄ nanowires: performance, mechanisms and DFT calculation.* **Chem Eng J**, 381, 2020, 122632.
13. P. Kovalakova, L. Cizmas, T.J. McDonald, B. Marsalek, M. Feng, & V.K. Sharma. *Occurrence and toxicity of antibiotics in the aquatic environment: A review.* **Chemosphere**, 251, 2020, 126351.
14. Z. Zhang, A. Zada, N. Cui, N. Liu, M. Liu, Y. Yang, D. Jiang, J. Jiang, & S. Liu. *Synthesis of Ag loaded ZnO/BiOCl with high photocatalytic performance for the removal of antibiotic pollutants.* **Crystals**, 11, 8, 2021, 981.
15. L. Yang, J. Wang, Y. Zhang, B. Zhou, P. Tan, & J. Pan. *Construction of S-scheme BiOCl/CdS composite for enhanced photocatalytic degradation of antibiotic.* *J. Mater. Sci. -Mater. El.* 33, 16, 2022, 13303–13315.
16. L. Serwecińska. *Antimicrobials and antibiotic-resistant bacteria: A risk to the environment and to public health.* **Water**. 12, 12, 2020, 3313.
17. D. Akhil, D. Lakshmi, P. Senthil Kumar, D.-V.N. Vo, & A. Kartik. *Occurrence and removal of antibiotics from industrial wastewater.* **Environ. Chem. Lett.** 19, 2, 2021, 1477–1507.
18. X. He, T. Kai, & P. Ding. *Heterojunction photocatalysts for degradation of the tetracycline antibiotic: a review.* **Environ. Chem. Lett.** 19, 6, 2021, 4563–4601.
19. H.M. Hamidi, A. Zarrineh, A. Es-Haghi, & A. Ghasempour. *Rapid and sensitive determination of neomycin and kanamycin in measles, mumps, and rubella vaccine via high-performance liquid chromatography-tandem mass spectrometry using modified super-paramagnetic Fe₃O₄ nanospheres.* **J Chromatogr A**, 1625, 2020, 461343.
20. M.E.A. El-sayed. **Nanoadsorbents for Water and Wastewater Remediation.** *Sci. Total Environ.* 2020, 739, 139903.
21. R. Medhi, M.D. Marquez, & T.R. Lee. *Visible-light-active doped metal oxide nanoparticles: review of their synthesis, properties, and applications.* **ACS Appl. Nano Mater.** 2020, 3, 6156–6185.

Chapter Two

Literature Review

2.1 Renewable Energy

The bedrock of the current energy system is fossil fuels, such as natural gas, oil and coal, which make up a large portion of the world's power production¹. Nevertheless, these non-renewable energy sources might eventually run out of fuel due to the substantial increase in global energy consumption brought on by population growth and economic progress^{2,3}. As a result, research interest in the investigation of clean energy sources has significantly increased in recent years. Because of the sun's capacity to produce heat and radiation, which enables the production of electricity and thermoelectric power, solar energy has become a particularly attractive energy source to address this problem. Solar energy is therefore a sustainable energy source that contributes to lowering the demand for fossil fuels and, ultimately, greenhouse gas emissions².

2.2 Solar Energy: Renewable Energy Source

The term "solar energy" refers to the energy that the sun releases as electromagnetic radiation in the radio and ultraviolet to infrared spectrum varies (0.2 nm to 3 nm). Solar cells are devices that use the photovoltaic effect to convert solar energy into electrical power. The energy is abundant, clean, and sustainable, and it has an endless lifespan of 10 billion years⁴. A year's worth of Earth's energy usage (4.1×10^{20} J) is less than the sun's entire energy in an hour (4.3×10^{20} J)⁵. Earth receives around 174 petawatts (PW) of insolation, which is the term for the sun's radiation. Time, location, and the sun's relative position, as well as the season and atmospheric reflection, diffusion, and absorption, all affect insolation. Thirty percent of this insolation is reflected back into space, while the remaining seventy percent is absorbed by the land masses, clouds, and

oceans, absorbing 3,850 ZJ of solar energy annually. There are four trillion 100-watt light bulbs' worth of incident solar energy on Earth per second⁶.

Despite all of this, solar energy has yet to reach its full potential; in 2012, 100 GW of solar energy were utilized globally⁷. The two primary functions of a solar cell are the photogeneration of charge carriers in a light-absorbing material and the separation of the charge carriers to a conductive contact that will transmit the electricity. This necessitates an electrolyte that can transfer the charge from the photo-acceptor to the electrodes in polymer and dye-sensitized solar cells. In nanoparticle-based solar cells, the particles need to be close to one another in order for charge to be transmitted directly. The combination of quantum dots (QDs) and nanocrystalline materials has resulted in significant improvements in the overall efficiency of solar cells. Solar PV systems and solar thermal systems are the two categories of solar energy technology. Figures 2.1 and 2.2 depict the solar PV and solar thermal systems, respectively⁷.



Figure 2.1: An illustration of a standard solar water heating system

Source⁷

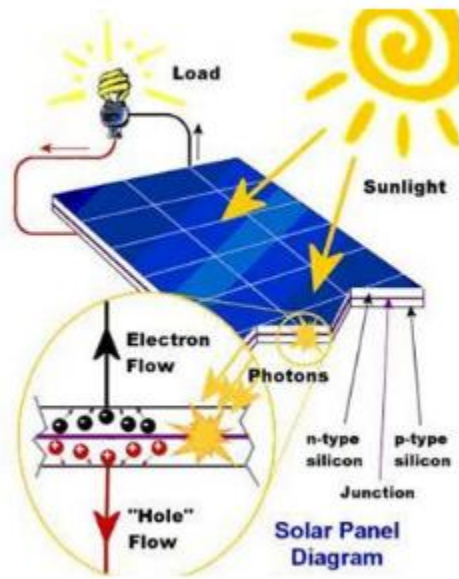


Figure 2.2: PV system

Source⁷

2.3 Green Synthesis of Nanoparticles

The synthesis of nanoparticles using plant extract and microorganisms provides an advantage over traditional approaches, according to the 12 principles of green chemistry⁸. This method offers a safer way to produce nanoparticles with the appropriate chemical and physical characteristics. However, as different synthesis techniques may produce different kinds of nanoparticles, there are several constraints to be aware of during the synthesis phase. First, the types of green synthesizers used, the amount of extract used, and the experiment parameters all affect the size and shape of the nanoparticles that are formed. These factors may also cause changes in the nucleation process and the number of functional groups that are deposited on the surface of the nanoparticles to prevent agglomeration⁸. A growing number of studies have concentrated on the production of nanoparticles using various methods because of their extensive applications in several branches of cutting-edge scientific fields. When preparing nanoparticles, metal salt is equivalent to metal nanoparticles that are synthesized from a selected precursor. When bioactive functional groups from natural sources are present, they are reduced to metal ions⁹.

2.3.1 Nanoparticles Synthesis Using Plant Extract

One emerging new field of study for the biological synthesis of metal nanoparticles is phyto-nanotechnology. Because plants include functional components that can be employed as a capping and reducing agent, plant extract is significantly more beneficial. This approach is superior because it offers superior control over the increase of particle sizes, which significantly stabilizes the synthesis process¹⁰. Specific nanoparticles with the required size and shape can be created for a wide range of nanotechnology applications by using plant extract. Metal nanoparticles can be synthesized from a variety of plant parts, including as leaves, stems, roots,

and seeds. According to reports, the natural resources recognized to be responsible for the reduction of metal salts are phytochemicals and their primary and secondary metabolites¹¹. The reducing power of the plant extract with the oxidation state of the reactive metal ion affects the extent of metal nanoparticle accumulation.

Cassia alata L., a member of the Fabaceae family, is employed in another study to synthesize CuO nanoparticles. It has been found to exhibit phytochemical activity. According to analysis, *Cassia alata* contains flavonoids with photocatalytic activity and active anthraquinones such as rhein, emodin, and physcion¹². A complex mixture of secondary metabolites, such as polyphenols, flavonoids, alkaloids, and terpenoids, can be found in plant extracts that are obtained from different plant species. Because of their reducing properties, these substances can aid in the reduction of metal ions and the consequent production of nanoparticles. Because plant extracts are naturally diverse, they offer a flexible toolkit for modifying the size, shape, and surface characteristics of nanoparticles, which enables them to be used in a variety of applications. The use of plant extracts stands out as a potential approach among the several green synthesis techniques available. As abundant sources of bioactive substances, plants provide a wide range of phytochemicals that can be used as capping and reducing agents when creating nanoparticles. In addition to doing away with the requirement for dangerous chemicals, this technique uses the inherent qualities of plant extracts to give the produced nanoparticles special qualities. The use of plant extracts stands out as a potential approach among the several green synthesis techniques available. It is already known that *Azadirachta indica* (neem), *Medicago sativa* (alfalfa), *Albizia lebbek*, and microbes can be used to synthesize gold and silver nanoparticles^{13,14}.

2.4 Use of Plant Extracts

The biosynthesis of nanoparticles is now being carried out using plant extracts, which may be more beneficial than the difficult process of maintaining cell cultures when using microbes. It is already known that *Azadirachta indica* (neem), *Medicago sativa* (alfalfa), Alovera, and microbes can be used to produce gold and silver nanoparticles¹⁵.

2.4.1 Description of *Syzygium malaccense* (Malay Apple)

The basil species *Syzygium malaccense*, popularly referred to as "Malay apple," is indigenous to Africa, Southeast Asia, and other tropical areas. *Syzygium malaccense* is a significant herb used in medicine. It is becoming more and more popular in pharmacological activities, such as general tonics, anti-hyperglycemic, anti-diabetic drugs, anti-leprotic, antiallergic, anticancer, and because of its enormous therapeutic potential. It scavenges free radicals, protects the stomach mucosa, and increases the phagocytic and bactericidal properties of polymorphs. This plant has been shown to have anti-fibrotic, anti-oxidant, anti-inflammatory, immunological modulating, radioprotective, and stimulatory properties for macrophage phagocytic and inhabitation activities¹⁶.

The vitamin-rich herb *Syzygium malaccense* is used to treat a variety of conditions, including bronchitis, diabetes, deep bone aches, yellow urine, and dreadful apatite. Anthocyanin, procyanidins, flavonols, and polyphenolic acids can all be identified in *Syzygium malaccense* fruit extract¹⁶. The sugar and organic acids in the fruit give it a sweet, sour taste. Using the green synthesis method, silver nanoparticles have been produced from *Syzygium malaccense* fruit extract. Terpenoids, polysaccharides, flavones, alkanoids, proteins, enzymes, amino acids, and alcoholic substances are examples of photochemicals that can stabilize or decrease nanoparticles^{17,18}. Non-toxic biomolecules like flavonoids and phenolic compounds inhibit and

prevent nanoparticle agglomeration. These days, the goal of nanocatalysts is to improve solar energy efficiency while also helping with cleanliness and the removal of organic pollutants. Significant amounts of dyes are disposed of with industrial effluent, which poses a risk to the environment. A hazardous cationic dye, methylene blue harms both the environment and anybody who come into touch with it. The removal of dye molecules from water and the environment is frequently accomplished with a photocatalyst. This work addresses the important problems of MB identification and removal from wastewater. Although everyone does chemical synthesis, the primary concern is the creation of nanoparticles through green synthesis. Since the nanoparticles are not produced by the process, the solutions are dispersed to the outlet. This impacts the system and is harmful to the environment. Ag nanoparticles are mostly utilized in industrial biomedical production and wound healing^{17,18}.

2.5 Definition of Metal Oxides

With a variety of structural, optical, magnetic, and electrical characteristics, these materials are special functional materials. Depending on the material's band gap, they behave as metallic, semiconducting, or insulators at ambient temperature. Sensors, piezoelectrics, fuel cells, solar cells, and magnetic memory are just a few of the uses for them. The particle sizes of metal oxides have an impact on their characteristics. Their characteristics tend to be distinct in the "nano" realm (10^{-9} m). This occurs because when particle size diminishes from bulk form to tens of nanometers, the surface-to-bulk ratio of the atoms increases. This results in changed density and chemically active locations. Material science, chemistry, and physics are interested in the characteristics of metal oxides¹⁹.

2.5.1 Metal Oxide Nanoparticles

Both physical and chemical approaches can be used to create these materials¹⁹. Either top-down or bottom-up methods can be used to prepare them. These methods make advantage of gas-solid or liquid-solid transition. Among semiconducting nanostructures, metal oxide nanostructures are distinct. Because of their features and attributes, they are the most prevalent, varied, and wealthy class. They exhibit a variety of intriguing qualities²⁰. Because of their unique and adjustable characteristics, metal oxides are a highly desired candidate for a wide range of technical applications. Applications for them are numerous and include gas sensors, solar cells, superconductivity, and more. Among the often produced nanostructured metal oxides are nickel oxide (NiO), copper oxide (CuO), aluminum oxide (Al₂O₃), and zinc oxide (ZnO). They can be made using a number of methods, such as chemical synthesis, thermal evaporation, and chemical vapour deposition²⁰.

2.6 Methods of Synthesizing Metal Oxides Nanoparticles

The development, property characterization, and subsequent use in a variety of technological domains include the research of metal oxide nanoparticle materials. Nanomaterials are synthesized using a variety of techniques. These consist of the liquid and gas phases. The gas phase is utilized to produce huge amounts of nanopowders at a low cost. The liquid phase provides greater control over the final product material's composition, shape, and structural variation²¹. Numerous chemical techniques, including sol-gel, precipitation, hydrothermal synthesis, chemical reduction, thermal breakdown, electrochemical, and wet chemical processes, can be used to create nanoparticles. The synthesis of metal nanoparticles using conventional chemical methods has several drawbacks, including being costly, requiring the use of chemicals, taking a long time, and posing environmental risks due to the production of waste products and

toxic solvents. As a result, there is a growing need to develop more environmentally friendly and sustainable methods. Numerous biological systems, including bacteria, fungus, algae, plants, and human cells, have been shown to be capable of converting metal ions into metal nanoparticles²¹. Metal oxide nanoparticles have garnered attention over the years due to their unique characteristics and adaptability to a wide range of uses, particularly optoelectronic ones. Numerous methods for creating metal oxide nanoparticles have been documented. These include, among others, hydrothermal, metal organic chemical vapour deposition, and evaporation. The gas-phase and solution-deposition procedures are examples of chemical methods. There are more subgroups within this. Atomic layer deposition (ALD), chemical vapour deposition (CVD), and atomic layer epitaxy are the gas-phase techniques. Spray pyrolysis, sol-gel, spin, and dip-coating are the techniques used for solution deposition. Molecular beam epitaxy, magnetron sputtering, physical vapour deposition (PVD), and pulsed laser deposition are examples of physical deposition techniques. Additional methods include anodic oxidation, vacuum evaporation, electron beam evaporation, chemical bath deposition, and advanced reactive gas deposition²¹.

2.6.1 Chemical Synthesis

Its foundation is the solid phase (NP) precipitation that results from supersaturation of the liquid medium made up of different reactants. Supersaturation can be accomplished by adding the required reactants or by quickly cooling a solution that has already been heated. Various surfactants can be used for chemical synthesis. By altering the particle's surface tension, surfactants allow for the control of the particle's size and structural shape. Additionally, they stop particles from clumping together²².

2.6.1.1 Sol-gel Method

The most common technique of producing metal oxide nanoparticles is most likely the sol-gel approach. The solution, which is made up of metal oxides scattered throughout an organic solvent, is referred to as "sol." Aqueous or non-aqueous methods can be specified based on whether the solvent is water. The hydrolysis, condensation, and polymerization processes make up the sol-gel transition. A dense, porous, three-dimensional gel is produced as the hydroxide polymerizes. As shown in Figure 2.3, the oxide's final form coatings, solid foam, fibers, nanoparticles, etc. can be adjusted by subjecting it to further drying and heating²².

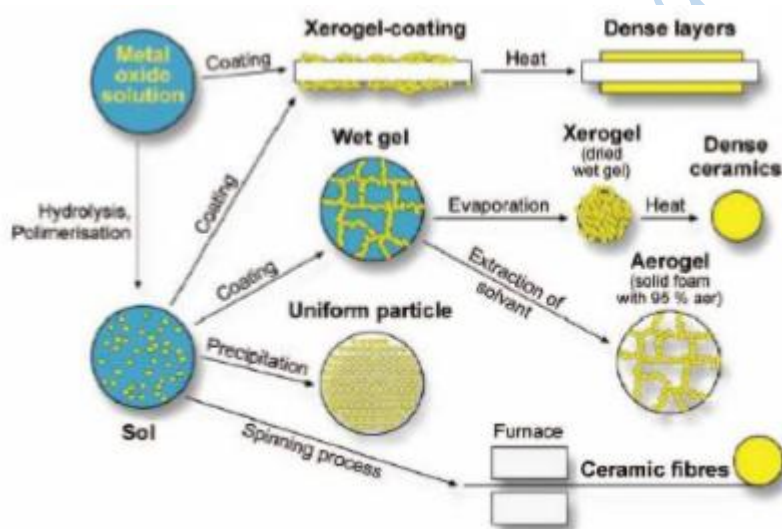


Figure 2.3: Diagram of the sol-gel process.

Source²²

2.6.1.2 Solvothermal Synthesis

Using this technique, the initial material is dissolved in a solvent (if the solvent is water, the process is called "hydrothermal synthesis") and heated to high pressure and temperature, which causes supersaturation and particle nucleation and growth. The reaction's chemical parameters the kind and proportion of the reactants as well as its thermodynamic parameters temperature, pressure, and time can regulate the size and form of the particles²¹.

2.6.2 Physical methods

In essence, physical synthesis involves breaking down a solid precursor into molecules or even individual atoms, which are subsequently deposited in the desired nanostructure form. Since they necessitate costly vacuum procedures and the deposited layer area is severely constrained by the chamber dimensions, these approaches are typically the most expensive²². Among the many different physical deposition techniques, the following have been effectively used to synthesize metal oxide nanoparticles:

- i. A plasma arc is applied to a solid target in Physical Vapour Synthesis (PVS) in order to produce vapour and initiate reactions that result in supersaturation. Upon cooling and combining the resulting atoms with the reactive gas, molecular clusters are created, which

subsequently come together to form particles. This approach uses the kind of reactant gas and cooling rate to adjust the particle properties. One variation of this technique, known as low energy cluster beam deposition (LECBD), is used for producing ZnO nanoparticles (NPs) when the supersaturated gas is additionally exposed to supersonic adiabatic expansion²².

- ii. A high-power laser beam is used in the pulsed laser ablation technique to evaporate the atoms from the solid target. The technique may be conducted in the presence of a background gas, such as oxygen, or in ultrahigh vacuum, with the goal being a bulk metal oxide. In the latter scenario, the target may be composed of pure metal, and the deposition process will cause it to oxidize²².

2.6.3 Mechanical Methods

The top-down way for creating nanostructures is mechanical processes. In order to obtain a fine grinding and homogeneous dispersion of particles in the pigment, those based on milling bulk metal oxides are frequently employed in the ink industry and pigment manufacturing. The obtained particle sizes are at least 200–300 nm in size. Even though mechanochemical processing, a mechanical technique, has been effectively used to produce metal oxide nanoparticles (NPs) of lower sizes²¹.

- i. Mechanochemical processing (MCP) is a synthesis technique that combines a chemical reaction that is activated at the nanoscale during grinding with a physical size reduction in a ball mill. When the right diluent is present, the precursors clash in the ball mill, causing an exchange reaction. Frequently, a heat treatment is used to further break down the product that forms (for example, heating ZnCO_3 produced during synthesis causes it to break down into ZnO). NPs with sizes ranging from 18 to 40 nm have been created

using this technique, contingent on the milling time and heat treatment temperature. This technique can be used to create MO NPs of oxides for which the appropriate precursors can be seen²¹.

Table 2.1: An overview of the updated fabrication process that includes the size of the NPs and the type of synthesized MO.

	Method	Types of Metal oxides synthesized	Nanoparticles size
Chemical	Solvothermal Synthesis	MgO, TiO ₂ , Fe ₃ O ₄ , WO _x , and many others	Ultra small, single nm
	Sol-gel	TiO ₂ , ZnO, MgO, CuO, ZrO ₂ , SnO ₂ and many others	>20 nm
Physical	Pulsed Laser Ablation	V ₂ O ₅ , WO ₃ , ZnO, SnO ₂ , NiO, ZrO ₂ , Cu/Cu ₂ O and many others	Av. Size–20 nm
	Physical Synthesis	Vapour ZnO	Av. size-8 to 75 nm
Mechanical	Milling	All	Larger than 200-300 nm
	Mechanochemical	ZnO	18-40nm.

2.7 Metal Oxide Nanoparticles' Characteristics for Solar Cell Electrodes

Owing to the extensive array of possible applications across several sectors, nanoparticle research is presently a vigorously pursued scientific domain²³. By their electronic structure, nanoparticles can be classified as semiconductors, metals, or insulators. It is believed that the unique chemical and physical properties of metal oxide nanoparticles are caused by their high density and microscopic corners and edges on their surface. Because of their potential technical applications, metal oxide nanoparticles are of interest to researchers in a wide range of fields, including materials information technology, chemistry, medicine, agriculture, biomedicine, sensing, optics, electronics, catalysis, energy, and the environment²¹. For instance, in nanoparticles of CuO, CeO₂, SnO₂, MgO, ZrO₂, Al₂O₃, AgO, ZnO, TiO₂, etc., size-related structural changes have been shown to cause changes in cell parameters. An increasing number of surface and interface atoms in the nanoparticles cause strain or stress and adjacent structural perturbations as their size decreases¹⁹. The nanoparticle's size can change its electrical, magnetic, conductive, and chemical characteristics. Because their size and form can be used to adjust their properties, magnetic metal oxide nanoparticles have attracted a lot of attention. The size of the nanoparticle material can affect its magnetic, electrical, and chemical characteristics. Materials scientists are particularly interested in iron oxides, specifically magnetite, because of their

numerous potential uses, which range from magnetic resonance imaging (MRI) contrast agents to magnetic storage devices (MSD)²³.

γ -Fe₂O₃ nanoparticles showed size-dependency, with ferromagnetic behavior seen in the 55 nm particles and super-paramagnetic behavior without hysteresis in the 12 nm particles²³. As the particle size decreases, the overall magnetic anisotropy will likewise decrease, causing the super-paramagnetic transition¹⁹. To achieve all the required magnetic, electrical, and chemical properties, new and simple techniques for producing metal oxide nanoparticles of the necessary size are crucial.

The size of these particles has a significant impact on their electrical characteristics (conductance), particularly when using oxides like In₂O₃, WO₃, and SnO₂, in gas sensing applications. TiO₂ materials' electrical/ionic conductivity can be adjusted to find applications in photovoltaics, optoelectronics, and sensors. At high temperatures, TiO₂ is readily decreased, which has an adverse effect on conductivity²³. With its wurtzite-type structure, one-dimensional (1-D) ZnO used in optoelectronic and electrical applications offers enormous promise for use in gas sensors and varistors, among other uses. The nanostructured oxide has either little or no long-range effects of the Madelung field, which is present in the electrical characteristics of a bulk oxide surface²¹.

As a redox catalyst and a catalyst in various oxidation processes, CuO nanoparticles are employed in photothermal and photoconductive applications as well as in the microwave irradiation process. In many different chemical sectors, magnesium oxide nanoparticles are widely used as a catalyst in organic synthesis and as a scrubber material to remove gaseous air pollutants (CO₂, CO, NO_x, and SO_x). In the field of catalysis, the new structure of Al₂O₃ serves as a foundation for active phases coated with other materials. Structural ceramics, solid

electrolytes, catalysts, and gas sensing materials are among applications for ZrO_2 nanoparticles. The fields of catalysis, gas sensing, electrochemistry, biomedicine, and material chemistry all make use of CeO_2 nanoparticles. Numerous industrial applications involving photocatalysis for pollutant removal, solar cells, material science, and engineering employ TiO_2 nanoparticles²². Although ZnO is a wide bandgap semiconductor material that has been thoroughly researched for its inherent qualities, it has relatively little industrial application as a UV blocker in sunscreen lotions and creams, mixed varistors, solar cells, partially as laser sources, optoelectronics, gas sensors, and as catalysts for a variety of organic reactions²³.

The structure, size, and form of the nanostructures are directly related to all of the stated characteristics and uses of specific metal oxide nanoparticles that have been discussed²³. It is obvious that a wide range of elements will impact the functional devices' primary attributes and structural features, which in turn will impact how well they work. The production of a nanostructure with ideal optical or electrical properties becomes a challenging issue when two distinct nano-oxides are combined, including the formation of a p-n junction or modification with a dopant. Furthermore, the best technique for creating metal oxide nanoparticles with adjustable structural parameters and attributes should optimize every process parameter that can negatively affect the final qualities. Because there are so many variables affecting the structural properties and functionality of the functional devices, it is challenging to replicate the outcomes²³.

2.8 Characterization Techniques for Nanoparticles

Characterization of nanoparticles is necessary to determine their identity, structural features, and textural attributes once they have been manufactured. scanning electron microscopy (SEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA), ultraviolet-visible spectroscopy (UV-Vis), photoluminescence (PL) spectroscopy, Raman spectroscopy, Brunauer-Emmett-Teller

(BET) surface area analysis, Fourier-transform infrared, and transmission electron microscopy (TEM)²⁴. As a result, the methods that have had their working concepts fully specified in the subsection are the ones that were previously discussed.

2.8.1 Fourier Transform Infrared Spectroscopy (FTIR)

One of the main non-destructive methods of infrared spectroscopy, Fourier transform infrared (FTIR) spectroscopy, usually uses an infrared light beam to identify a functional group in a material (solid, liquid, or gas). The device measures the amount of IR light absorption by each link in the molecule. Plotting of the resulting spectrum against wavenumber (cm^{-1}) and transmittance percentage is done. Infrared electromagnetic radiation can be absorbed by materials that are covalently bonded. In order to identify IR active chemicals in a molecule, functional groups must be identified. A molecule is IR-active if its dipole moment remains constant. When infrared light interacts with a substance's covalent bond with an electric dipole, the bond absorbs energy and oscillates²⁵.

2.8.2 X-ray Diffraction

X-ray diffraction (XRD) is an effective non-destructive method for examining the crystalline structures of materials. It provides details on a material's structures, crystalline phases, and crystal orientations in addition to other structural characteristics including . crystal defects, crystallinity, strain, and average grain size. The foundation of XRD is a crystalline sample and the constructive interference of monochromatic X-rays. X-rays are produced by a cathode ray tube, collimated, filtered to produce monochromatic radiation, and then directed onto the sample²⁵.

This rule links the diffraction angle and lattice spacing in a crystalline sample to the electromagnetic radiation wavelength. After that, these diffracted X-rays are found, examined, and tallied. Due to the powdered material's unpredictable orientation, the sample needs be scanned from two different angles to get all potential lattice diffraction directions. Translating the diffraction peaks to d-spacings allows for chemical identification because each compound has a distinct collection of d-spacings. This is frequently accomplished by comparing the d-spacings to established reference patterns²⁵.

2.8.3 Scanning Electron Microscopy and Energy-dispersive x-ray spectroscopy (EDXs)

SEM is a potent non-destructive research method that creates finely detailed, high-magnification pictures of a subject's surface topography using a focused electron beam. Energy-dispersive x-ray spectroscopy (EDXs) can be used to offer a more comprehensive knowledge of the material's elemental makeup once a region of interest has been identified on the sample and assessed using SEM. This approach is particularly effective for solid inorganic material microanalysis and failure analysis²⁵.

2.8.4 Raman Spectroscopy

An analytical technique called Raman spectroscopy employs scattered light to determine a material's vibrational energy modes. It is called C. V. Raman in honor of the Indian scientist who was the first to observe Raman scattering in 1928 alongside K. S. Krishnan. Compounds can be identified by their unique Raman "fingerprint," which can also provide structural and molecular details, according to Raman spectroscopy. Raman spectroscopy, which searches for Raman scattering in the material, is used to gather this data. Raman has been characterized as a useful technique for determining the crystalline phases and chemical composition of titania²⁵.

2.8.5 Ultraviolet-Visible Spectroscopy

The diffuse reflection of light from a sample's surface is commonly studied using UV-visible diffuse reflectance spectroscopy (UV-Vis), which operates in the UV-Vis wavelength range (190-800 nm). This method is frequently used to examine the optical characteristics of opaque solid materials. Light is reflected off the surface of solid (opaque) materials because it cannot travel through them. The surface of most materials is composed of a non-absorbing powder, which causes it to reflect both diffuse and specular light. Diffuse reflection is rarely produced by surface roughness of a solid material. Diffuse reflection is still feasible even when specular reflection is produced by the flat surface²⁵. The incident light is reflected at multiple angles due to diffuse reflection, as opposed to specular reflection, which only reflects the light at one angle. Integrating spheres are used to enable the measurement²⁵.

When light is aimed at the sample at a 0° angle, only diffuse reflected light rather than the specular light that is already present in the sphere is measured. Nevertheless, models of integrating spheres with different incident light angles allow for the detection of both diffuse and specular reflected information. One of the well-developed and widely recognized theories for the optical phenomena caused by diffuse reflection is the Kubelka Munk hypothesis. The partial scattering and absorption of light is the foundation of this theory. Assuming that just two light pathways absorbed and scattered light are traveling in opposing directions, it was created to mimic the light that results from transparent and opaque materials. The Kubelka-Munk equation is expressed using Equation 2.5²⁵.

$$F(R) = \frac{(1 - R_{\infty})^2}{2R_{\infty}} = \frac{k}{s} = \frac{2.303\epsilon C}{s}$$

3.1

Where R_{∞} is the reflectance at infinite thickness, K is the absorption coefficient (which is twice the Beer's law absorption coefficient), S is the sample's scattering coefficient, M is the molar absorptivity, and C is the analyte concentration.

Plotting $(F(R) \text{ energy})$ versus energy ($h\nu$) enables easy estimation of the optical bandgap energy of nanoparticles from diffuse UV-Vis data²⁵.

2.9 History and Current Research in Photovoltaics

Although silicon solar cells are inexpensive to operate and maintain, their high production costs prevent photovoltaic technology from becoming widely used. Current research is predicated on the assumption that, for commercial applications, either photo-conversion efficiency must be increased or manufacturing costs must be reduced¹⁸.

2.9.1 First-Generation

Both crystalline and polycrystalline silicon solar cells are included in the first generation of solar cells. These silicon solar cells have been the industry standard for more than 50 years and provide almost 90% of photovoltaic energy. Phosphorus is diffusely doped into the upper surface of crystalline silicon (c-Si) solar cells. The front and back of the cell are connected using the screen printing technique¹⁹. On a lab scale, silicon solar cells have a maximum photo-conversion efficiency (PCE) of only approximately 25%, whereas commercial silicon cells have a PCE of roughly 22%. High-purity preparation The production of c-Si solar cells requires 99.999 percent precursors, which is a costly and time-consuming procedure. The capital cost of the manufacturing facility and solar modules are directly increased by this procedure²⁰. The high cost of silicon solar cells is preventing their widespread use in the generation of power. The main benefits of silicon solar cells are higher efficiencies and carrier mobility with a wide spectrum absorption range. One significant drawback of silicon solar cells is their manufacturing costs.

Heat is the waste product of photon energy produced at short wavelengths. This technology's energy payback time (EPP) is around two to three years²⁰.

2.9.2 Second Generation / Thin-Film Solar Cells

Thin-film solar cells are made of copper indium gallium diselenide (CIGS), cadmium telluride (CdTe), thin-film crystalline silicon, copper zinc tin sulphide (CZTS), and amorphous silicon (a-Si). Thin-film methods are used to produce the photoactive material for thin-film solar cells on a flexible substrate or glass²⁰. As a result, these gadgets are known as thin-film solar cells. Second-generation solar cells, in contrast to first-generation ones, have broad area deposition, cheap production costs, and less materials needed. Because of their high absorption coefficient, direct bandgap photoactive materials need to be thinner than a micron in order to absorb incoming sunlight. Thin-film technology-based solar cells employ a variety of thin-film technologies, including PVD, plasma-based, CVD, and others, to sequentially deposit the required thin films, which range in thickness from 1 to 10 μm , in a vacuum on a variety of substrates, including glass, polymers, metal, etc., over large areas with integrated module manufacturing by scribing the layers for interconnections²⁰.

The a-Si solar cell's structure is made up of layers that are n-doped (p-i-n), intrinsic, and p-doped. These a-Si cells demonstrated the highest photo-conversion efficiency of 10.1%; nevertheless, substantial power-conversion efficiency losses are seen during exposure to sunlight²¹. Thin coatings of photoactive material are employed to improve stability and efficiency. These thin coatings lower the photo-conversion efficiency by obstructing the absorption of solar energy. When CdTe is deposited over cadmium sulfide (CdS), it often creates p-n junction solar cells with a bandgap that is near to the ideal bandgap of 1.48 eV. First Solar Inc. U.S.A.'s demonstration of 21% photo-conversion efficiency (PCE) with CdTe solar cells and 17% using

CdTe solar modules has sustained interest in this technology in both research and commerce¹⁹. A notable efficiency of 21.7% with exceptional stability is obtained when gallium is added to copper indium diselenide (CIS). The efficiency of the CIGS solar module is 16.5%. The photo-conversion efficiency of the CIGS module, which was constructed using a buffer devoid of cadmium, was 13.5%. A promising option for thin-film photovoltaics are solar cells based on CIGS²⁰.

The materials InSb, GaAs, InAs, InP, GaInAsP, and GaAlAs are classified within the Periodic Table's III-V group. The ease of preparation of these materials and alloys makes them suitable for the development of monolithic multilayer tandems with solar cells and absorbers that function at various sun spectrum wavelengths. In this manner, the combination may collect the solar spectrum to create a high-efficiency device²¹. GaInAsP, GaAs, InSb, GaAlAs, InP, and InAs materials are restricted to concentrated photovoltaics and space. GaAs, as a single junction cell, has attained 29.1% PCE. The greatest 46% PCE is found in GaInP/GaAs/GaInAs multi-junction solar cells. Second-generation solar cells are far better at absorbing incoming solar light than first-generation solar cells. The efficiency of second-generation solar cells has been reported to be between 15% and 20%. One of the limitations of second-generation solar cells is poor charge transmission²². Due of this, second-generation photovoltaics cannot be commercialized, which has prompted research into newer PV technologies²¹.

2.9.3 Emerging Photovoltaics or Third Generation

Researchers have initiated the development of an advanced classification of solar cells, designated as third-generation or emerging photovoltaics, with the objective of addressing the limitations associated with first and second-generation solar cells. The subsequent categories are pertinent to emerging photovoltaics, perovskite solar cells Dye-sensitized solar cells (DSSC)

Quantum dot solar cells (QDSSC) Bulk heterojunction solar cells (BHJ)¹⁷. These emerging photovoltaics present a multitude of advantages, encompassing cost-effective materials, simplified manufacturing processes, an abundant supply of resources, and the capability to be fabricated on both flexible and rigid substrates for solar cell production. In DSSC, both inorganic-organic and organic dye compounds are utilized as sensitizers. Conversely, in quantum dot solar cells, inorganic quantum dots serve as sensitizers, and due to their tunable bandgap properties, they exhibit numerous advantages over dye molecules²¹. Nonetheless, a significant challenge arises in the form of sensitization and the selection of an effective electrolyte, which may lead to the degradation of the quantum dots. Carbon-based compounds such as C60 act as acceptor materials in BHJ, while conjugated conductive polymers function as donor materials. The primary limitations of BHJ are attributed to moisture and ambient light, which can drastically hinder cell performance. Recent investigations into Perovskite and CZTS solar cells have revealed that the former achieved an efficiency of 23.3%, whereas the latter attained an efficiency of 12.6%²². DSSC, recognized as a member of the third generation, is approaching readiness for commercialization and can be manufactured on both rigid and flexible substrates²¹.

2.9.3.1 Dye-sensitized Solar Cells

Using very clean semiconductor materials (avoid flaws and interfaces) and depending on an inherent electrical field to help separate photogenerated electron-hole pairs is the widely recognized paradigm in conventional solar energy conversion²³. Furthermore, it is preferable for a semiconductor's band gap to be around an optimal value for solar energy absorption. Due to their reliance on wide band gap, nanostructured semiconductors, dye-sensitized solar cells (DSCs) represented a significant advancement in this area. DSCs function without an internal electrical field or stringent material purity controls, yet their large internal interface is essential to their

proper operation²⁴. A mesoporous layer of semiconductor oxide nanoparticles, sintered together to create a good electric contact between the particles, forms the backbone of a dye-sensitized solar cell. The nanoparticles have a diameter of around 25 nm, and the film thickness (d) is typically about 10 μm . In order to let light into the cell, this film is placed over a glass plate coated with transparent conducting oxide (TCO).

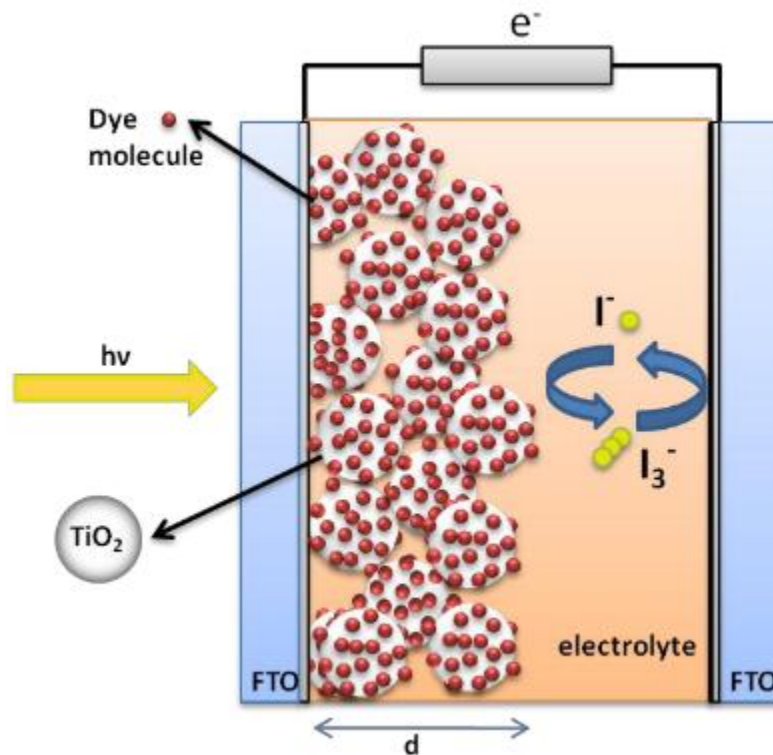


Figure 2.4: Schematic view of a dye-sensitized solar cell device

Source²⁵

Harvesting the light is done by a monolayer of dye molecules that are affixed to the oxide's surface. An electrolyte solution with a high ionic strength, typically made of an organic solvent with a redox pair, envelops the sensitive screen (Figure 2.4)²⁵.

Almost every part of a DSC can be adjusted. The most effective material combination to date is still the one described in the groundbreaking study by the Grätzel group, which launched the dye-sensitized solar cell research field. The primary constituents of this configuration consist of an organic solvent that serves as the redox mediator and a layer of titanium dioxide nanoparticles sensitized by a ruthenium-complex dye with an I-/I³⁺- redox pair²⁶. Grätzel and O'Regan successfully combined an effective and stable dye with a nanostructured semiconductor electrode. As was previously noted for ZnO mesoporous electrodes in 1976, the surface area was the crucial component in that combination²⁶. Even if there is only a single layer of dye covering the surface, incoming photons can be efficiently collected in a mesoporous film. The rationale is that compared to a flat electrode of the same geometric area, a mesoporous structure can have a surface area available for dye adsorption that is more than a thousand times bigger. Alternative materials to this conventional design serve as the foundation for the work in this thesis²⁶.

2.9.3.1.1 Operational Principles of Dye-Sensitized Solar Cells

In photo-electrochemical dye-sensitized solar cells, multiple electron transfer mechanisms operate concurrently and competitively. Charge production and optical absorption are two distinct processes in a DSSC²⁷. Similar to chlorophyll in leaves, dye molecules have to absorb incident sunlight and trigger an electron transfer reaction. Photo-regenerative devices are dye-sensitized solar cells. A schematic of their fundamental operating principles is shown in Figure 2.4.

When exposed to light, the dye is photoexcited, which causes an electron to be injected into the oxide's conduction band. The resulting oxidized sensitizer can either recombine with the injected electron or be renewed by the electrolyte's electron donor. Additionally, the excited dye may relax prior to electron injection²⁸. Through a random walk mechanism, the photogenerated electron moves toward the external contact through the mesoporous oxide sheet. After being removed, the electron can return to the counter electrode and work in an external circuit. The regenerative cycle is completed when the oxidized species in the electrolyte synthesized during the dye regeneration phase diffuses to the counter electrode coated in platinum and is reduced back there. The process's main loss pathway is the injected electrons' recombination with the oxidized redox mediator²⁸.

Reactions that explain how a DSC operates. S stands for fundamental state, S* for excited state, S⁺ for oxidized state, SC for semiconductor, CB for conduction band, and TCO for transparent conducting oxide.

The potential difference between the redox potential of the I⁻/I₃⁻ couple in the electrolyte and the conduction band edge of the TiO₂ determines the maximum theoretical value for the photovoltage under open circuit conditions²⁹. Dye-sensitized solar cells are extremely intricate

devices. Numerous activities are interrelated, and the device's chemical complexity makes it challenging to investigate each individual activity that influences cell performance independently. Since their features are influenced by the overall functioning, these processes actually need to be researched in whole devices²⁹.

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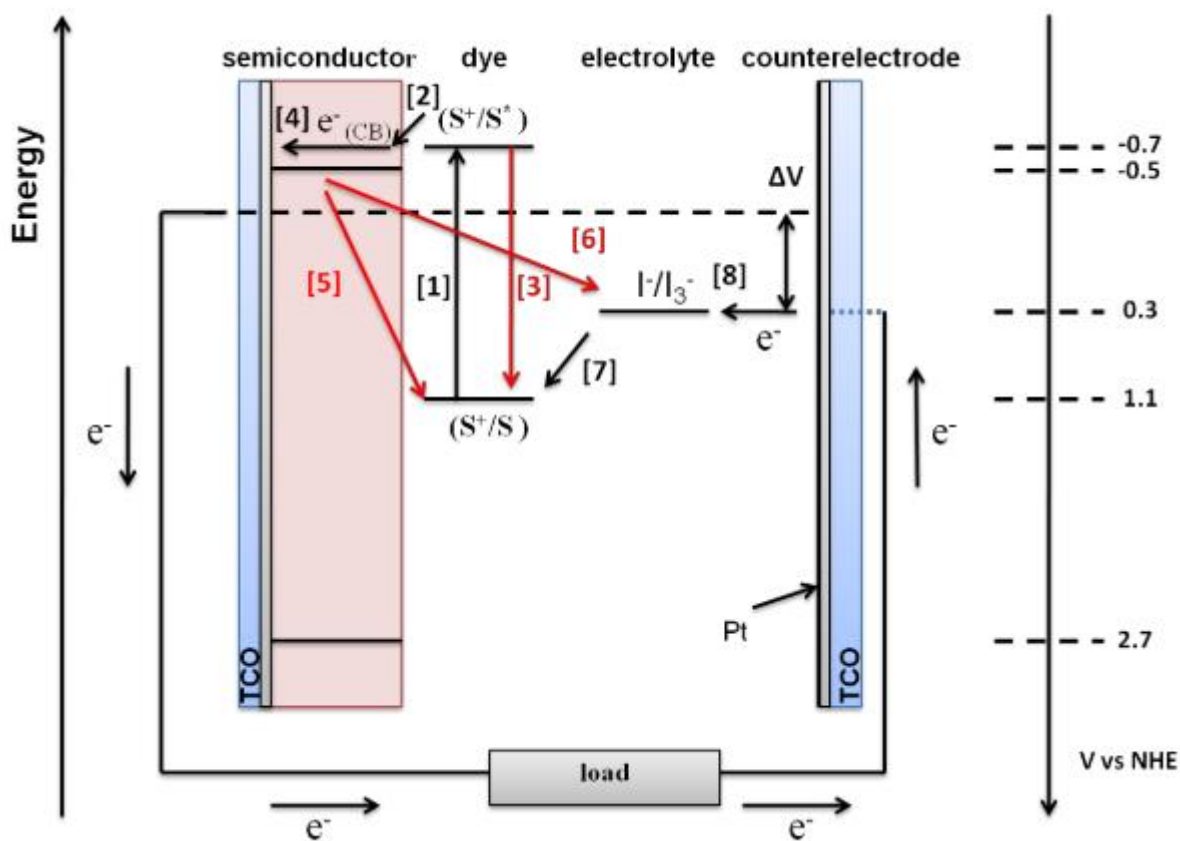


Figure 2.5: Dynamics of several electron transfer mechanisms that occur during a DSSC's photo-conversion

Source²⁸

[1] Photoexcitation	$S + h\nu \rightarrow S^*$
[2] Electron injection	$S^* \rightarrow e^-_{(CB)} (SC) + S^+$
[3] Relaxation	$S^* \rightarrow S + h\nu$
[4] Electron transport	$e^-_{(CB)} (SC) \rightsquigarrow e^- (TCO)$
[5] Recombination with the dye	$S^+ + e^-_{(CB)} (SC) \rightarrow S$
[6] Recombination	$2 e^-_{(CB)} (SC) + I_3^- \rightarrow 3I^-$
[7] Dye regeneration	$2S^+ + 3I^- \rightarrow 2S + I_3^-$
[8] Reaction at the counter electrode	$I_3^- + 2e^- (Pt) \rightarrow 3I^-$

The creation of photocurrent is sustained when the liquid redox electrolyte penetrates the photoelectrode and conducts the hole carriers and dye molecule regeneration. To prevent liquid electrolyte leakage, a thermoplastic polymer is positioned between the counter electrode and photoanode to seal the device. The next subsection provides an explanation of the device's components²⁹.

2.9.3.1.1.1 TCO Substrates

The photoelectrode and counter electrode for the device assembly are made using TCO substrates. It supports the counter electrode catalyst (such as platinum) and photoanode material (such as TiO₂ nanoparticles)³⁰. Chemical vapor deposition (CVD) or sputtering techniques are used to deposit TCOs. Sputtering produces flat TCOs that require a chemical wet etching process to provide a nano-texture for improved surface adherence and light scattering characteristics. When opposed to sputtering technology, the TCOs deposited using CVD technology offer extra benefits. This method has good surface texture, high deposition speeds, and is readily scalable. Tin-doped indium oxide (ITO) and fluoride-doped tin oxide (FTO) are the two best TCOs that have been created in the past three decades. Because FTO substrates are less expensive and more

robust up to 550 °C than ITO, they are the ideal option for DSSC. However, FTO has less optical transparency and electrical conductivity than ITO³⁰.

2.9.3.1.1.2 Photoanodes

Photoanodes are made from semiconductor oxides with a wide bandgap (such as ≥ 3 eV). The majority of incident sunlight is absorbed by these metal oxides, which are stable against photo-corrosion and optical excitation across the bandgap. Because of its affordability, stability, catalytic activity, and ease of preparation, titanium dioxide (TiO₂) is a photoanode material that is being studied extensively for DSSC³¹. There are four polymorphs of TiO₂. They are TiO₂(B), rutile, anatase, and brookite. The most stable of them is rutile, whereas the other three are metastable and can change into rutile when exposed to high temperatures³⁰. When it comes to photocatalytic activity, anatase is more active than rutile, and its electron mobility is 40 times greater. The LUMO energy levels of many dyes are located just above the conduction band edge of TiO₂, which makes it easier to inject electrons. TiO₂ has a bandgap of 3.37 eV. Because of TiO₂ high dielectric constant ($\epsilon = 80$ for the anatase phase), the injected electrons are well shielded electrostatically from the excited dye molecules. TiO₂ key characteristics are its non-toxicity, affordability, and accessibility. It is the primary ingredient in cosmetics and paintings³².

In DSSC, mesoporous TiO₂ nanoparticles having a surface area of 50–250 m²/g are primarily used to generate the photoelectrode. The TiO₂ film is applied to the TCO substrate using either the doctor blade or the screen printing technique. Organic binders are then removed by high-temperature treatment, which produces pure TiO₂ film and enhances the inter-particle necking between the TiO₂ nanoparticles³³. A variety of morphologies, including hierarchical structures, aerogels, mesoporous/nanoporous nanowires, nanorods, nanotubes, nanoparticles, and nanobelts, are becoming more and more common. Made with nanoparticles of size less than 20 nm,

transparent TiO₂ paste initially covers a TCO substrate. Made with size 400 nm nanoparticles, light scattering paste is then covered over transparent TiO₂ film layers³³.

In addition to TiO₂, various metal oxides and composite materials are being researched as photoanode materials, including Au-TiO₂, ZnO, Ag₂O-ZnO, Nb₂O₅, SnO₂, WO₃, and Fe₂O₃³². ZnO is thought to be the finest substitute for TiO₂ among them when it comes to creating the photoanode for DSSC. ZnO has a bandgap of 3.3 eV, and the conduction band edge's energy levels are at the same level as TiO₂. One crucial aspect of DSSC is that ZnO has better electron mobility and carrier lifetime than TiO₂³¹. facile development of many morphologies including nanoparticles, nanowires, nanorods, nanotubes, and tetrapods corresponds with facile production of ZnO. Photoconversion efficiency of the ZnO photoanode-based DSSC is now 8.0%³⁰. However, ZnO reduces efficiency by dissolving in iodide/triiodide electrolyte and forming Zn²⁺ ions. Layered double hydroxide is being researched as a photo-anode material for DSSC in order to get around ZnO's drawbacks when an electrolyte of corrosive redox iodide/triiodide is present. New architectures, materials, and structures are still possible to achieve the DSSC's superior performance^{31,32}.

2.9.3.1.1.3 Sensitizers

The dye molecules, often referred to as sensitizers, are important components of the DSSC. When sunlight is absorbed by these sensitizers, excitons are produced. The LUMO level injects electrons into the photo-anode's conduction band, while the HOMO level injects holes into the redox electrolyte. The photo-conversion efficiency is determined by how much photons are absorbed by sensitizers³³.

2.9.3.1.1.4 Counter Electrodes

The TCO substrates are coated with the catalyst, which guarantees the electrons' catalytic activity toward the reduction of tri-iodide and the electrons' charge transfer kinetics at the cathode. Common catalyst materials for the usage of counter electrodes include platinum and carbon-related compounds³⁴. Of these, platinum has the highest electrical conductivity and functions as a better catalyst. Electrochemical, spin coating, sputtering, and vapor deposition techniques are used to prepare the platinum counter electrode. The commercialization of DSSC is limited by the price of platinum. Because it is inexpensive and simple to prepare, graphite is regarded as one of the platinum substitutes³³. However, as compared to platinum-based DSSC, graphite-based DSSC has lower efficiency. As counter electrodes, other materials such as graphene and graphene-related materials, conductive polymers like PEDOT:PSS, chalcogenides, and p-type metal oxides are studied, although platinum remains the most popular of all³¹.

2.9.3.1.1.5 Electrolytes

Redox electrolyte's primary function in DSSC is to renew the oxidized sensitizers and introduce holes into the electrolyte. Any electrolyte used in the DSSC needs to meet these specifications:

- i. In addition to exhibiting thermal, chemical, optical, and electrochemical stability, the electrolyte must also inhibit dye degradation.
- ii. The oxidized dye molecules must be restored to their ground state by injecting the hole carriers into the electrolyte.
- iii. There should be no overlap between the electrolyte's absorption spectrum and the dye's or the visible spectrum³¹.

Solid, liquid, and quasi-solid electrolyte types are distinguished by their viscosity and chemical components. Because of its distinct slow recombination rates, the redox couple iodide/triiodide (I^-/I_3^-) in DSSC is being studied extensively. In addition to reacting with the injected electrons, triiodide ions absorb visible light. For improved performance, iodide and triiodide ion optimization is required. Because I^-/I_3^- electrolyte is corrosive, research is being done to prepare novel redox electrolytes such $SCN^-/(SCN)_3^-$, $SeCN^-/(SeCN)_3^-$, and Br^-/Br_3^- . Although these electrolytes' results are encouraging, their chemical stability is lacking. Coordination compounds based on copper and cobalt have the ability to function as redox couples. Cobalt-based coordination compounds performed exceptionally well in photo-conversion among them. With modified Y123 dye, the state-of-the-art for DSSC based on a cobalt-based redox pair is 14.3%. The cobalt-based redox couple's key characteristics were its transparency, non-volatile nature, and lack of corrosion³⁰.

2.10 Fabrication Techniques of DSSCs

Screen printing, doctor blade, electro-phoretic coating, and spin coating are the most widely used fabrication techniques for DSSCs, and they have a considerable impact on the cell's efficiency and cost, as will be discussed in the following sections³¹.

2.10.1 Screen-printing

The techniques utilized to develop DSSCs have a big impact on the cell's cost and efficiency. Screen printing, spin coating, electrophoretic coating, and doctor blade are the fabrication methods that are most frequently utilized. A 2020 research indicated that the photoanode included TiO_2 on rGO sheets embedded with Ag, while the counter electrode consisted of silver (Ag) nanoparticles attached to a reduced graphene oxide-platinum composite (Ag-rGO/Pt), as seen in Figure 2.5.

Under 1.5 AM solar irradiation, the DSSC with the 1:2 Ag-rGO/Pt CE and 0.5% TiO₂-rGO/Ag photoelectrode demonstrated an overall maximum PCE of 9.15%³².

2.10.2 Spin-coating

Spin-coating is a simple technique for rapidly coating a substrate's surface with consistently thin layers. A typical approach starts with a material solution made from a volatile solvent, which is then dropped onto the center of the substrate surface and spun up and off. Both the spin-off and spin-up procedures use the solvent evaporation step. Once placed in the center of the substrate's surface, the material solution is dispersed using centrifugal force. The next step requires the thin layer of material applied to a glass substrate to dry.

The relationship between the layer's thickness and several other properties can be explained using Equation 2.1:

$$h = \left(1 - \frac{\rho_A}{\rho_{A0}}\right) \left(\frac{3\eta \times m}{2\rho_{A0} \times \omega^2}\right)^{\frac{1}{3}} \quad 2.1$$

where thickness is indicated by h. The symbols A, m, and angular speed represent the density of a volatile liquid, the viscosity of the solution, and the rate of evaporation, respectively. This equation shows that the angular speed, solution viscosity, and spinning duration all affect the thickness of the formed layer. When the substrate spins at a greater angle, the film is thinner. The spin-coating technique has been used in a number of published papers. A 2019 study, for instance, described a thin-film TiO₂ photoanode created using a spin-coating process to increase the efficiency of natural and organic DSSCs³³.

2.10.3 Electrophoretic Deposition

When materials are treated using electrophoretic deposition (EPD), charged particles in a stable colloidal suspension are deposited onto a conductive substrate, which acts as one of the two electrodes in the EPD cell with opposite charges. Applying a suitable solvent to the surface of a conductive substrate is a quick and economical process. It involves four main steps;

- Electrophoresis
- Deposition.
- Dispersion
- Electrochemical charging

EPD is developed when charged particles move in an aqueous solution or solvent while being exposed to an electric field. A recent publication describes the CdSe-TiO₂ nanocomposite film produced by EPD for quantum dot-sensitive solar cells³⁴. Additionally, Cao has documented the use of the EPD technique to create mesoporous TiO₂ photoanodes and employ them in DSSCs³⁵.

2.10.4 Doctor-blade Coating

Doctor-blade coating is a high-throughput, low-solution-wastage thin film, roll-to-roll compatible, manufacturing technique. This technique is widely used to create a thin liquid substrate layer on top of a large-surface-area glass conducting substrate. It provides easily adjustable layers that range in thickness from 10 to 150 μm . To create counter electrodes for DSSCs, Al-Bahrani employed the Doctor-blade technique. To create a nanocomposite, reduced graphene oxide, nickel oxide, and multi-walled carbon nanotubes were mixed together³⁶. Furthermore, a study was published on a possible counter electrode for DSSCs composed of a hydrophilic carbon (HC)/TiO₂ colloid composite covered with a doctor blade³⁷. The cell's PCE was found to be 1.9% under standard test settings. Development of Cu₂ZnSnS₄ counter

electrodes for DSSCs using Doctor-blade coating has been documented in a study³⁸. This method uses less of the original components and is less expensive than other methods. is therefore thought to be the most straightforward printing method for modern devices and one of the simplest, least expensive methods for depositing semiconductor paste. This method uses less of the original components and is less expensive than other methods. It is therefore thought to be the most fundamental printing method for modern electronics and one of the simplest, least expensive processes for depositing semiconductor paste.

2.11 Electrical Characteristics Parameters

The solar cells are tested using photovoltaic metrics such the J_{sc} , V_{oc} FF, and PCE when illuminated. solar parameters are used to validate the J-V properties of solar cells³⁹.

2.11.1 Open-Circuit Voltage

The external current ($J=0$) does not flow when illuminated at the open-circuit voltage (V_{oc}), also called a bias voltage, which is applied to solar cells to destroy the current generated during illumination. The V_{oc} in DSSC is identified by the Fermi energy work function of the electrolyte and photoanode. The experimentally determined V_{oc} is relatively low because of charge carrier recombination³⁹.

2.11.2 Short-circuit Current Density (J_{sc})

J_{sc} is the word used to describe the current density produced in a solar cell at applied zero bias. Charge transfer and exciton dissociation provide the build-in potential. A DSSC's J_{sc} is reliant on exciton production and incident light. Second, a broad photoactive layer absorption spectrum allows for the harvesting of more excitons in the terrestrial solar spectrum, resulting in the highest J_{sc} of the DSSC. The solar cell's J_{sc} is determined by the active layer's charge carrier mobility³⁹.

2.11.3 Fill Factor (FF %)

Figure 2.6 displays the J-V characteristics of DSSC. A solar cell's primary goal is to convert sunlight into electrical power. The J-V curve allows us to determine $P_{\max}$, which stands for the maximum deliverable power. The following phrase is used to determine the DSSC's fill factor;

$$\text{FF \%} = \frac{P_{\max}}{J_{\text{sc}} \times V_{\text{oc}}} = \frac{J_{\max} \times V_{\max}}{J_{\text{sc}} \times V_{\text{oc}}}$$

Equation 2.2

With the FF, the diode properties of solar cells may be measured. The FF needs to be unity for a perfect diode. The diode will be more perfect as the FF increases. Because to recombination and transport losses, the FF in DSSC was between 0.6 and 0.85. Shunt and series resistance have been shown to function as limiting variables in solar cells. High fill factor FF is the result of solar cells having large shunt resistance and low series resistance³⁹.

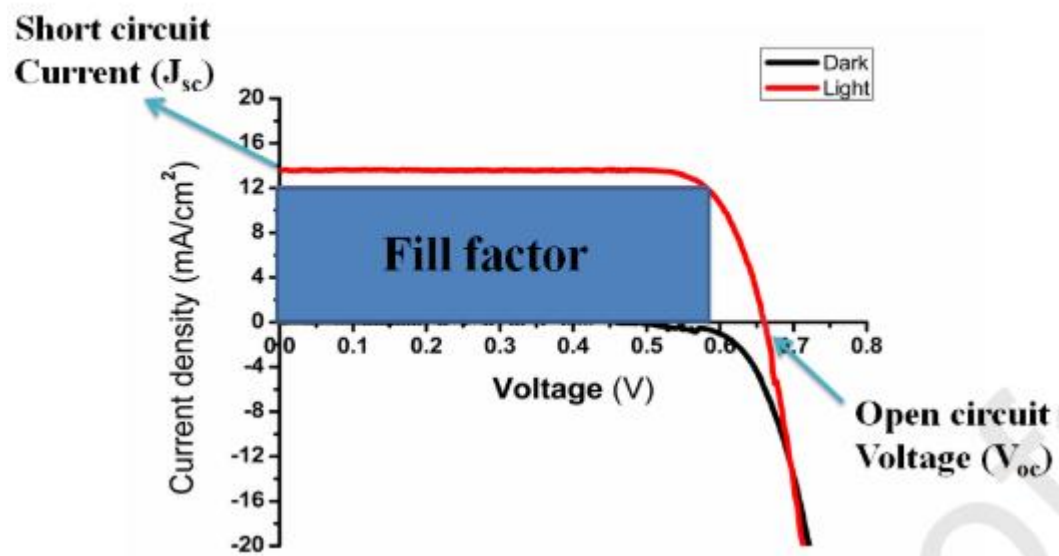


Figure 2.6: Diagrammatic illustration of the DSSC's J-V characteristic curve.

Source³⁹.

2.11.4 Power Conversion Efficiency (η)

The ratio of incident light power (P_{in}) to supplied power (P_{max}) is a measure of a DSSC's efficiency. The following formula is used to determine the solar cell's photo conversion efficiency;

$$\eta = \frac{P_{max}}{P_{in}} = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}}$$

Equation 2.3

The η provides information on the DSSC's output power as well as photovoltaic characteristics and how light is converted into energy³⁹.

2.11.5 Dark Current

Dark current is the phrase used to describe the current flowing through the diode while it is dark. The dark current production is based on the recombination of charge carriers or any surface leakage in the depletion area, which is the perfect diode current. To generate the potential difference between the solar cell's terminals, a forward bias load must be provided. The current created by this potential difference operates in the opposite direction of the photocurrent, lowering the net current from its short circuit value³⁹. Similar to the current I_{dark} (V), which runs across the device when a voltage is applied in the dark, this reverse current is typically referred to as dark current. When exposed to darkness, solar cells function similarly to a diode, accepting a higher current under forward bias ($V > 0$) than reverse bias ($V < 0$). Solar cells exhibit this behavior because asymmetry is necessary to accomplish charge separation³⁹.

2.12 Review of Metal Oxides Nanoparticles

Fe_2CuO_4 nanoparticles were produced using UV-irradiation¹¹. XRD, EDX, FE-SEM, TEM, and photoluminescence spectroscopy were among the methods used to examine the shape, structure,

and optical characteristics of the produced nanoparticles. The average particle size of the produced Fe_2CuO_4 NPs was 11.7 nm, and their FE-SEM and crystal structure were validated by TEM pictures. No contaminant peaks were found in an XRD analytical analysis. Using photoluminescence spectroscopy (PL) to evaluate the optical characteristics, the energy gap was found to be 1.95 eV. Using nanopowder and cibacron brilliant red B as a photosensitizer, an effective photo-sensitizing solar cell was developed with an energy conversion efficiency ranging from 6.47 to 10.39%. A novel technique that does not require significant testing has made it possible to swiftly and easily control nano-particulate composites. Their study could look at the possibilities of producing nanomaterials, such as photoanodes, very quickly¹¹.

A research demonstrates how to modify both of a plasmonic dye-sensitized solar cell's (PDSSC) functional electrodes in order to produce a cost-effective and efficient solar device³⁶. A straightforward one-step wet synthesis approach and inexpensive, non-toxic precursors were used to create the hybrid magnetite nanoparticles decorated reduction graphene oxide ($\text{rGO}/\text{Fe}_3\text{O}_4$) and copper-doped titania (Cu/TiO_2) nanocomposite. The as-prepared nanocomposites were carefully analyzed using SEM, energy dispersive X-ray spectroscopy, X-ray diffraction, thermogravimetric analysis, and UV-Vis spectroscopic methods, proving the successful formation of Cu/TiO_2 and hybrid $\text{rGO}/\text{Fe}_3\text{O}_4$ nanocomposites. The photovoltaic features of the PDSSCs were investigated by the analysis of IPCE spectra and J-V characteristics. In PDSSCs, the Cu/TiO_2 -based photoanode's power conversion efficiency (PCE) was 3.89% when using platinum (Pt) and 2.20% when using hybrid $\text{rGO}/\text{Fe}_3\text{O}_4$ counter electrodes (CEs). The hybrid $\text{rGO}/\text{Fe}_3\text{O}_4$ CE-based PDSSC was around 70% more efficient than pure TiO_2 -based photoanodes and 57% more efficient than the traditional platinum electrode with Cu/TiO_2 . The homogeneous distribution of catalytic Fe_3O_4 nanoparticles on the surface of rGO nanosheets and

the plasmonic effect of the Cu nanoparticles may be responsible for the respectable efficiency gain. According to the results, the synergistic combination of modified functional electrodes in plasmonic DSSCs demonstrated a respectable efficiency and might thus work well as a substitute for traditional and expensive Pt³⁶.

Another work used the photoirradiation approach for fabricating Fe₂O₃ nanoparticles from iron complex solutions³⁷. The generated nanoparticles are identified by ultraviolet visible spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The results show that the nanoparticles are homogenous rhombohedral in form and range in size from 11 to 29 nm. A novel dye solar cell with an energy conversion efficiency of about 2.5% was made using hematite nanoparticles, ITO, -Fe₂O₃ NPs, dye (Rhodamine 6 G), iodine, and Ag film³⁷.

A counter electrode was suggested in a work using a mixture of low-cost carbon black and tin selenide components³⁸. TiO₂ is used as the photoanode in the solar cell's architecture. The physicochemical properties of the CEs are investigated using XRD, TEM, RAMAN, BET, and EDX. CV and EIS studies were carried out to evaluate the electrocatalytic and charge transport characteristics. The DSSC with the SnSe/CB-200 CE electrode showed a PCE of 8.17 ± 0.02% with an open-circuit voltage of 0.797 ± 0.03 V and a short circuit current density of 19.78 ± 0.02 mA/cm², whereas the DSSC with the platinum counter electrode had a PCE of 5.81 ± 0.03%³⁸.

A study was conducted on copper polypyrrol functionalized multiwall carbon nanotubes (Cu-PPy-FWCNTS) nanocomposite CE utilizing a two-step electrodeposition process on a stainless-steel substrate to provide a simple and cost-effective substitute for Pt CE in dye-sensitized solar cells (DSSC)³⁹. The surface morphology, electrical conductivity, and electrochemical properties of Cu-PPy-FWCNTS nanocomposite CE electrodes were investigated using SEM, the four-probe

technique, and an electrochemical workstation. According to Fourier transform infrared (FTIR) spectroscopy, the PPy-FMWCNTS nanocomposite comprises FMWCNTS, and XRD examination verified the presence of Cu nanostructures. The cyclic voltammogram and Tafel polarization measurement demonstrated that the solution-processed Cu-PPy-FWCNTS nanocomposites CE had a higher electrocatalytic performance for I₃/I redox solution. The photovoltaic efficiency of DSSCs produced with Cu-PPy-FWCNTS nanocomposite CE and Platinized CE was compared. According to the results, the CE of DSSC with Cu-PPy-FWCNTS nanocomposites was 7.1%, higher than that of Platinized CE (6.4%). Cu-PPy-FMWCNTS film's enhanced photovoltaic efficiency is due to copper nanostructures, which enhance the cathodic current density (2.35 mA/cm²). Cu-PPy-FWCNTS nanocomposites' simple manufacturing method, strong electrocatalytic properties, and photovoltaic capabilities make them a viable CE substitute that can lower the cost of DSSC³⁹.

In a different study, Ni_{0.5}Zn_{0.5}Fe₂O₄/carbon (NZF/C) composites with different carbon content ratios were used to generate novel counter electrodes⁴⁰. According to the characterization data, NZF/Cs had bandgap energies of 2.36-2.99 eV, pore diameters of 99.4-119.6, and specific surface areas of 109.3-128.6 m² g⁻¹. The catalytic activity of the NZF/C CEs was verified by electrochemical impedance spectroscopy and cyclic voltammetry. NZF/Cs had remarkable catalytic activity and outperformed Pt CEs in the dye-sensitized AgNP/TiO₂ DSSCs while reducing I₃. Pt CE's 2.83% efficiency was very comparable with NZF/C-1 CE's 2.75% efficiency for the natural betalain dye. With a fill factor of 50.71% and a short circuit current density of 4.13 mA cm², this efficiency was attained. During a 30-day stability test, NZF/C-1 CE was able to maintain a fill factor of 55.57% and a photon conversion efficiency of 7.18% for Z-907 synthetic dye. The high conductivity of carbon black and the strong electrocatalytic activity of

NZF are responsible for the NZF/C performance. The results show that NZF/C may be utilized in DSSCs as a workable and reasonably priced substitute for Pt⁴⁰.

2.13 Antibiotics in the Environment

Veterinary care, human medicine, and aquaculture all often employ antibiotics as a class of drugs⁴¹. When antibiotics are used, the majority eventually end up in the environment. Several nations have reported antibiotic contamination of their environments in recent years, including those in the South America (Brazil, Canada, and USA), Africa (South Africa, Kenya), Asia (China, India, and Japan), and Europe (Germany Portugal and France)⁴¹.

Among the top 20 active nations are four Asian countries, one South American country, two North American countries, one Oceanian country, eleven European countries and one African country. The number of publications regarding antibiotics in the environment rose progressively between 2011 and 2020. These results showed that the environmental presence of antibiotics has become a global problem. In addition, China has published more articles than any other nation about the prevalence of antibiotics in the environment. This may be due to the fact that China is the biggest producer, exporter, and consumer of antibiotics worldwide⁴².

2.13.1 Occurrence of Antibiotics in Waste, Surface, Sea, Ground, and Drinking Water

Aquaculture and animal husbandry, the pharmaceutical sector, hospitals, and municipal wastewaters are the main sources of antibiotics⁴³. Regularly detected in the waste waters are 21 antibiotics, including TMP, 6 FQs, 4 SAs, 4 MAs, 5 TCs, and AMX. WWTP influents or effluents can include antibiotic concentrations ranging from a few hundred ng/L to a few ten µg/L, which is a quite high concentration. The range of AMX concentrations in influents and effluents, which are 200–6, 516 ng/L and not detected (ND)–1,600 ng/L, respectively, indicates that WWTPs can remove AMX pollution. The following sequence describes the concentrations

of the different antibiotic classes in influents: For effluents, the order is SAs (ND – 12,848 ng/L) > FQs (ND – 9,347 ng/L) > TCs (ND – 2,014) > MAs (ND – 1,492 ng/L); for SAs (ND – 34,500 ng/L) > TCs (ND – 30,049 ng/L) > FQs (ND – 6,453 ng/L) > MAs (3–2,951 ng/L). Naturally, WWTPs cannot completely remove antibiotics from wastewater. Relatively high levels of SAs and TCs are found in WWTP influents as a result of the substantial use of SAs and TCs in veterinary pharmaceuticals and feed additives⁴⁴.

FQs that are most commonly found in effluents include ofloxacin (OFL, 47.4–8,637 ng/L), CIP (ND – 3,403 ng/L), NOR (36.7–9,347 ng/L), and doxycycline (DOX), which ranges from ND to 1,492 ng/L. Chlortetracycline (CTC, ND – 1,986 ng/L), oxytetracycline (OTC, 10.7–8,014 ng/L), and TC (ND – 1,536 ng/L) are the most common TCs detected in effluents. The combination of TMP and SMX is commonly used to treat bacterial infections⁴⁵. The treated effluents contain significant amounts of TMP and SMX, which are frequently found to be 12,848 ng/L and 5,316 ng/L, respectively. Additionally, a variety of degradation products, ranging from ND to 1,245 ng/L, are present in effluents. These compounds include AMX penilloic acid, ERY-H₂O, and N-acetyl SMX. Overall, the most common antibiotics found in WWTP effluents are ERY, TC, TMP, CTC, OTC, CIP, NOR, SMX, and OFL.

Antibiotic-containing wastewater will have an effect on the receiving river water. According to certain research that looked at the distribution of antibiotics in these two water phases, WWTP upstream and downstream water have higher antibiotic concentrations than upstream water. TMP, for instance, was found in downstream waters at significant concentrations (11–140 ng/L), despite being absent in downstream waters⁴⁶. Antibiotics are partially eliminated from wastewaters following treatment, as evidenced by the greater antibiotic concentrations in downstream water discharged from WWTPs compared to upstream water. Additionally, because

of the high population density and increased wastewater inputs brought on by human activity, urban rivers have higher antibiotic levels than suburban or rural ones. The GDP of a nation is connected with antibiotic contamination. Because low-income nations lack wastewater treatment facilities, their environmental antibiotic concentrations are far higher than those of high-income nations⁴⁶.

2.13.2 Antibiotics Routes of Entry into Wastewater and Its Consequences

Given that antibiotics are used to cure ailments, the sharp rise in human antibiotic use may not appear alarming⁴¹. However, excessive use of antibiotics is harmful to both people and the environment. Antibiotics have disadvantages that go beyond consumption; they also affect disposal. Usually present in wastewater, antibiotics are challenging to eliminate using standard degrading methods⁴⁴.

Due to the growing demands of the population, antibiotics are being used in domains other than medicine. Animals and veterinary care are two areas where antibiotics are used extensively. In some countries, antibiotics are used not only to treat animals but also to promote animal growth and increase productivity⁴¹. However, there won't be any appreciable antibiotic concentrations in the meat if the treatment is halted for a few days because all of the antibiotics will be completely removed from the animal's blood. However, due to their inadequate digestion, antibiotics will either be used as agricultural fertilizer or released as animal waste and disposed of in wastewater⁴¹. Few studies assess the efficacy of plants' absorption of antibiotics from fertilizers. For example, a study to measure the concentration of antibiotics in different vegetables fertilized with animal dung found that the concentrations of various antibiotics were below the detection limit, at less than 10 µg/Kg. However, this result is concerning if antibiotics are used frequently⁴¹. Further investigation revealed that the antibiotic chlortetracycline was absorbed by cabbage,

onions, and maize. However, the vegetables did not absorb the tyrosine antibiotic, even though its molecular size was vast. The findings of these studies show that various plants can absorb different antibiotics at varied rates, depending on the kind of plant and the molecular size of the antibiotic⁴⁴.

The primary problem with antibiotics in wastewater is the development of antibiotic-resistant microorganisms. Because they are so challenging to cure, antibiotic-resistant bacterial strains represent a threat to both human health and the environment. Bacterial resistance is particularly common in hospital wastewater due to the frequent and high dosages of antibiotics used. When bacterial resistance becomes a serious issue, antibiotic degradation becomes crucial. Figure 2.7 provides a summary of the many routes via which antibiotics might enter wastewater⁴¹.

2.14 Degradation and Removal Methods

Because antibiotics are frequently found in the environment and may harm the ecosystem, the present review also focuses on methods for removing and degrading them. Table 2.2 provides a summary of previous research on antibiotics and their breakdown products⁴⁷.

2.14.1 Photodegradation and Oxidization

Direct photodegradation, sensitized photodegradation, and photo-oxidation are all forms of photodegradation that can uniformly break down organic contaminants. The structure and properties of organic pollutants, temperature and pH, photosource, photocatalyst, water composition (including inorganic compounds, kinds and quantities of dissolved organic matter), and other factors all affect the photolysis process of antibiotics. For instance, protonation in aqueous solutions with varied pH values can cause certain antibiotics, such as NOR and OTC, to take on distinct forms. This may affect their absorbance and cause changes in the kinetics of photolysis⁴⁷.

FQs are sensitive to light. Because FQs can exist in cationic, zwitterionic, or anionic forms depending on the pH of the solution, pH had an effect on the direct photolysis rates of FQs. The fastest deterioration occurred under simulated sun light irradiation in neutral or slightly alkaline settings due to the predominance of zwitterionic FQs.

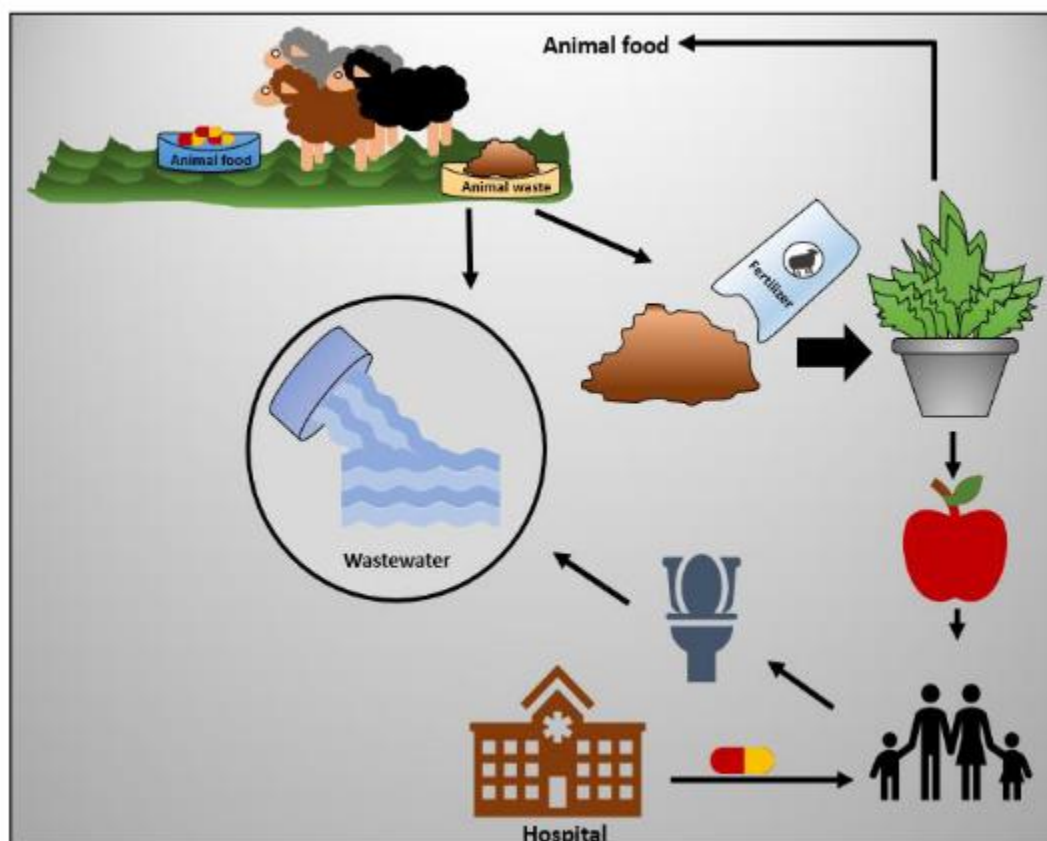


Figure 2.7: Potential pathways by which antibiotics could enter wastewater
Source⁴¹

Table 2.2: Summary of previous studies using different strategies to improve photocatalytic degradation of antibiotics

Catalysts and concentration	Light source	Antibiotic and concentration	Degradation efficiency	References
Fe, Co, Ni, Fe-Co-, and Fe-Ni-doped ZnO 0.6 g/L	300-W Xe lamp ($\lambda=365$ nm)	Oxytetracycline 20 mg/L	Approximately 87% optimum within 2h (continued	48
CQDs modified Bi_2MoO_6 1 g/L	300-W Xe lamp ($\lambda>400$ nm)	Ciprofloxacin 20 mg/L	88% optimum within 2h	49
Ti^{3+}/N co-doped TiO_2 /diatomite granule 5 g/L	150-W Xenon lamp with a UV light filter	Tetracycline 10 mg/L	92% optimum within 150 min	50
P-O co-doped $\text{g-C}_3\text{N}_4$ 1 g/L	350-W Xe lamp ($\lambda>420$ nm)	Enrofloxacin 10 mg/L	Approximately 90% within 80 min	51
$\text{Bi}^{3+}/\text{g-C}_3\text{N}_4$ 0.2 g/L	300-W Xe lamp ($\lambda>420$ nm)	Tetracycline 10 mg/L	Approximately 94% optimum within 30 min	52
Z-scheme $\text{AgI}/\text{Ag}/\text{Bi}_3\text{TaO}_7$ 0.5 g/L	300-W Xe lamp (visible light)	Sulfamethoxazole 5 mg/L	Approximately 98% optimum within 100 min	53
$\text{CuBi}_2\text{O}_4/\text{CuO}$ 1 g/L	Visible light ($\lambda>400$ nm)	Metronidazole 50 mg/L	36% optimum within 120 min	54
$\text{AgCl}/\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4$ 1 mg/L	Visible-light irradiation ($\lambda>400$ nm)	Sulfamethoxazole 50 mg/L	Approximately 100% optimum within 90 min	55

CQDs/BiOBr microspheres	1	Visible irradiation	light	Ciprofloxacin g/L	1	Approximately 65% optimum within 180 min	56
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Source: Field survey, 2024.

ENR photoproducts remained considerably active in the *Escherichia coli* DH5 α growth suppression assay, but NOR and OFL photoproducts failed. The photoproducts from ENR in Ge's investigation exhibit activity consistent with the results of Wammer's study⁴⁷. Additionally, they discovered that six fluorescent chemicals undergoing solar-mediated direct photodegradation had half-lives ranging from 0.56 to 28.8 minutes in surface waters. When exposed to radiation, photosensitizers such as humic substances (HSs) have been shown to accelerate photolysis. According to Porras's research, administering HSs and CIP together can speed up CIP's photo-decomposition in both neutral and alkaline solutions⁴⁸. In particular, the half-life of CIP ($40 \text{ min} < t_{1/2} < 60 \text{ min}$) was significantly shortened in the presence of HSs compared to CIP Al₂O₃ne ($t_{1/2} = 2 \text{ h}$). Interestingly, HSs did not affect the photodegradation pathways. The photolysis products of CIP were generated by di-hydroxylation, oxidation of the piperazine ring following defluorination, and substitution of hydroxyl (-OH) for the fluorine atom (F), all of which were derived from the parent molecule. The authors also found that, although direct photolysis only slightly decreased the anti-microbial efficacy of CIP, irradiation in the presence of humic acid (HA) led to a significant reduction in the results of both the *Staphylococcus aureus* and *Escherichia coli* inhibition experiment. The removal of FQs by photo-oxidation process can also be an effective option because the intense oxidizing radicals (like hydroxyl and sulfate radicals) generated by photolysis of oxidants (like H₂O₂, persulfate, and peroxymonosulfate) can electrophilically attack the piperazine moiety of FQs; additionally, the toxicity of FQs and obtained products decreased significantly⁴⁹.

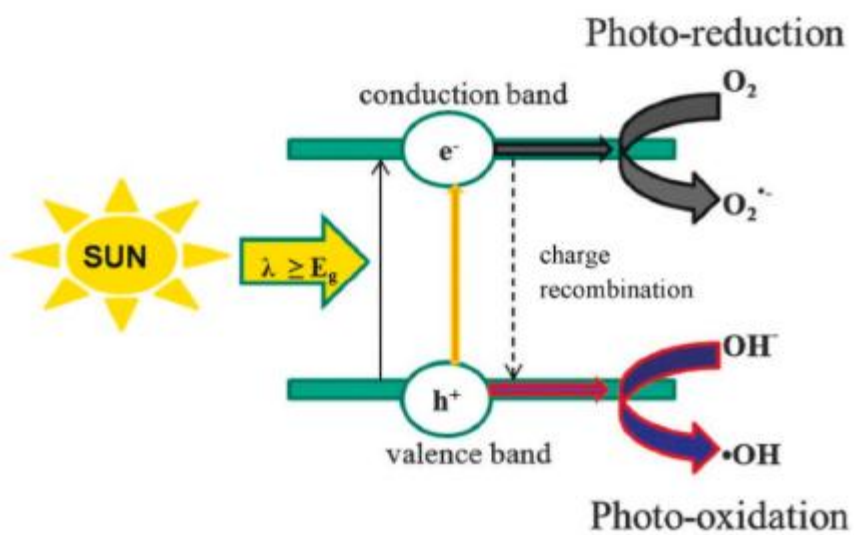


Figure 2.8: Schematic representation of the semiconductor photocatalysis process

Source⁴⁵

2.15 Fundamentals of Photodegradation

When exposed to radiation with energy higher than the optical band gap, the electrons in a semiconductor are excited and transported from the valence band (VB) to the conduction band (CB). As a result, the VB has an equal number of positively charged holes⁴⁵.

When the semiconductor's VB + potential against NHE is greater than that of $\text{H}_2\text{O}/\text{OH}$ ($+2.72\text{V vs NHE}$)₂ or $+\text{OH}/\text{OH}^-$ ($+1.89\text{V vs NHE}$), and when its CB potential against NHE is greater than that of O_2/O_2^- (-0.33 V vs NHE), it can produce $\cdot\text{OH}$ and O_2 . The photo-induced electrons and holes then separate and migrate to the surface of the semiconductor, where redox reactions occur at the reactive site (Figure 2.8).⁴⁵ These chemical reactions allow for the direct transformation and efficient utilization of solar energy. ZnSe quantum dot (QD)/g-C₃N₄ composites, for instance, were synthesized and utilized in a study to photocatalytically degrade ceftriaxone sodium; the main active ingredients were identified as OH and h^+ based on the results³⁷. However, the effects of photocatalytic activity are reduced by limited optical usage and the quick annihilation of photo-excited electron-hole pairs, which can be addressed by photocatalysts provided they meet the following criteria:

1. The proper spectrum of absorption.
2. The right band energy structure for sufficient electron-hole pair transit and separation.
3. Adsorption or reaction sites that are enough

All three of the aforementioned conditions must be satisfied in order to boost photocatalytic efficiency, and several attempts have been made to maximize photocatalytic dynamics and systematically develop photocatalysts⁵¹.

2.15.1 Origins, Manufacturing, and Enhancement of Photocatalysts

Many different types of photocatalysts have been developed to photodegrade antibiotics in aqueous solution. Because single component photocatalysts are so stable and simple to synthesize, they were used first. A variety of techniques have also been developed to improve antibiotics' visible light activity and photodegradation efficiency (Figure 2.9)⁴⁵.

2.15.1.1 Methods to Increase Activity in Visible Light

Several methods have been employed to enhance the visible light activity of photocatalysts for antibiotic degradation, namely semiconductor coupling, hydrogenation, ligand-to-metal charge transfer action, metal or non-metal doping, and the formation of perovskite structures.

These techniques can stimulate the visible light activity of wide band gap photocatalysts by sensitizing the semiconductors with narrow band gap or by narrowing the band gap by adding a new middle energy level⁴⁵.

2.15.1.3 Metal Oxides-Based Photocatalysts with Semi-conductivity

To aid in the degradation of organic pollutants such as dyes, insecticides, and polycyclic aromatic hydrocarbons (PAHs), metal oxide semiconductors have been used as pure photocatalysts, hybrids, or in conjunction with other materials⁴². Additionally, researchers have recently become more interested in and focused on the use of metal oxide-based photocatalysts for antibiotic degradation due to their excellent light absorption under UV, visible, or both, as well as their biocompatibility, safety, and stability under various conditions⁴³.

Metal oxides frequently struggle with photocatalytic activity ineffectiveness or non-absorbance⁴⁴ due to their high band gap and fast electron-hole pair recombination. For example, TiO_2 is the most often utilized metal oxide for photocatalysis because of its advantageous optical and electrical properties, chemical stability and reusability, non-toxicity, and reasonable cost

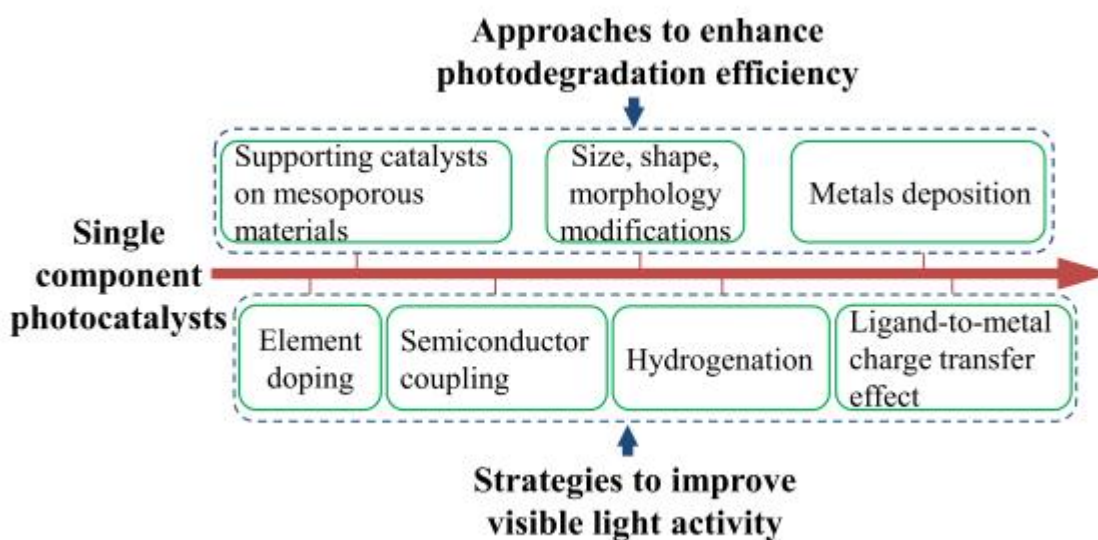


Figure 2.9: Different methods for improving the photodegradation efficiency and visible light activity of single component photocatalysts for the photodegradation of antibiotics.

Source⁴⁵

When compared to TiO_2 , ZnO is another semiconducting material that shows stronger photocatalytic performance and improved quantum efficiency. This is particularly true when ZnO is used at a neutral pH for photocatalytic antibiotic breakdown. However, because of its high rate of electron-hole pair recombination, ZnO cannot be completely used without functionalization. Numerous investigations have shown that doping ZnO with metals like Ag and Fe or non-metals like N and C enhanced the activity of photocatalytic antibiotic degradation^{45,46}. WO_3 is another interesting metal oxide that has attracted a lot of attention due to its abundance, affordability, and lack of toxicity. Furthermore, $\text{W}_{18}\text{O}_{49}$ was believed to have a higher photocatalytic degradation efficiency than WO_3 , making it a superior photocatalyst. It is oxidizable to WO_3 in spite of its great photocatalytic effectiveness. It is possible to develop a hybrid of $\text{W}_{18}\text{O}_{49}$ and other metal oxides to overcome this oxidation barrier⁴⁷.

2.16 Factors Influencing Antibiotics in Photodegradation

Several factors, some of which will be discussed in this section, can significantly impact the photocatalytic degradation of antibiotics.

2.16.1 Light Wavelength

There is a clear correlation between the wavelength of the light and the photocatalyst's capacity to be activated by it. An investigation revealed that sulfanilamide calcified and decomposed more effectively when exposed to LED white and blue light than when exposed to LED green

and yellow light⁵⁷. This was explained by the fact that photographs with higher energy may be created by shorter light wavelengths, which increases the number of $e^- h^+$ pairs that are formed by photos. These findings were found in a study on the photocatalytic degradation of aqueous ciprofloxacin and moxifloxacin under UV-A and UV-C light irradiations; however, excessively high energy photon light may cause light waste, so it can be concluded that the wavelength of light influences the photocatalytic breakdown efficiency of antibiotics⁵⁷.

2.16.2 Size, Morphology, Size and Dosage of Photocatalysts

As was previously mentioned, the electrical and optical properties of photocatalysts, as well as the effectiveness of antibiotic adsorption when isolated from photogenerated charges, can be influenced by their size, shape, and morphology. These components are therefore essential to the photodegradation of antibiotics. A research synthesized polymeric carbon nitride foam with a high surface area and a mesoporous structure for the photodegradation of tetracycline hydrochloride⁵⁷. The substantial photocatalytic activity was responsible for the large specific surface area, increased availability of exposed active sites, enhanced conveyance, and enhanced separation efficiency of the photogenerated charges. Nanomaterials were also designed to promote the photodegradation efficiency of antibiotics due to their large specific surface area, which can increase the antibiotics' adsorption capacity and light absorption. However, simple aggregation will limit the service life of these materials⁵⁷. Antibiotic photodegradation efficiency can also be significantly influenced by the amount of photocatalyst used; specifically, the addition of more catalyst to the mixture increases the number of active sites, which in turn increases the number of reaction sites and light absorption, improving the production of active species and increasing the efficiency of antibiotic photodegradation⁵⁷. However, an excessive catalyst dosage can lead to several issues:

1. Blocking some of the photosensitive surface and making the solution more turbid, which prevents light from penetrating.
2. Increasing the catalyst surface's ability to reflect light.
3. Speeding up the catalyst particles' agglomeration, which reduces light absorption and antibiotic adsorption while preventing more light penetration. These elements reduce the effectiveness of antibiotic photodegradation⁵⁷.

2.16.3 Antibiotics Concentration

Antibiotic concentration has been demonstrated to significantly affect photodegradation efficiency⁵⁷. More active sites on the photocatalyst are occupied, and more light is absorbed by antibiotic molecules as a result of rising antibiotic concentrations. For antibiotic photodegradation, these two effects lower the amount of photons absorbed by the catalyst and, consequently, the generation of reactive species⁵⁷. The production of more organic intermediates and end products may also hinder the photocatalytic breakdown of antibiotics by competing with the parent antibiotic molecules for the catalyst's few adsorption and photocatalytic sites. The photocatalytic degradation of the antibiotic sulfamethoxazole by the UV-A/TiO₂ combination likewise showed a similar effect. An increase in antibiotic concentration usually has a negative impact on their photocatalytic degradation because more intermediates and end products compete with one another for adsorption and photocatalytic sites on the catalyst surface⁵⁷.



2.16.4 Solution pH

The different charges that the surfaces of photocatalysts and antibiotic molecules may have under different pH settings affect the adsorption of antibiotics onto the surface of photocatalysts

and the accompanying photodegradation efficiency⁵⁷. For instance, the tricarbonyl system, phenolic diketone moiety, and dimethylammonium group make tetracycline an amphoteric molecule. Consequently, it has pKa values of 3.3, 7.68, and 9.7. 6.25 is TiO₂'s point of zero charge (pzc). At pH values below 3.3, tetracycline and TiO₂ both show positive charge, which has the repelling effect of preventing the antibiotics from sticking to the TiO₂ surface and further reducing the photocatalytic efficiency.

At pH >7.68, their negative charge also makes the repelling action stronger; at pH >9.7, the double negative charge of tetracycline will increase this effect. Neutral pH would be a preferable environment for the degradation process because photocatalytic efficiency for tetracycline degradation over TiO₂ is weak in acidic and alkaline settings. Similar results have also been reported for the photodegradation of ciprofloxacin and sulfamethoxazole 98, 99. Nevertheless, a study found that the optimal norfloxacin degradation occurred at pH >10.5, when negative charges were present in both Bi₂WO₆ and norfloxacin⁵⁷. It may be explained by a greater concentration of OH serving as a source of OH, which can increase OH concentration and improve antibiotic breakdown. Furthermore, the present form of the photocatalyst may be affected by pH. At pH levels close to pH_{pzc}, RGO-WO₃ composites showed fast precipitation and particle agglomerations. Poor dispersion and particle agglomeration development would significantly hinder the photocatalytic activity, lowering the reactive sites of the photocatalyst and perhaps reducing antibiotic adsorption and light absorption⁵⁷. In summary, a number of antibiotic classes (including sulphonamide, simidazoles, quinolones, tetracyclines, and >β-lactams) are affected by pH in terms of their adsorption and photodegradation over photocatalysts.

Endnotes

1. G. Mutezo, & J. Mulopo. *A review of Africa's transition from fossil fuels to renewable energy using circular economy principles*. **Renewable and Sustainable Energy Reviews**, 137, 2021, 110609.
2. K. Nwaigwe, P. Mutabilwa, & E. Dintwa. *An overview of solar power (PV systems) integration into electricity grids*. **Materials Science for Energy Technologies**, 2, 2019, 629-633.
3. S.M. Jowitt, G.M. Mudd, & J.F.H. Thompson. *Future availability of non-renewable metal resources and the influence of environmental, social, and governance conflicts on metal production*. **Communications Earth & Environment**, 1, 2020, 13.
4. A. K. Pandey, & M. Samykano. *Solar energy: direct and indirect methods to harvest usable energy, in Dye-sensitized solar cells*. **Academic Press, Massachusetts, United States**, 2022, 1-24.
5. T. F. Yadeta, & T. Imae. *Effect of carbon dot on photovoltaic performance of n-TiO₂/p-NiO and n-TiO₂/p-CuO heterojunctions in dye-sensitized solar cells*. **Applied Surface Science**, 2023, 157880.
6. M.M.A. Moon, M. Rahman, J. Hossain, & A.B.M. Ismail. *Comparative study of the second generation a-Si:H, CdTe, and CIGS thin-film solar cells*. **Advanced Materials Research**, 1154, 2019, 102-111.
7. N. A. Tegegne, & F. G. Hone. *Solar cell technology: challenges and progress, in Electrode materials for energy storage and conversion*. **CRC Press, Boca Raton, United states**, 2020, 437-471.
8. A.F. Kamil, H. I. Abdullah, A. M. Rheima, & S. H. Mohammed. *Impact of Fe₂NiO₄ nanoparticles to increase efficiency of dye-sensitized solar cells*. **Materials Today: Proceedings**, 49, 2022, 2727-2732.
9. P. Suman, Sharma, P. & P. Goyal. *Evolution of PV technology from conventional to nano-materials*. **Materials Today: Proceeding**, 28, 2020, 1593-1597.

10. J. Ali, S. Bibi, W. B. Jatoy, M. Tuzen, M. A. Jakhrani, X. Feng, & T. A. Saleh. *Green synthesized zinc oxide nanostructures and their applications in dye-sensitized solar cells and photocatalysis: A review*. **Materials Today Communications**, 2023, 106840.
11. A. F. Kamil, H. I. Abdullah, A. M. Rheima, S. H. Mohammed, S. J. Tumaa, & R. M. Abed. *Fabrication of Fe_2CuO_4 nanoparticles via photolysis technique for improved performance in dye-sensitized solar cells*. **Digest Journal of Nanomaterials & Biostructures (DJNB)**, 2021, 16, 4.
12. M. Memari, & N. Memarian. *Designed structure of bilayer $TiO_2-Nb_2O_5$ photoanode for increasing the performance of dye-sensitized solar cells*. **Journal of Materials Science: Materials in Electronics**, 31, 2020, 2298-2307.
13. M. Imran, A. Abutaleb, M. A. Ali, T. Ahamad, A. Ansari, M. Shariq, & A. Khan. *UV light enabled photocatalytic activity of $\alpha-Fe_2O_3$ nanoparticles synthesized via phase transformation*. **Materials Letters**, 258, 2020, 126748.
14. T. Zahid, N. Arshed, M. Munir, & K. Hameed. *Role of energy consumption preferences on human development: a study of SAARC region*. **Economic Change and Restructuring**, 54, 2021, 121-144.
15. S.S. Thakar, K.R. Jha, Y. Phasinam, Y. Qureshi, & V.H. Babu. *X ray diffraction analysis and evaluation of antioxidant activity of copper oxide nanoparticles synthesized from leaf extract of *Cissus vitiginea**. **Mater. Today Proc.** 2021.
16. B. Arumugam, T. Manaharan, C.K. Heng, U.R. Kuppusamy, & U.D. Palanisamy. *Antioxidant and antiglycemic potentials of a standardized extract of *Syzygium malaccense**. **LWT-Food Sci. Technol.** 59, 2, 2014, 707–712.
17. F.I. Oliveira, M.I. Gallão, S. Rodrigues, & F.A.N. Fernandes. *Dehydration of Malay apple (*Syzygium malaccense* L.) using ultra- sound as pre-treatment*. **Food Bioprocess Technol.** 4, 4, 2011, 610–615.
18. Â.G. Batista, M.C. Mendonça, E.S. Soares, J.K. da Silva-Maia, A.P. Dionísio, C.R. Sartori, M.A. da Cruz-Höfling, & M.R. Júnior. **Syzygium malaccense* fruit supplementation protects mice brain against high-fat diet impairment and improves cognitive functions*. **J. Funct. Foods**, 65, 2020, 103745.
19. S. Akin. *Boosting the efficiency and stability of perovskite solar cells through facile molecular engineering approaches*. **Sol Energy**, 199, 2020, 136–142.

20. F. Borousan, R. Yousefi, & P. Shabani. *Tuning the size of PbSe nanocubes for solar-cell applications*. **Mater Lett**, 268, 2020, 127590.
21. A. Naganthran, G. Verasoundarapandian, F.E. Khalid, M.J. Masarudin, A. Zulkharnain, N.M., Nawawi, & S.A. Ahmad. *Synthesis, characterization and biomedical application of silver nanoparticles*. **Materials**, 15, 2, 2022, 427.
22. S.J. Begum, S. Pratibha, J.M. Rawat, D. Venugopal, P. Sahu, A. Gowda, & M. Jaremko. *Recent advances in green synthesis, characterization, and applications of bioactive metallic nanoparticles*. **Pharmaceuticals**, 15, 4, 2022, 455.
23. M. Olga, M. Jana, M. Anna, K. Irena, M. Jan, C. & C. Alena. *Antimicrobial properties and applications of metal nanoparticles biosynthesized by green methods*. **Biotechnol Adv**, 2022, 107905.
24. B. Guan, J. Yu, S. Guo, S. Yu, & S. Han. *Porous nickel doped titanium dioxide nanoparticles with improved visible light photocatalytic activity*. **Nanoscale Adv**, 2, 2020, 1352–1357.
25. S. Vijayaram, H. Razafindralambo, Y.Z. Sun, S. Vasantharaj, H. Ghafarifarsani, S.H. Hoseinifar, & M. Raeeszadeh. *Applications of green synthesized metal nanoparticles: a review*. **Biological Trace Element Research**, 202, 1, 2024, 360-386.
26. M. Agha, M. El-Kemary, A. H. Oraby, & E. Salim. *Efficient multilayers organic solar cells with hybrid interfacial layer-based P3HT and CuO nanoparticles*. **Journal of Inorganic and Organometallic Polymers and Materials**, 34, 2, 2024, 557-564.
27. A. Zatirostami. *Fabrication of dye-sensitized solar cells based on the composite TiO₂ nanoparticles/ZnO nanorods: investigating the role of photoanode porosity*. **Materials Today Communications**, 26, 2021, 102033.
28. K. Valadi, S. Gharibi, R. Taheri-Ledari, S. Akin, A. Maleki, & A. E. Shalan. *Metal oxide electron transport materials for perovskite solar cells: a review*. *Environmental Chemistry Letters*, 19, 3, 2021, 2185-2207.
29. S. Thambidurai, P. Gowthaman, M. Venkatachalam, S. Suresh, & M. Kandasamy. *Morphology dependent photovoltaic performance of zinc oxide-cobalt oxide nanoparticle/nanorod composites synthesized by simple chemical co-precipitation method*. **Journal of Alloys and Compounds**, 852, 2021, 156997.
30. Z. K. Yildiz, A. Atilgan, A. Atli, K. Ozel, C. Altinkaya, & A. Yildiz. *Enhancement of efficiency of natural and organic dye sensitized solar cells using thin film TiO₂*

- photoanodes fabricated by spin-coating. Journal of Photochemistry and Photobiology A: Chemistry*, 368, 2019, 23-29.
31. H. M. Aung Kyaw, K. A. Yaacob, A. F. Mohd Noor, A. Matsuda, & G. Kawamura. *Effect of deposition time CdSe-TiO₂ nanocomposite film by electrophoretic deposition for quantum dot sensitized solar cell. Materials Today: Proceedings*, 17, 2019, 736-742.
 32. D. Cao, H. Yin, X. Yu, J. Zhang, Y. Jiao, W. Zheng, B. Mi, & Z. Gao. *Role of modifying photoanodes by organic titanium on charge collection efficiency enhancement in dye-sensitized solar cells. Advanced Engineering Materials*, 22, 2019, 1901071.
 33. M. R. Al-bahrani, W. Ahmad, H. F. Mehnane, Y. Chen, Z. Cheng, & Y. Gao. *Enhanced electrocatalytic activity by rGO/MWCNTs/NiO counter electrode for dye-sensitized solar cells. Nano-Micro Letters*, 7, 2015, 298-306.
 34. M. Kouhnavard, N. A. Ludin, B. V. Ghaffari, S. Ikeda, K. Sopian, & M. Miyake. *Hydrophilic carbon/TiO₂ colloid composite: a potential counter electrode for dye-sensitized solar cells. Journal of Applied Electrochemistry*, 46, 2016, 259-266.
 35. J. P. Sawant, & R. B. Kale. *CZTS counter electrode in dye-sensitized solar cell: enhancement in photo conversion efficiency with morphology of TiO₂ nanostructured thin films. Journal of Solid State Electrochemistry*, 24, 2020, 461-472.
 36. A. A. Qureshi, S. Javed, H. M. Asif Javed, A. Akram, M. Jamshaid, & A. Shaheen. *Strategic design of Cu/TiO₂-based photoanode and rGO-Fe₃O₄-based counter electrode for optimized plasmonic dye-sensitized solar cells. Optical Materials*, 2020, 109.
 37. H. I. Abdulah, A. M. Rheima, D. H. Hussain, & H. J. Abed. *Synthesis of Fe₂O₃ nanoparticles by photolysis method for novel dye-sensitized solar cell. Journal of Advanced Sciences and Nanotechnology*, 1, 1, 2022, 1-8.
 38. M. Gomathi, A. Sankar, S. Kannan, M. Shkir, & V. R. M. Reddy. *Tin selenide/carbon black nanocomposite-based high efficiency counter electrode for dye-sensitized solar cells (DSSCs). Chemical Physics Letters*, 802, 2022, 139802.
 39. S. Rafique, I. Rashid, & R. Sharif. *Cost effective dye sensitized solar cell based on novel Cu polypyrrole multiwall carbon nanotubes nanocomposites counter electrode. Scientific Reports*, 11, 1, 2021, 14830.
 40. A. A. Oladipo, & M. Gazi. *Ternary Ni_{0.5}Zn_{0.5}Fe₂O₄/carbon nanocomposite as counter electrode for natural dye-sensitized solar cells: Electro-photovoltaic characterizations. Journal of Photochemistry and Photobiology A: Chemistry*, 425, 2022, 113665.

41. D. Jassby, T.Y. Cath, & H. Buisson. *The role of nanotechnology in industrial water treatment*. **Nat. Nanotechnol.** 13, 2018, 670–672.
42. B. Deshpande, P. Agrawal, M. Yenkie, & S. Dhoble. *Prospective of nanotechnology in degradation of waste water: A new challenges*. **Nano-Struct. Nano-Objects**, 22, 2020, 100442.
43. F. Ahmadi, A.A. Zinatizadeh, A. Asadi, T. McKay, & S. Azizi. *Simultaneous carbon and nutrients removal and PHA production in a novel single air lift bioreactor treating an industrial wastewater*. **Environ. Technol. Innov.** 18, 2020, 100776.
44. E.F. Aboelfetoh, M.E.Z. Elabedien, & E.Z.M. Ebeid. *Effective treatment of industrial wastewater applying SBA-15 mesoporous silica modified with graphene oxide and hematite nanoparticles*. **J. Environ. Chem. Eng.** 9, 2021, 104817.
45. F. Sher, K. Hanif, S.Z. Iqbal, & M. Imran. *Implications of advanced wastewater treatment: Electrocoagulation and electroflocculation of effluent discharged from a wastewater treatment plant*. **J. Water Process Eng.** 33, 2020, 101101.
46. T. Runguphan, & J. Kitpichai. *Coaction of bio-sorption and bio-filtration for the remediation of domestic and agricultural wastewater contaminated with heavy metal*. **IOP Conf. Ser. Mater. Sci. Eng.** 965, 2020, 012010.
47. A. Kalfa, B. Shapira, A. Shopin, I. Cohen, E. Avraham, & D. Aurbach. *Capacitive deionization for wastewater treatment: Opportunities and challenges*. **Chemosphere**, 241, 2020, 125003.
48. J. Guo, Y. Li, D. Hu, & H. Liu. *Preparation of transition-metal-doped ZnO nano-photocatalysts and their performance on photocatalytic degradation of antibiotic wastewater*. **Desalin. Water Treat.** 2014, 1–8.
49. J. Di, J. Xia, M. Ji, H. Li, H. Xu, H. Li, R. Chen. *The synergistic role of carbon quantum dots for the improved photocatalytic performance of Bi₂MoO₆*. **Nanoscale** 7, 2015, 11433–11443.
50. S. Chang, X. Yang, Y. Sang, & H. Liu. *Highly efficient photocatalysts and continuous-flow photocatalytic reactors for degradation of organic pollutants in wastewater*. **Chem Asian J** 11, 2016, 2352–2371
51. J. Huang, D. Li, R. Li, Q. Zhang, T. Chen, H. Liu, Y. Liu, W. Lv, & G. Liu. *An efficient metal-free phosphorus and oxygen co-doped g-C₃N₄ photocatalyst with enhanced visible*

light photocatalytic activity for the degradation of fluoroquinolone antibiotics. Chem. Eng. J. 374, 2019, 242–253.

52. M. Wang, C. Jin, Z. Li, M. You, Y. Zhang, & T. Zhu. *The effects of bismuth (III) doping and ultrathin nanosheets construction on the photocatalytic performance of graphitic carbon nitride for antibiotic degradation. J. Colloid Interface Sci.* 533, 2019, 513–525.
53. M. Ren, J. Chen, P. Wang, J. Hou, J. Qian, C. Wang, & Y. Ao. *Construction of silver iodide/silver/Bismuth Tantalate Z-scheme photocatalyst for effective visible light degradation of organic pollutants. J. Colloid Interface Sci.* 532, 2018, 190–200.
54. A.C. Nogueira, L.E. Gomes, J.A.P. Ferencz, J.E.F.S. Rodrigues, R.V. Gonçalves, & H. Wender. *Improved visible light photoactivity of CuBi₂O₄/CuO heterojunctions for photodegradation of methylene blue and metronidazole. The Journal of Physical Chemistry C*, 123, 2019, 25680–25690.
55. L. Zhou, W. Zhang, L. Chen, H. Deng, & J. Wan. *A novel ternary visible-light-driven photocatalyst AgCl/Ag₃PO₄/g-C₃N₄: Synthesis, characterization, photocatalytic activity for antibiotic degradation and mechanism analysis. Catal. Commun.* 100, 2017, 191–195.
56. Z. Liang, J. Yang, C. Zhou, Q. Mo, & Y. Zhang. *Carbon quantum dots modified BiOBr microspheres with enhanced visible light photocatalytic performance. Inorg. Chem. Commun.* 90, 2018, 97–100.
57. X. Yang, Z. Chen, W. Zhao, C. Liu, X. Qian, M. Zhang, & Y.S. Ok. *Recent advances in photodegradation of antibiotic residues in water. Chemical Engineering Journal*, 405, 2021, 126806.

Chapter Three

Methodology

3.1 Materials and Chemical Used

3.1.1 Materials

The leaves of the *Syzygium malaccense* (Malay Apple), which are obtained from Covenant University in Ota, Ogun State, was primarily used for the environmentally friendly production of nanoparticles. The leaves of the *Syzygium malaccense* (Malay Apple) was identified by University of Ibadan, Botanical Department with identification number of UIH-23559.

3.1.2 Chemical/Reagents Used

All of the reagents, chemicals, and solvents utilized in the synthesis was used exactly as supplied, without any additional purification, regardless of their origins, purity, or grade. Water from a double-distilled machine will be utilized for the synthesis. Distilled water, 97% iron (III) chloride (Sigma Aldrich), 97% copper oxide (Sigma Aldrich), 95% ethanol (Sigma Aldrich), argon gas, chlorine, acetylacetone (MERCK), titanium (IV) chloride, acetonitrile (Aldrich), and neomycin.

3.1.3 Apparatus/Instruments Used

The instruments are Stuart hot plate and stirrer (Magnetic stirrer), heater, Thermometer, Gallen Kamp moisture extraction oven, Glassware (Beaker, conical flask, measuring cylinder, standard flask, round bottom flask), Digital Balance BL3001, Spatula, Crucible, Samples bottles, UV-Visible spectroscopy (Spectrumlab 752), SEM (JSM-7800), X-Ray diffraction (XRD 4154),

FTIR (630 FT-IR), Solar Simulator (Newport Oriel, instrument model 65194A - 100 solar simulator), UV light, UV spectrophotometer, desiccator, etching machine, and glass cutter.

3.2 Methods

3.2.1 Preparation of *Syzygium malaccense* (Malay Apple) Leaf Extract

A green synthesis method was adopted to synthesize the Al_2O_3 nanoparticles, CuO nanoparticles, and ZnO nanoparticles. The *Syzygium malaccense* (Malay Apple) leaves were collected locally at Covenant University, Ota, Nigeria. The reason for plant biosynthesis is that they are reported to contain organic products that can serve as both reducing and capping agents such as flavonoids, and extracellular electron shuttles which could play important roles in the biosynthesis of metallic nanoparticles. The leaves were newly gathered, rinsed with deionized water, air-dried, and powdered individually into a fine powder. 100 grams of the dried fine powder was boiled in 500 ml of distilled water in a 1000 ml flask for 30 minutes, and the extract was filtered using Whatman No. 1 filter paper.

3.2.2 Synthesis of Aluminum Oxide (Al_2O_3) Nanoparticles

Using plant leaf extracts from the Malay apple (*Syzygium malaccense*), aluminum oxide nanoparticles have been successfully developed. To produce a complex formation, extract was added progressively in a 2:4 ratio to the solution of IM of aluminum sulphate octadecahydrate while being stirred magnetically at 50 °C for approximately two hours. The complex that formed at 4500 rpm for 15 minutes was separated using centrifugation. After being washed with distilled water, the complex was centrifuged for ten minutes at 4500 rpm. After being dried for eight hours at 40 °C, the isolated complex was calcined at 450 °C in a muffle furnace.



Figure 3.1: Photograph of *Syzygium malaccense* (Malay apple) leaves

Source: Field Survey, 2025

3.2.3 Synthesis of Copper oxide (CuO) Nanoparticles

The synthesis of copper oxide nanoparticles was successfully accomplished using plant leaf extracts from *Syzygium malaccense*, or the Malay apple. To achieve a complex formation, extract was added progressively in a 2:4 ratio to a solution of 1M copper sulphate heptahydrate under magnetic stirring for approximately 4 hours at 80 °C. The complex that formed at 4500 rpm for 15 minutes will be separated by centrifugation. After being washed with distilled water, the complex was centrifuged for ten minutes at 4500 rpm. Following hours of drying at 40 °C, the isolated complex was calcined at 450 °C in a muffle furnace.

3.2.4 Synthesis of Zinc oxide (ZnO) Nanoparticles

Effective production of zinc oxide nanoparticles was achieved using plant leaf extracts of *Syzygium malaccense* (Malay apple). For approximately four hours, extract was added progressively in a 2:4 ratio to a solution of 1M zinc sulphate heptahydrate under magnetic stirring at 80 °C to create a complex formation. After 15 minutes at 4500 rpm, the complex was separated using centrifugation. The complex that had formed was then centrifuged for 10 minutes at 4500 rpm after being washed with distilled water. After drying at 40 °C for several hours, the isolated complex was calcined at 450 °C in a muffle furnace.



Figure 3.2: Synthesis of Al_2O_3 , CuO , and ZnO biosynthesized nanoparticles

Source: Field Survey, 2025

3.3 Characterization Techniques of the Bio-synthesized Nanoparticles

3.3.1 Optical Properties Measured by UV-VIS Spectroscopy

The extract and nanoparticles' UV-visible absorption spectra was examined using a Spectrumlab 752 single-beam ultraviolet-visible (UV-vis) spectrometer, which operates at room temperature in the 200–800 nm range. The samples was ultrasonically dispersed in deionized water for the optical property study, and the solution was then poured into quartz cuvettes for the measurement¹. Additionally, a Tauc plot which plots a graph of $(\alpha h\nu)^2$ versus $h\nu$ using Tauc's equation was used to determine the band gap energy of the catalysts.

Tauc's equation: $(\alpha h\nu)^n = A(h\nu - E_g)$

Where $\alpha = 2.302A$

A = absorbance

h = Planck's constant

ν = frequency of light absorbed.

3.3.2 FT-IR for surface chemistry analysis

The pellet will be positioned beneath the pinhole location, and the holder will be used to press the particle so that the IR beam can pass through it². The primary goal of analyzing the FT-IR spectrum is to determine the chemical bonding and interaction within the nanoparticles. FT-IR spectroscopy studies of the nanoparticles will be carried out using Agilent Technologies Cary 630 FT-IR, with scanning spectra recorded in the range of 400 to 4000 cm^{-1} .

3.3.3 Determination of the Crystalline Structure by XRD

One of the most important methods for figuring out a material's crystalline structures and phase composition is X-ray diffraction (XRD). In this study, XRD 4154 with monochromatized Cu K α radiation and wavelength $\lambda = 1.5418 \text{ \AA}$ will be used to investigate the solid powder's XRD pattern. The system covered a 2θ range of 10° to 80° at a scanning rate of 0.02° per second. The diffraction peak's sharpness relates to its crystal structure; crystalline structures have sharp peaks, whereas amorphous structures have wide peaks. JCPDS is a non-profit scientific organization that collects, edits, publishes, and disseminates powder diffraction data to identify inorganic and organic compounds with a crystal structure. Additionally, the Miller index, diffraction peak position, and relative intensity of unknown materials can be ascertained by comparing the diffraction data with the diffraction pattern from the Joint Committee on Powder Diffraction Standard (JCPDS)^{2,3}.

3.3.4 SEM-EDX analysis

A high-resolution field emission scanning electron microscope was used to examine the nanoparticles' surface characteristics and size or form³. SEM was used to capture the pictures for this study (JSM-7800). This model's field emission gun electron source produces enough current to allow imaging with a resolution of up to 3 nm and a magnification of up to 250,000. Every nanoparticle that will be evaluated will be in powder form.

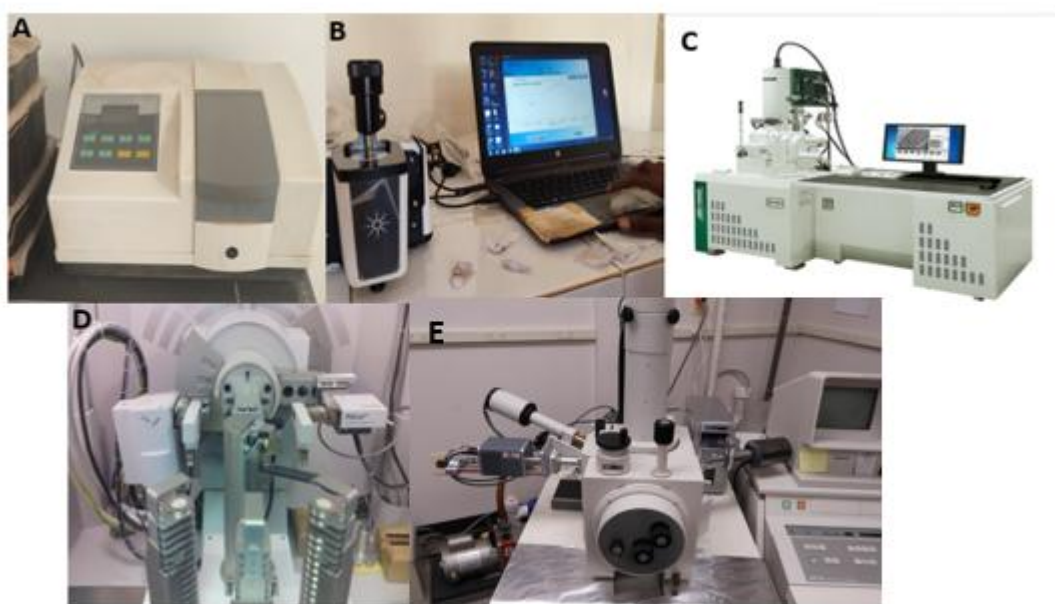


Figure 3.3: Nanoparticles Characterization Instrumentation (A) UV Spectroscopy (B) FT-IR (C) FE-SEM (D) XRD (E) EDX
Source: Field Survey, 2025

3.4 Fabrication of Monolithic DSSC

FTO glass plates (TEC-15, Nippon Sheet Glass Co., Ltd., Japan) were employed in the fabrication of monolithic electrodes. The FTO substrate underwent preliminary cleaning through the application of propanol followed by drying in a spin coater (Labscience model 800) operating at 3000 rpm. To synthesize mesoporous TiO_2 , Ti-Nanoxide was deposited via screen printing and subsequently subjected to annealing for a duration of 30 minutes at 450°C . Following the treatment of the mesoporous films with a 70 mM solution of TiCl_4 for 30 minutes at 70°C , the films were rinsed with water and then annealed for an additional 30 minutes at 500°C . ZrO_2 paste was subsequently applied to the TiO_2 layer to encapsulate the porous TiO_2 layer once the substrate had cooled. Thereafter, the ZrO_2 paste was annealed for 30 minutes at 450°C to yield the Al_2O_3 , CuO , and ZnO layers. A screen printer equipped with a 70 mesh screen was utilized for all screen printing operations. The Al_2O_3 , CuO , and ZnO paste was formulated using Al_2O_3 , CuO , and ZnO nanoparticles ($d=40\text{--}50\text{ nm}$; Fulka, USA) in accordance with a previously established methodology⁴. Following the cooling of the substrate, doctor blading was employed to deposit the Al_2O_3 , CuO , and ZnO layers utilizing carbon conductive paste (Elcocarb solaronix) as the back contact. The carbon layer was concurrently connected to the secondary FTO layer. A dye solution comprising chlorine dissolved in toluene was applied to the cell stack, which was subsequently allowed to remain at ambient temperature for an entire night. The dye-adsorbed photoanode was removed from the solution, rinsed with toluene, and permitted to dry in the dark on a hot plate maintained at 60°C . The glass plates and dye-coated electrodes were bonded by heating a hot-melted adhesive film ($150\text{ }\mu\text{m}$ thick; Bynel 4164, DuPont, USA) to 250°C for one minute, followed by an increase in temperature to 80°C while the electrodes remained on the hot

plate. To construct the final cell, a droplet of the electrolyte solution, specifically a 0.05 M solution of CuI dissolved in acetonitrile, was introduced by drop casting into a perforation drilled into the glass of the assembled cell, which was subsequently sealed with 0.1 mm thick aluminum foil. The electrolyte, provided by Solaronix, is utilized in dye-sensitized solar cells (DSCCs) exhibiting exceptional durability⁵.

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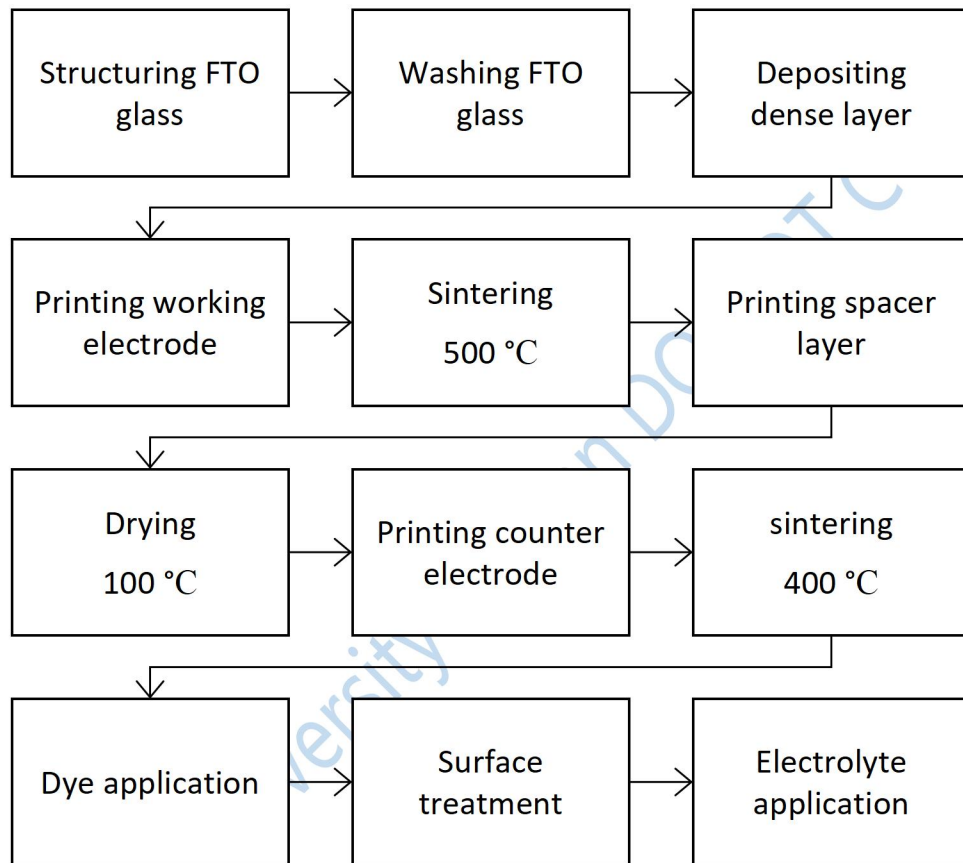


Figure 3.4: Fabrication process steps for Monolithic DSSC.

Source: Field Survey, 2025

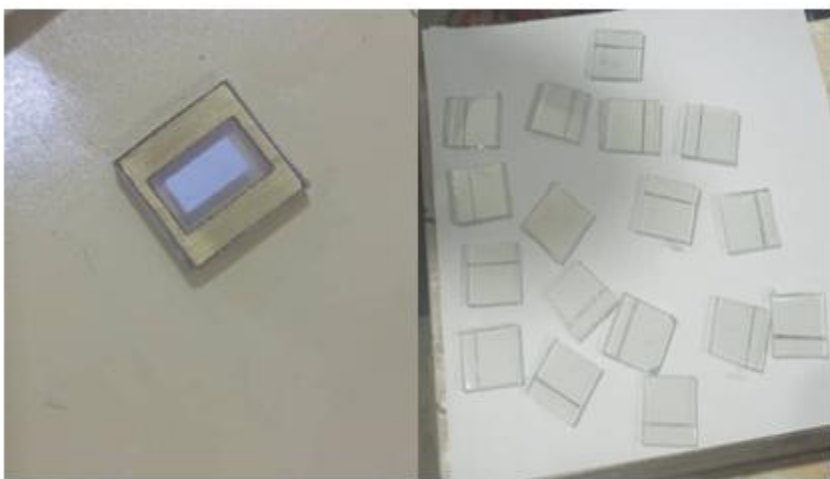


Figure 3.5: Fabricated DSSCs using Al_2O_3 , CuO , and ZnO biosynthesized nanoparticles

Source: Field Survey, 2025

3.6 Photocurrent Voltage Behaviors of the DSSCs

Utilizing a solar simulator (Newport Oriel, instrument model 65194A-100 solar simulator) at $100\text{mW}/\text{cm}^2$ in conjunction with a source measure unit Kethley Model 2400 source meter, the current-voltage characteristics was performed in order to analyze the photovoltaic properties of the cells. The characterization was take place at Namiroth Nigeria Limited in Abuja. The measurements was carried out in a lighted environment at room temperature. Every cell was have an active area of $0.5 \times 0.5 \text{ cm}^2$. Furthermore, the solar cell's capacity to generate electricity was evaluated using:

$$= \frac{P_{max}}{P_{in}} = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}} * 100 \quad 3.1$$

Where V_{oc} , J_{sc} , P_{in} represent the open-circuit photo-voltage, the short-circuit density photocurrent and the incident light power respectively. Furthermore, the fill factor is given by

$$FF = \frac{V_{max} \times J_{max}}{V_{oc} \times J_{sc}} \quad 3.2$$

Where; V_{max} and J_{max} represent the voltage and the current density at the maximum output power point respectively, while the efficiency is given by;

$$\text{Efficiency} = \frac{I_m \times V_m}{\text{Input photon power}} \times 100\% = \frac{I_{sc} \times V_{oc} \times FF}{\text{Input Photon Power}} \times 100\% \quad 3.3$$

3.4 Photodegradation Experiment

1, 2, 3, and 5 ppm of the antibiotic were prepared from 100 ppm stock solution. Using a UV–vis absorption spectrometer, 5 ppm was employed for scanning at 150–400 nm. The measured absorbance of 1, 2, 3, and 5 ppm was used to prepare the calibration plot.

The photodegradation of the antibiotics was carried out for 120 minutes in order to determine the photocatalytic activity of the catalyst. 0.3 g of the catalyst was added to 50 mL (10 ppm) of the antibiotics. The solutions were continuously stirred using a magnetic stirrer while being kept in the dark in order to achieve the absorption-desorption equilibrium. The photodegradation experiment was conducted under UV light for varying durations of 20, 40, 60, 80, 100, and 120 minutes while being continuously stirred. Every 20 minutes, 5 mL aliquots from each beaker were taken, and the photocatalyst was extracted by centrifuging the aliquots.

Using a UV–vis absorption spectrometer, the amount of antibiotics in each sample was measured.

The following formula was used to determine the degradation percentage:

$$\text{Removal efficiency (\%)} = \frac{C_o - C_t}{C_o} \times 100 \quad 3.4$$

Where C_o is the initial dye concentration, and C_t is the concentration of antibiotics at time t .



Figure 3.6: Photocatalytic degradation of antibiotics using UV-light

Source: Author's Field Work, 2025



Figure 3.7: Centrifuging reaction after photodegradation to extract the biosynthesized nanoparticles.

Source: Author's Field Work, 2025

Endnotes

1. M. Memari, & N. Memarian. *Designed structure of bilayer $\text{TiO}_2\text{-Nb}_2\text{O}_5$ photoanode for increasing the performance of dye-sensitized solar cells.* **Journal of Materials Science: Materials in Electronics**, 31, 2020, 2298-2307.
2. M. Imran, A. Abutaleb, M. A. Ali, T. Ahamad, A. Ansari, M. Shariq, & A. Khan. *UV light enabled photocatalytic activity of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles synthesized via phase transformation.* **Materials Letters**, 258, 2020, 126748.
3. T. Zahid, N. Arshed, M. Munir, & K. Hameed. *Role of energy consumption preferences on human development: a study of SAARC region.* **Economic Change and Restructuring**, 54, 2021, 121-144.
4. S.S. Thakar, K.R. Jha, Y. Phasinam, Y. Qureshi, & V.H. Babu. *X ray diffraction analysis and evaluation of antioxidant activity of copper oxide nanoparticles synthesized from leaf extract of *Cissus vitiginea*.* **Mater. Today Proc.** 2021.
5. B. Arumugam, T. Manaharan, C.K. Heng, U.R. Kuppusamy, & U.D. Palanisamy. *Antioxidant and antiglycemic potentials of a standardized extract of *Syzygium malaccense*.* **LWT-Food Sci. Technol.** 59, 2, 2014, 707–712.

Chapter Four

Results and Discussion of Findings

4.1 Characterization of Biosynthesized Al₂O₃, CuO, and ZnO Nanoparticles using *Syzygium malaccense*

4.1.1 Ultraviolet–Visible (UV–Vis) Analysis

One crucial and useful method for the thorough evaluation of biosynthesized nanoparticles is UV-vis spectroscopy. The stability and production procedures of Al₂O₃, CuO, and ZnO nanoparticles are also investigated using this technology. The unique optical properties of Al₂O₃, CuO, and ZnO nanoparticles cause them to interact strongly with particular light wavelengths¹. Furthermore, UV-Vis spectroscopy is acknowledged for its rapidity, simplicity, and user-friendliness. It efficiently quantifies various types of nanoparticles and exhibits both sensitivity and selectivity toward them. Metallic nanoparticles have the capacity to enhance the reaction rate by increasing the adsorption of reactants onto their surface, consequently reducing the activation energy barriers¹.

The ultraviolet-visible (UV-Vis) absorption spectra and the bandgap energy of aluminum oxide (Al₂O₃), copper oxide (CuO), and zinc oxide (ZnO) nanoparticles are illustrated in Figures 4.1 through 4.3, respectively. The optical absorbance spectra pertaining to aluminum oxide nanoparticles synthesized utilizing *Syzygium malaccense* (commonly known as malay apple) is depicted in Figure 4.1a. This figure reveals an optical absorbance spectrum band at 371.61 nm, which corroborates the presence of aluminum oxide nanoparticles. The phenomenon of surface plasmon resonance (SPR) arises from the interaction of electromagnetic radiation from light with the free electrons of aluminum oxide nanoparticles. These findings are consistent with prior research². The collective excitation oscillations generated as a consequence significantly enhance the surrounding electromagnetic fields adjacent to the nanoparticles. The band gap energy (E_g)

of the synthesized Al_2O_3 nanoparticles is illustrated in Figure 4.1b. The band gap energy of the synthesized Al_2O_3 nanoparticles is measured to be (2.09 eV). This observation suggests that the band gap of the semiconductor materials exhibits a dependence on the size of the particles. The band gap tends to increase as the particle size diminishes, while the absorption edge shifts towards a higher energy as the particle size decreased³.

The optical characteristics and bandgap energy of CuO NPs are displayed using the Tauc plot in Figure 4.2a,b. Following electron transfer from the valence band to the conduction band, the spectrum showed a distinct absorption peak at 370 nm that was linked to the intrinsic bandgap absorption of CuO NPs. This result is consistent with earlier research⁴. Moreover, CuO NP absorption spectra showed a limited nanoparticle dispersion⁵. CuO NPs and other semiconductors have a distinct bandgap energy, in contrast to metals that have integral electron levels. As shown in Figure 4.2b, the optical bandgap energy for CuO NPs was determined to be around 2.05 eV. Excellent electronic transaction and photocatalytic capabilities were inherited by the as-synthesised CuO NPs, as evidenced by the reported reduced bandgap energy numerical values⁶.

The UV-Vis plot and Tauc Plot (Bandgap analysis) of ZnO NP are displayed in Figs. 4.3a and b. The sample's absorption spectrum was recorded in the 350–500 nm range, with the absorbance peak at 371 nm corresponding to the characteristic band of zinc oxide nanoparticles. This was found to be consistent with previous research that demonstrated ZnO NP absorb light in this region⁷. The extrapolation of the Tauc's plot was then used to determine the bandgap. A bandgap of 3.23 eV is visually displayed in Figure 4.3b, which is consistent with the bandgap of ZnO (3.20 eV) NPs documented in the literature⁷. The apparent redshift is indicative of a strong

electronic interaction between the ZnO NPs. Therefore, when exposed to visible light, the ZnO NPs can show an accelerated photodegradation response⁷.

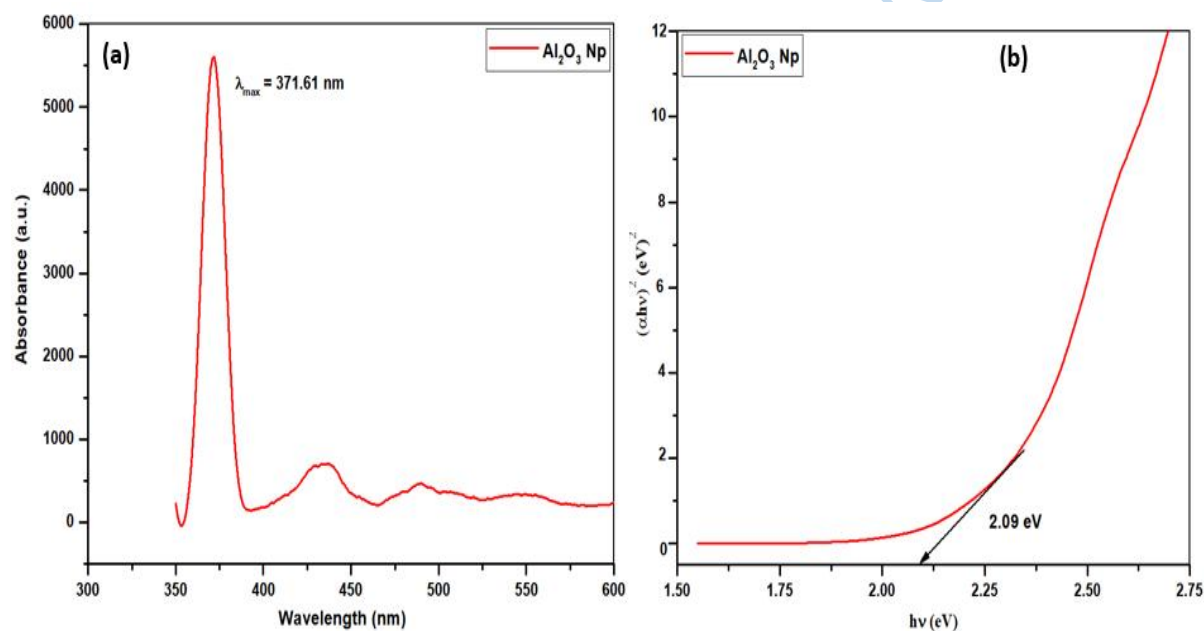


Figure 4.1: UV-visible spectra (a) Tauc plot of *Syzygium malaccense* extract synthesized Al_2O_3 NPs (b) and bandgap energy.

Source: Field Survey, 2025

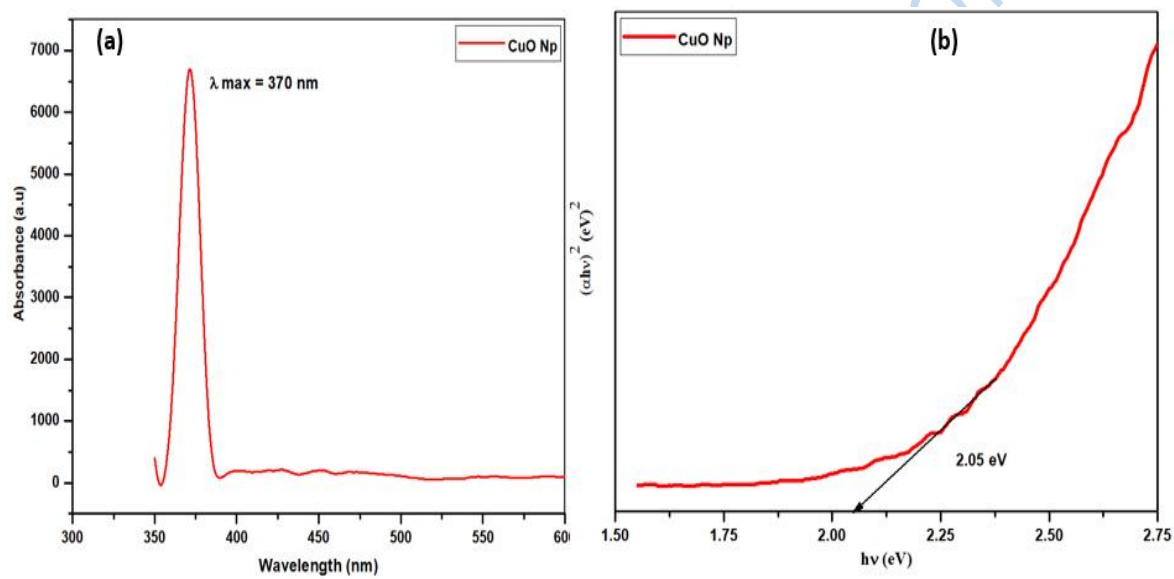


Figure 4.2: UV-visible spectra (a) Tauc plot of *Syzygium malaccense* extract synthesized CuO NPs (b) and bandgap energy.

Source: Field Survey, 2025

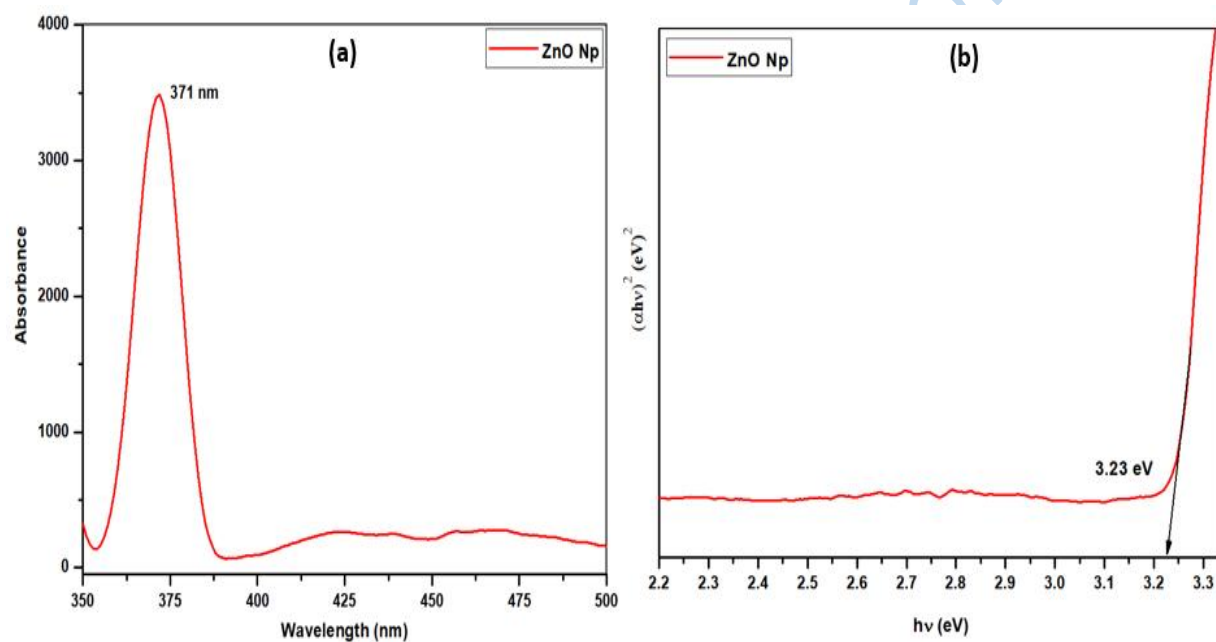


Figure 4.3: UV–visible spectra (a) Tauc plot of *Syzygium malaccense* extract synthesized ZnO NPs (b) and bandgap energy.

Source: Field Survey, 2025

4.1.2 FT-IR Analysis of Biosynthesized Al₂O₃, CuO and ZnO NPs using *Syzygium malaccense*

Characterization of biosynthesized nanoparticles through Fourier transform infrared (FTIR) spectroscopy is commonly employed to identify and classify potential biomolecules that may serve effectively as capping agents, thereby enhancing the stability of Al₂O₃, CuO, and ZnO nanoparticles. The identification of functional groups present on the surfaces of the nanoparticles was conducted utilizing FTIR spectroscopy. According to a hypothesis proposed by various studies, which identified numerous organic extracts across diverse materials, the amines and carboxylate functional groups may function as organic reducing agents or capping agents in the synthesis of Al₂O₃, CuO, and ZnO nanoparticles. Table 4.1 and Figures 4.4 to 4.6 illustrate the Fourier Transform Infrared (FTIR) spectra corresponding to the extract of *Syzygium malaccense* (Malay apple), highlighting the existence of various phytochemical constituents, including cellulose, hemicellulose, polyphenols, and biomolecules.

According to Table 4.1 and Figure 4.4, the presence of hydroxyl groups in cellulose, glycosides, and saponins as well as free and bound moisture were responsible for the observed valence vibrations of O-H bonds, which were 3600 cm⁻¹. Saturated carbon aromatic rings and vibration bonds in the -CH₂-groups were identified as the sources of the valence vibrations of C-H bonds that were detected in the 2700 cm⁻¹ region. Vibrational bands in the 2000–2400 cm⁻¹ range indicated the existence of flavonoid main amine–N–H bond vibration. At 1600 cm⁻¹, valence vibrations of C=O bonds in various functional groups (ketonic, ester, etc.) were detected.

The absence of this band in the case of stabilized Al_2O_3 NP, however, demonstrated that flavonoids and pectin biomolecules decreased and stabilized the Al^{2+} ions. The deformation vibrations of the terminal group $-\text{CH}_2\text{OH}$ and the C-H and -O-H bonds in hexagonal saturated rings were identified as the source of the broadband in Figure 4.4 at 1300 cm^{-1} . The sharp band in the 1100 cm^{-1} range was ascribed to the valence vibrations of C-O in the methoxy groups (pectin) and C-C and C-O bonds in hexagonal saturated rings^{2,9}.

Table 4.1 and Figure 4.5 display the FTIR spectra of CuO NPs that were biosynthesized using extract from *Syzygium malaccense*, or Malay apples. The bands at 400 cm^{-1} in the spectrum are attributed to Cu-O (M-O) stretching¹⁰. The strong and wide absorption bands at 3400 cm^{-1} are associated with C-H stretching aldehydes, phenols, and O-H stretching H-bonded alcohols. Stretching alkanes and vibration bonds in the $-\text{CH}_2$ -groups were responsible for the valence vibrations of C-H bonds that were detected in the 2900 cm^{-1} range. At 1600 cm^{-1} , valence vibrations of C=O bonds in various functional groups (ketonic, ester, etc.) were detected. Primary N-H bend 1° amine vibration of flavonoids was shown by vibrational bands in the 1400 cm^{-1} range. The valence vibrations of C-O stretching were identified as the cause of the sharp band in the 1000 cm^{-1} region².

Table 4.1 and Figure 4.6 list the functional groups found in the *Syzygium malaccense* ZnO NPs leaf extract. The presence of an O-H group with either intramolecular or intermolecular hydrogen bonding was established by the wide peak in the IR spectra that corresponded to an O-H stretching frequency of 3000 cm^{-1} . α , a β -unsaturated ketone of leaf extract, and conjugated alkene both respond to C=C stretching at a frequency of 1600 cm^{-1} . This has also been demonstrated by the O-H bending vibrations of the leaf extract measured by its medium intensity band at 1400 cm^{-1} . Additionally, the spectrum was seen with a weak band at 1300 cm^{-1}

indicating C-N stretching. The existence of C-O stretching¹¹ was carefully allocated to the stretching vibrations at 1100 cm⁻¹¹¹. It is possible to attribute a peak observed at 700 cm⁻¹ to the C-H bending vibrations of the leaf extract.

Wavenumber (cm ⁻¹)			Intensity	Possible assignments
Al ₂ O ₃	CuO	ZnO		
3600	3400	3000	Strong	O-H stretching alcohol
2700	2900			C-H
1600	1600	1600	Medium	C=C stretching in conjugated alkene
1300	1400	1400	Medium	O-H bending carboxylic acid
-	-	1300	Strong	O-H bending carboxylic acid
1100	1000	1100	Strong	1266 C-O stretching tertiary alcohol
-	600	600	Strong	C-Br stretching in Al ₂ O ₃ compounds
-	-	400	Strong	Al-O, Cu-O and Zn-O bond

Table 4.1: FTIR spectra with possible assignments using *Syzygium malaccense* leaf based biosynthesis Al₂O₃, CuO and ZnO NPs .

Source: Field survey, 2025

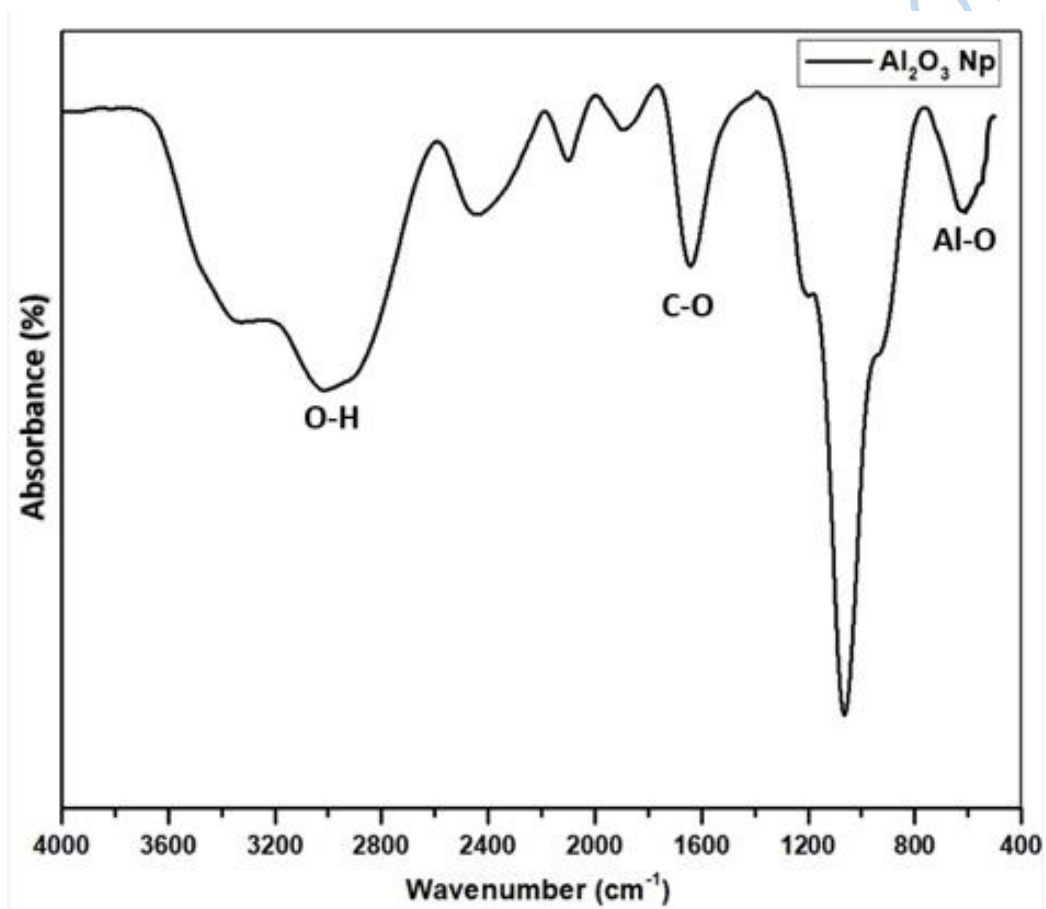


Figure 4.4: FT-IR Spectra of biosynthesized Al_2O_3 NP using *Syzygium malaccense*

Source: Field survey, 2025

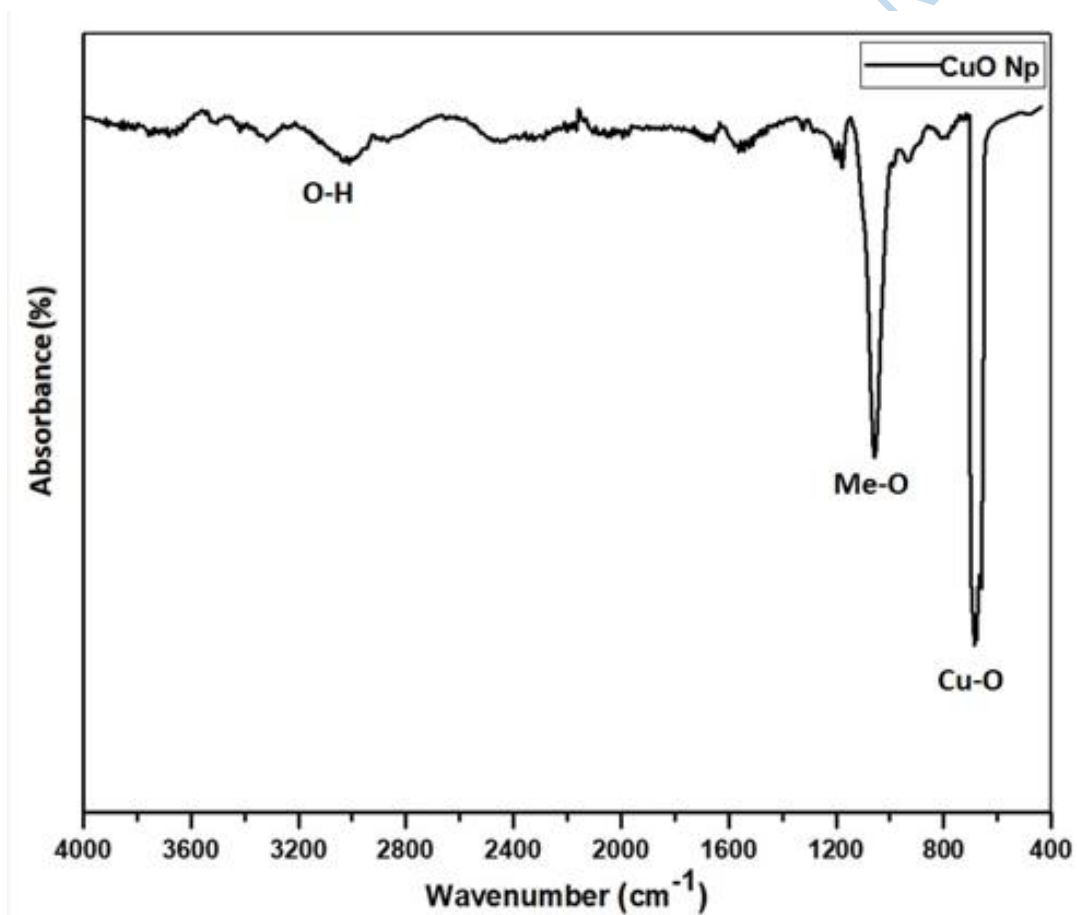


Figure 4.5: FT-IR Spectra of biosynthesized CuO NP using *Syzygium malaccense*

Source: Field survey, 2025

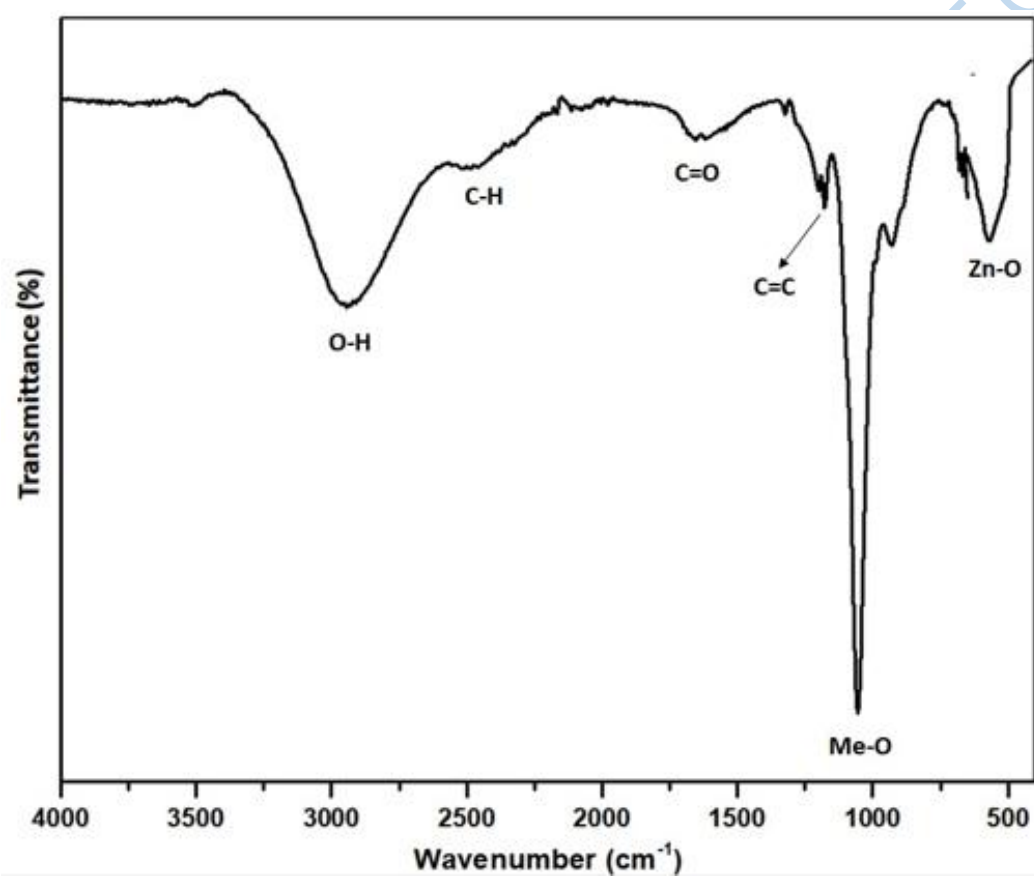


Figure 4.6: FT-IR Spectra of Biosynthesized ZnO NP using *Syzygium malaccense*

Source: Field survey, 2025

At 600 cm^{-1} of leaf extract, a discernible study band was seen that was attributed to the existence of either the C-Br or C-Cl band. The generation of ZnO NPs was confirmed by the Zn-O stretching frequency, which was 400 cm^{-1} . This aligns with the documented ZnO nanoparticles made from *Berberis aristata*¹².

4.1.3 XRD Analysis of Biosynthesized Al₂O₃, CuO and ZnO NPs using *Syzygium malaccense*

X-ray Diffraction (XRD) Analysis of Al₂O₃, CuO, and ZnO Nanoparticles characteristics including crystal structure/phase, lattice parameters, crystallite dimensions, single crystal orientation, preferred polycrystalline orientation, defects, stresses, and additional parameters are elucidated through the application of the XRD methodology. Figure 4.7 illustrates the intensity of the XRD spectrum for Al₂O₃ nanomaterials, plotted against the scattering angle 2θ . The preponderance of the diffraction peaks in the XRD pattern of Al₂O₃ nanoparticles were identified at 2θ angles of 22.52° , 25.75° , 27.76° , 30.29° , 35.30° , and 38.02° . A concurrent investigation arrived at a corresponding conclusion². These peaks corroborated the formation of Al₂O₃ nanoparticles of diverse dimensions, with analogous XRD patterns having been previously documented in the scientific literature^{2,3}. The broadening of peaks in the XRD patterns of Al₂O₃ nanoparticles can be attributed to variations in particle size. The crystalline dimension of Al₂O₃ nanoparticles was determined to be 22 nm, which correlates with the most pronounced peak.

Figure 4.8 presents the X-ray powder diffraction profiles for CuO nanoparticles. The diffraction peaks exhibit a nano-crystalline characteristic, featuring seven prominent peaks at the scattering angles (2θ) of 10.00° , 13.00° , 25.00° , 33.00° , 35.00° , 40.00° , and 45.00° . The sharpness of the

diffraction peaks depicted in the figure signifies the commendable crystallinity of the CuO nanoparticles, with the most substantial peak estimated to be 25 nm. The absence of characteristic peaks indicative of any alternative phase of CuO or any impurities substantiates the high purity of the CuO nanoparticles. A similar finding was reported in an earlier study⁶. The diffraction peaks of ZnO nanoparticles at 2θ angles (19.52° , 21.75° , 25.76° , 28.29° , 32.30° , 36.02°) are illustrated in Figure 4.8. These peaks confirmed the formation of ZnO nanoparticles of varying sizes, and analogous XRD patterns have been documented in prior literature^{13,14}. The widening of peaks in the XRD patterns of ZnO nanoparticles is attributable to fluctuations in particle size. A crystalline dimension of 27 nm was established for ZnO nanoparticles, corresponding to the apex peak.

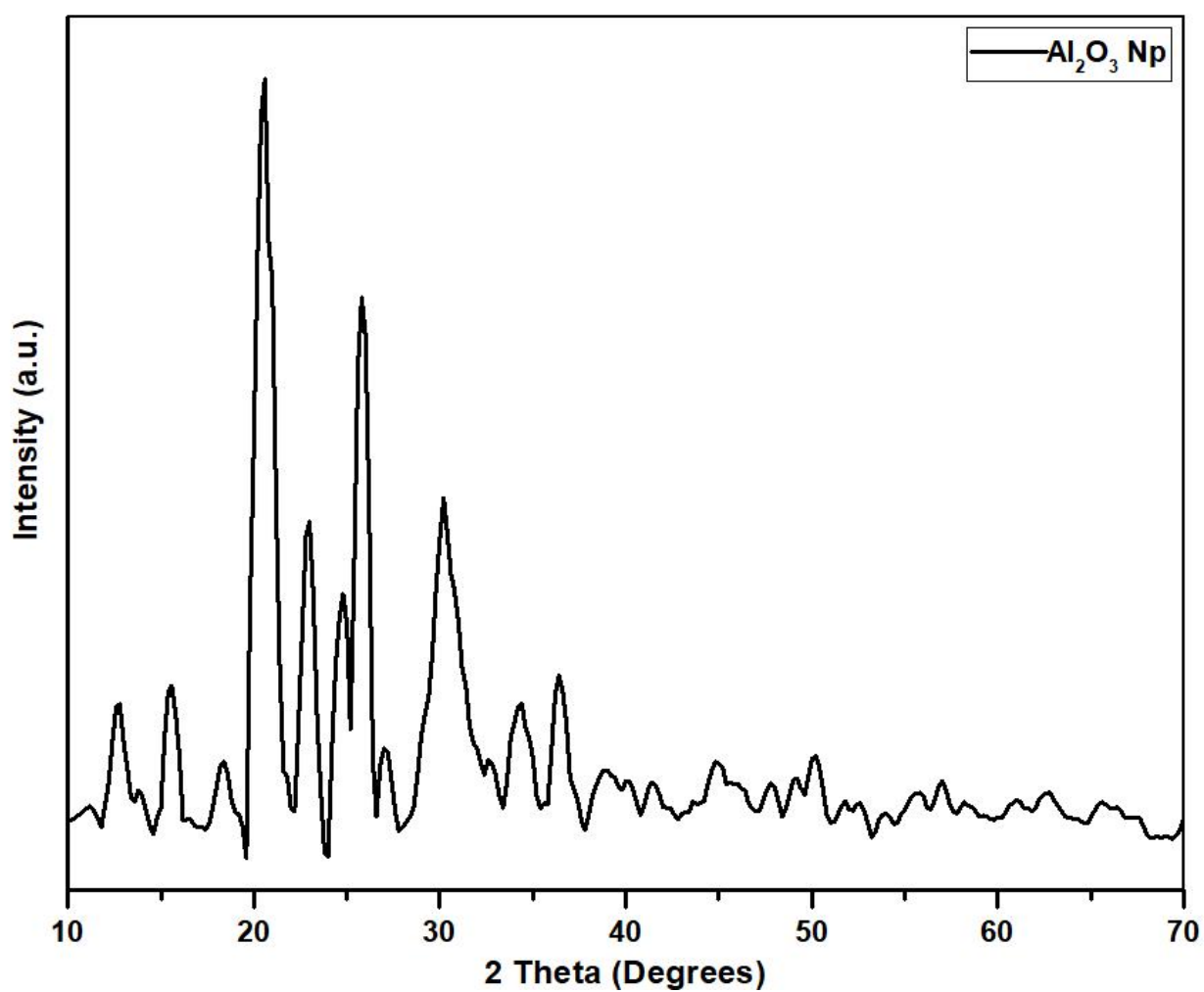


Figure 4.7: XRD Pattern of Biosynthesized Al₂O₃ NPs using *Syzygium malaccense*

Source: Field survey, 2025

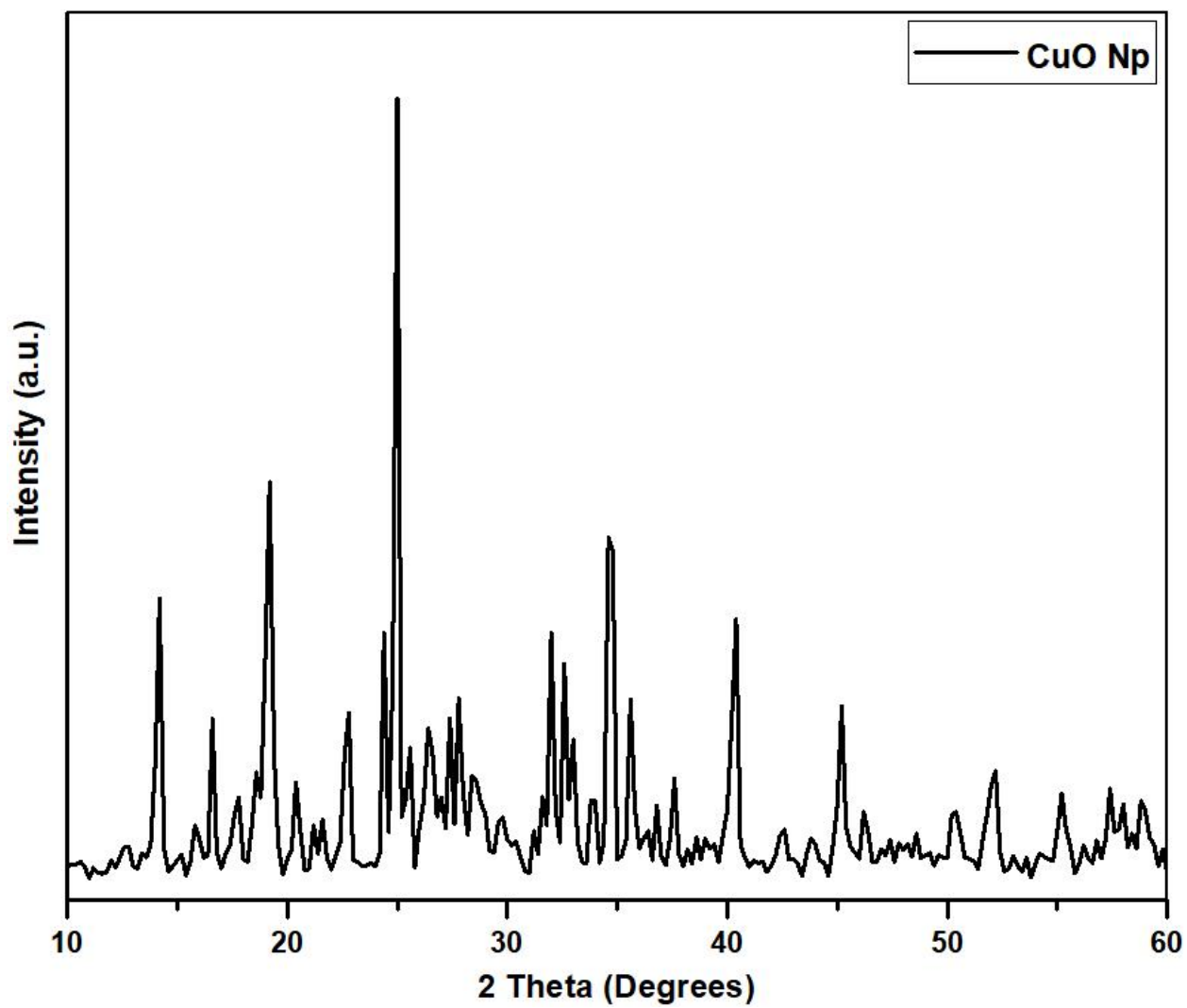


Figure 4.8: XRD Pattern of Biosynthesized CuO NPs using *Syzygium malaccense*

Source: Field survey, 2025

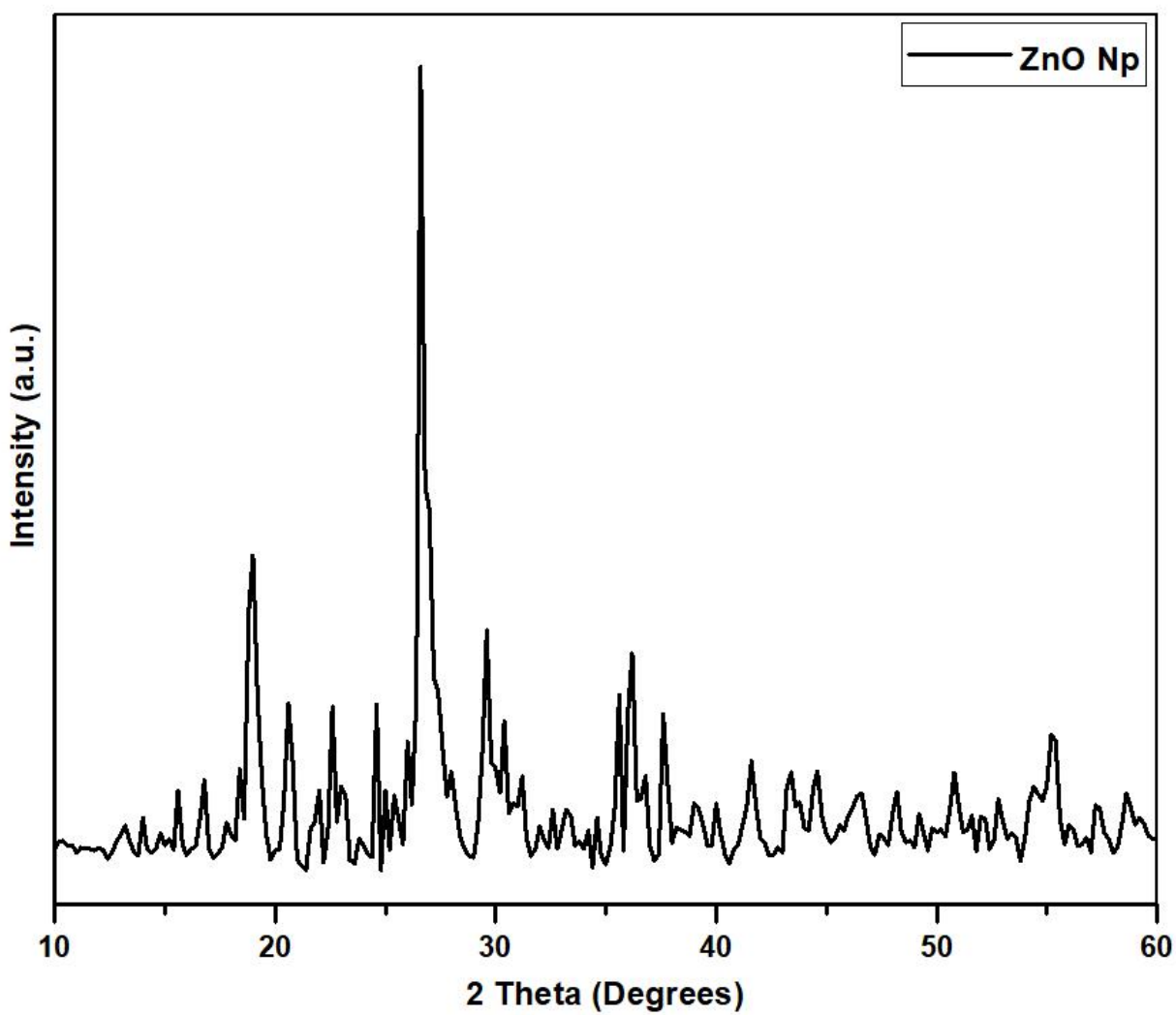


Figure 4.9: XRD Pattern of Biosynthesized ZnO NPs using *Syzygium malaccense*

Source: Field survey, 2025

4.1.4 SEM and EDX Analysis

The SEM is a highly helpful tool for learning about the composition, morphology, and topography of materials. This kind of electron microscope may generate pictures of a sample's surface with great resolution. SEM pictures have a distinctive three-dimensional look because of the way they are produced, and they may be used to assess the sample's surface morphology⁴. Scanning electron microscopy (SEM) was used to examine the morphological structures of biosynthesized Al_2O_3 , CuO, and ZnO NPs using leaf extract from *Syzygium malaccense*. Figures 4.10, 4.12, and 4.14 show SEM micrographs of Al_2O_3 , CuO, and ZnO NPs using leaf extract from *Syzygium malaccense*. The particles had a homogeneous spherical shape, with average sizes of 27.50 nm, 11.01 nm, and 21.98 nm, respectively. Figures 4.10, 4.12, and 4.14 showed the histograms illustrating the size distribution of the Al_2O_3 , CuO, and ZnO NPs.

Additionally, an energy dispersive X-ray spectroscopy (EDX) was used to determine the composition of the Al_2O_3 , CuO, and ZnO NPs utilizing leaf extract from *Syzygium malaccense*. The Al_2O_3 -NPs from the plant extract were shown to have an aggregated or spherically cluster-like structure by SEM examination. The outcome is consistent with a comparable outcome². Aluminum (Al), oxygen (O), sulfur (S), and carbon (C) components were present in the produced catalyst without any impurity peaks, according to the EDX spectrum of the Al_2O_3 NP in Figure 4.11. Al, O, S, and C have relative weight percentages of 10.68%, 76.07%, 8.47%, and 4.77%. Al, O, S, and C have atomic concentration percentages of 18.56%, 65.95%, 12.38%, and 3.11%, respectively. The outcome validated the 1:0.5 atomic ratio of S to C and the 1:6

stoichiometry between Al and O. The outcomes unequivocally demonstrated the produced Al_2O_3 NP's homogeneity and great purity².

A sphere-shaped morphology and enhanced crystallinity are shown in the SEM picture. Previous research have looked at similar results^{4,15}. Copper (Cu), oxygen (O), and sulfur (S) atoms were present in the produced nanoparticles without any impurity peaks, according to the EDX spectrum of the CuO NP in Figure 4.13. Cu, O, and S have respective weight percentages of 33.25%, 57.24%, and 9.51%. Cu, O, and S have respective atomic concentration percentages of 63.38%, 27.47%, and 9.15%. The outcome validated the 1 atomic ratio of S and the 6:2 stoichiometry between Cu and O. The outcomes unequivocally demonstrated the produced CuO NP's homogeneity and great purity¹⁵.

Many spherical and almost spherical particles were grouped together and shown in rod-like patterns in the SEM picture. The produced nanoparticles included zinc (Zn), oxygen (O), and sulfur (S) components without any impurity peaks, according to the ZnO NP's EDX spectrum in Figure 4.15. The synthesized ZnO NP's homogeneity and excellent purity were firmly validated by the results. Cu, O, and S have relative weight percentages of 27.77%, 61.07%, and 11.16%. Zn, O, and S have respective atomic concentration percentages of 57.63%, 31.02%, and 11.36%. The outcome validated the 1 atomic ratio of S and the 5:3 stoichiometry between Zn and O.

The SEM picture revealed an array of agglomerated, rod-like spherical and almost spherical particles. The ZnO NP's EDX spectrum, shown in Figure 4.15, showed that the produced nanoparticles included the elements zinc (Zn), oxygen (O), and sulfur (S) without any impurity peaks. The outcomes unequivocally demonstrated the produced ZnO NP's great purity and homogeneity⁷. Cu, O, and S make up 27.77%, 61.07%, and 11.16% of the total weight, respectively. The percentages of Zn, O, and S that have atomic concentrations are 57.63%,

31.02%, and 11.36%, respectively. Both the 1 atomic ratio of S and the 5:3 stoichiometry between Zn and O were validated by the findings.

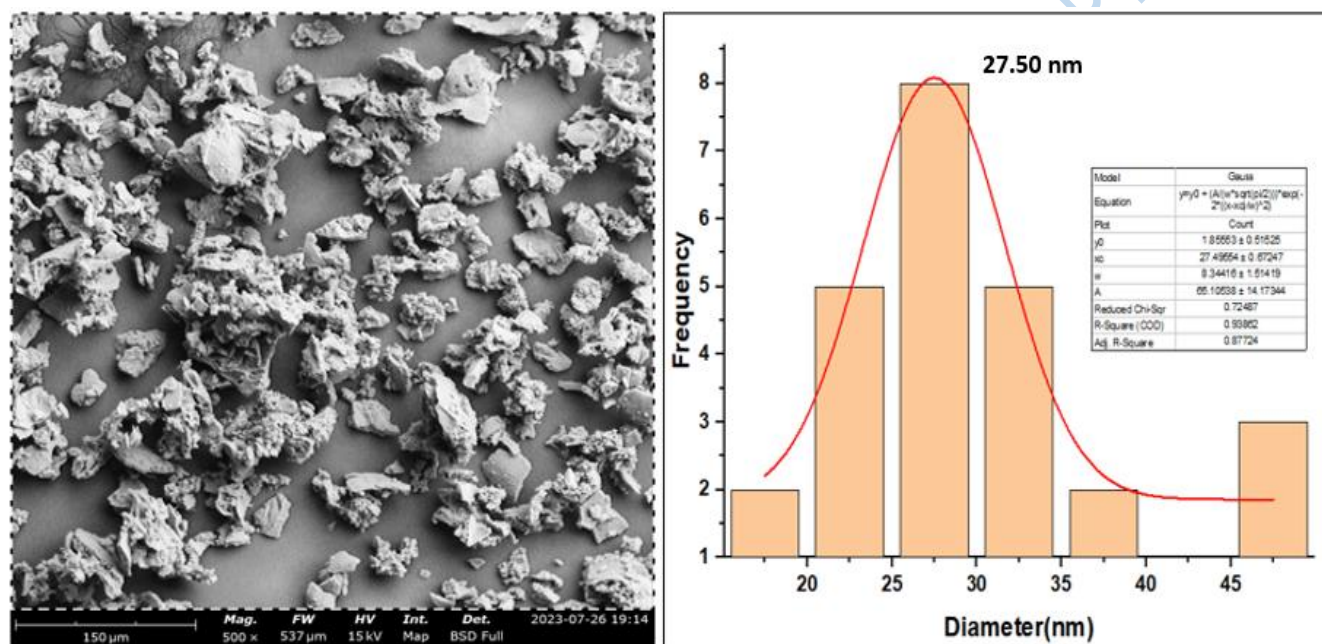


Figure 4.10: SEM micrographs and size distribution of Biosynthesized Al_2O_3 NP

Source: Author's Field Work, 2025

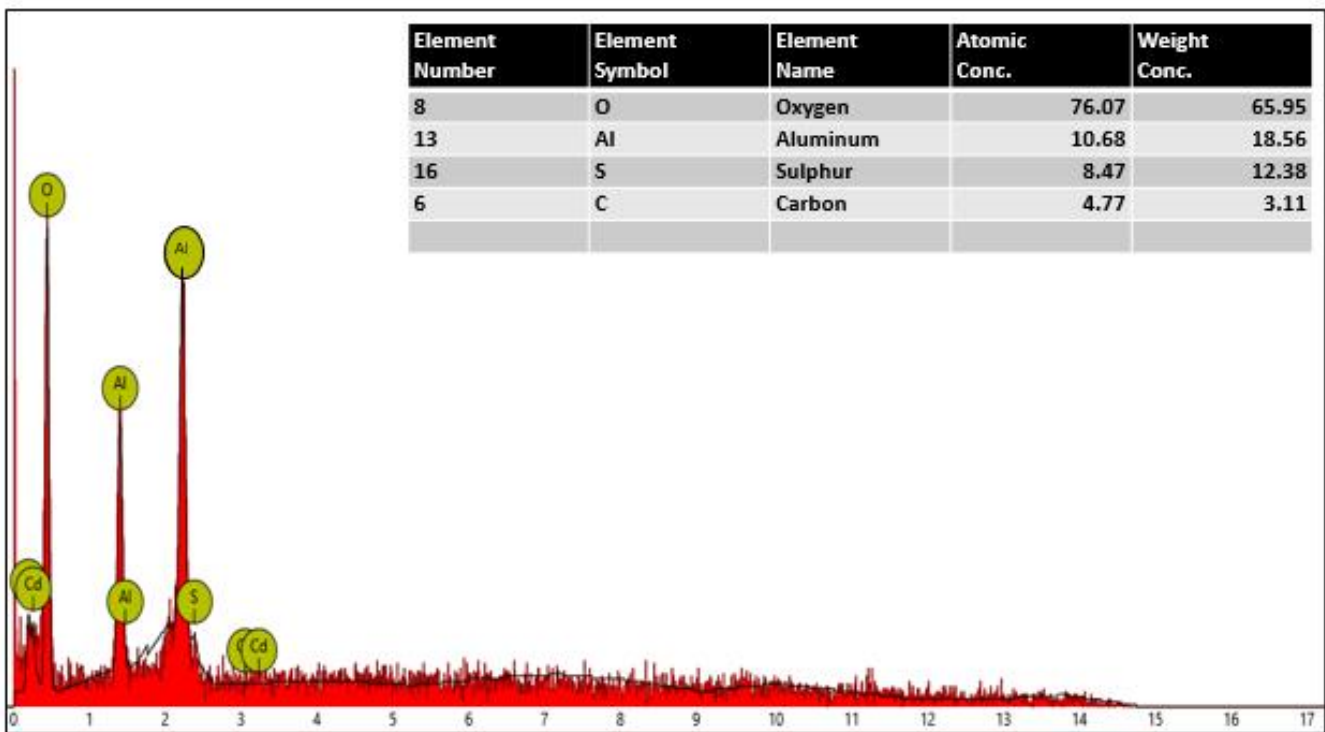


Figure 4.11: EDX spectrum and elemental composition of Al_2O_3 NP

Source: Author's Field Work, 2025

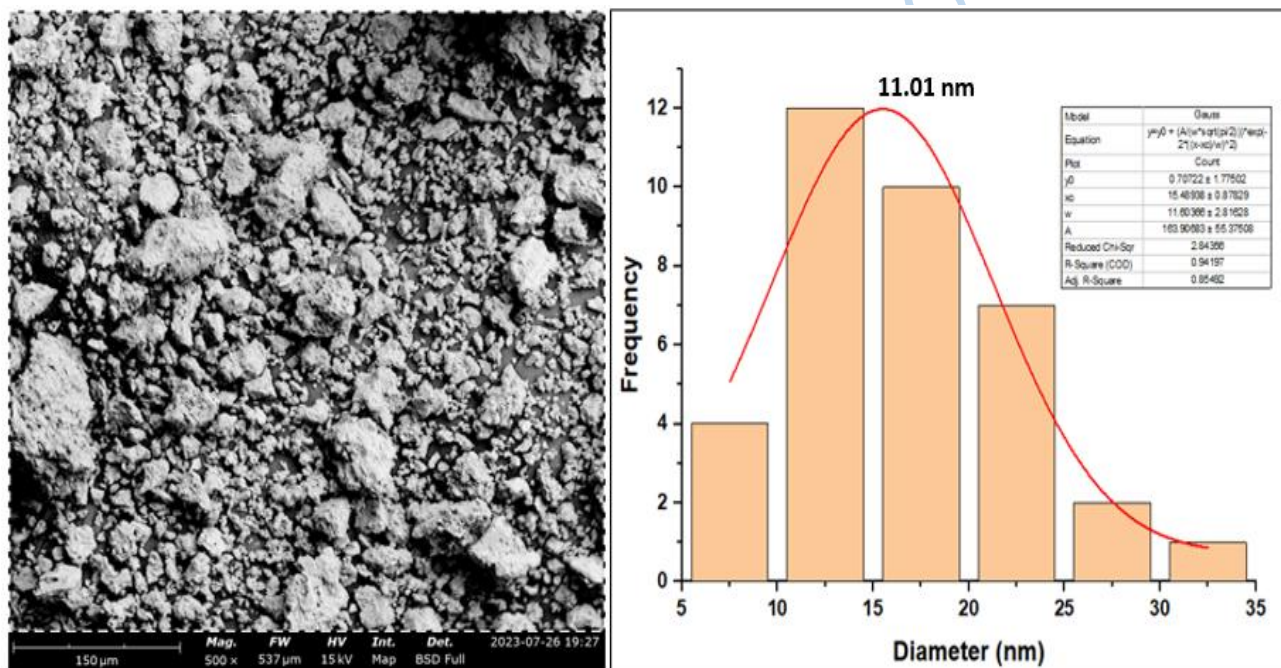


Figure 4.12: SEM micrographs and size distribution of Biosynthesized CuO NP

Source: Author's Field Work, 2025

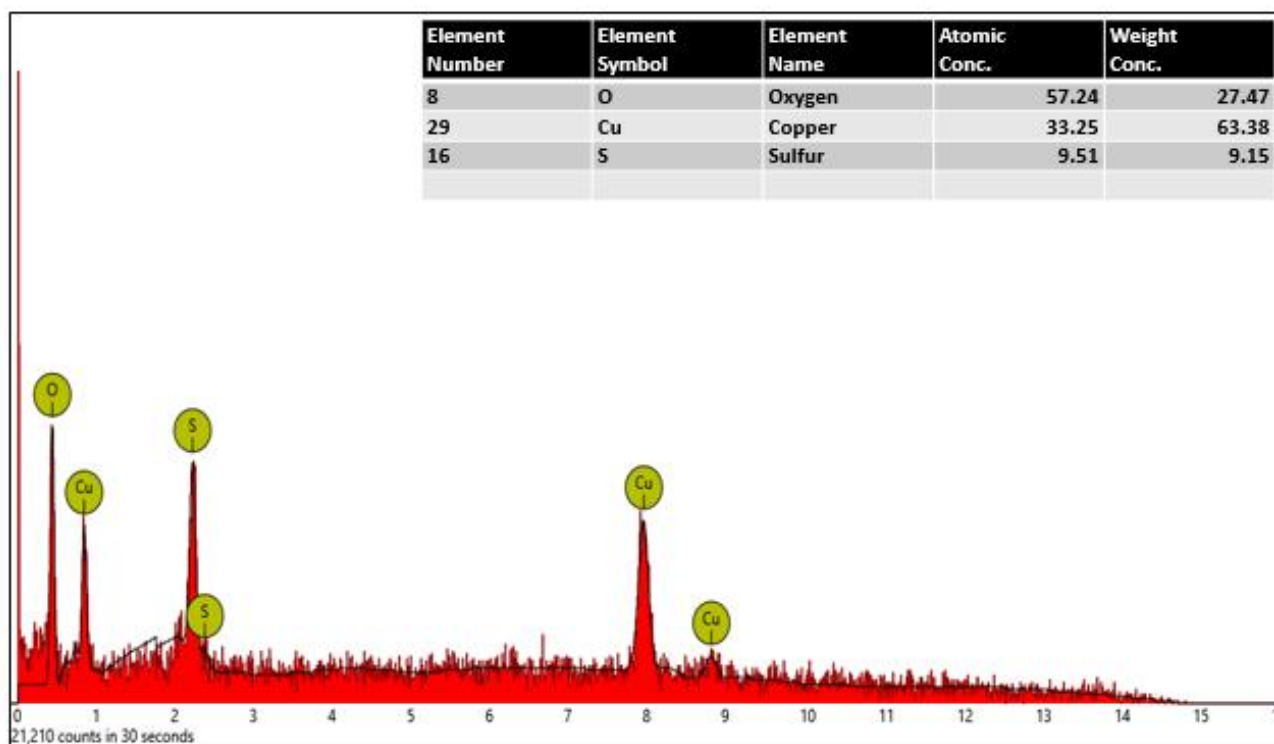


Figure 4.13: EDX spectrum and elemental composition of CuO NP

Source: Author's Field Work, 2025

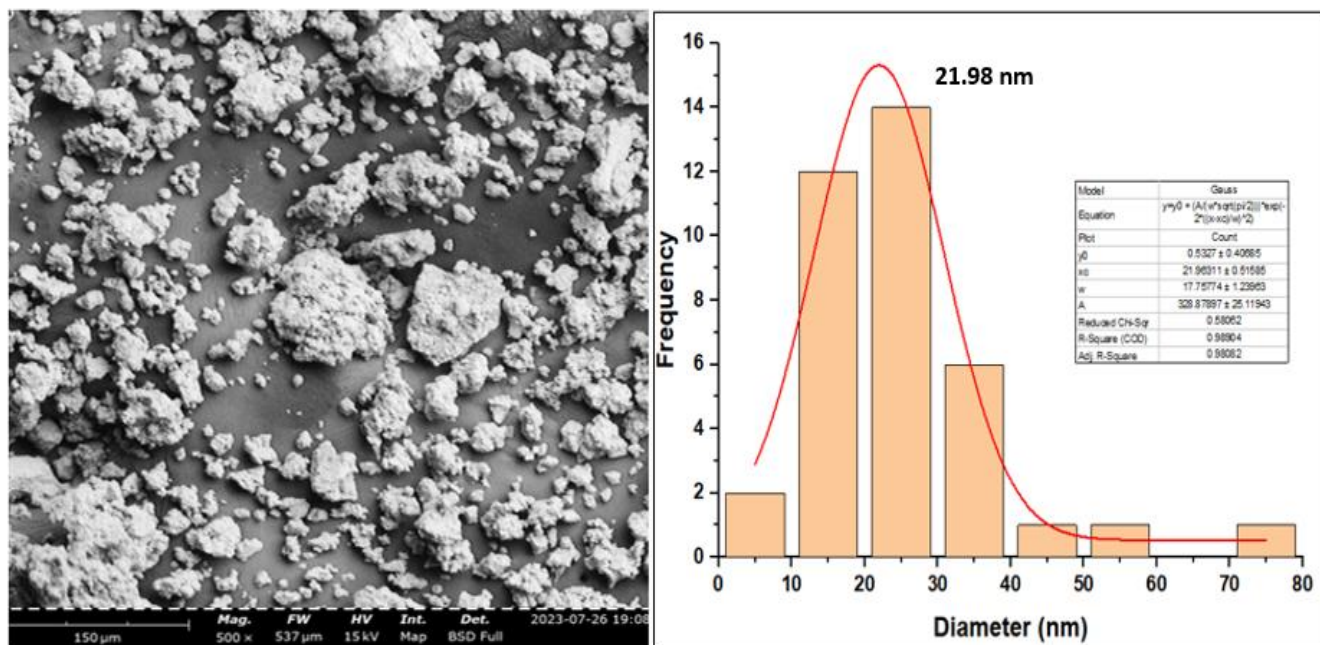


Figure 4.14: SEM micrographs and size distribution of Biosynthesized ZnO NP

Source: Author's Field Work, 2025

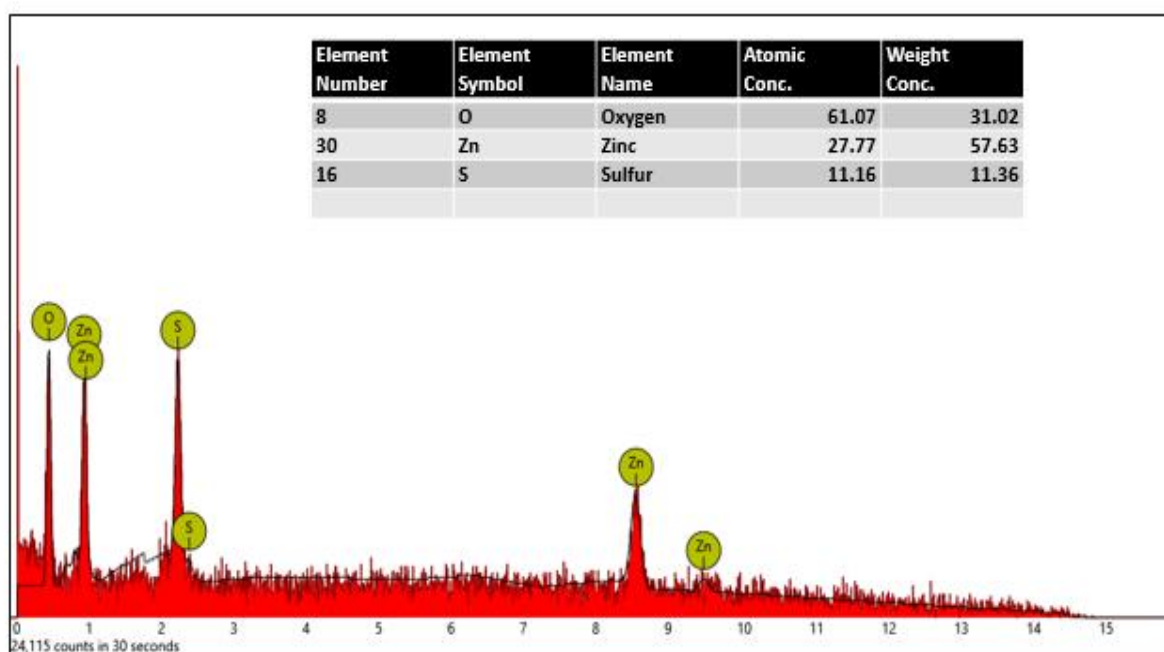


Figure 4.15: EDX spectrum and elemental composition of ZnO NP

Source: Author's Field Work, 2024

4.2 Current Density Versus Voltage Characteristics of Fabricated Monolithic DSSCs

The performance of the biosynthesized nanoparticles of zinc oxide (ZnO), copper oxide (CuO), and aluminum oxide (Al_2O_3) as CEs in DSSCs has been evaluated by screen-printing them onto the FTO. Performance of the DSSC was evaluated by measuring the maximum voltage, maximum current, fill factor, open-circuit voltage, and short-circuit current of the cell. The performance parameters of monolithic dye-sensitized solar cells (DSSCs) with varying nanoparticle compositions monolithic, CuO , and ZnO biosynthesized nanoparticles are shown in Table 4.2. Open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor, overall efficiency, voltage at maximum power (V_{mp}), and current at maximum power (I_{mp}) are among the characteristics that are observed.

By acting as a surface passivation layer over TiO_2 , the wide-bandgap insulator Al_2O_3 lowers recombination at the electrolyte contact. The efficiency of solar-to-power conversion of DSSCs using Al_2O_3 biosynthesized nanoparticles was 1.79%, with an open circuit voltage of 0.48 V, a short-circuit current of 7.2 mA/cm^2 , a V_{mp} of 0.35, an I_{mp} of 5.3 mA/cm^2 , and a fill factor of 0.53. These results are displayed in Figure 4.18 and Table 4.2. With an efficiency of 1.76%, an open circuit voltage of 0.36 V, a short-circuit current of 4.9 mA/cm^2 , a V_{mp} of 0.29, an I_{mp} of 0.2 mA/cm^2 , and a fill factor of 0.29, the DSSC without nanoparticles had the lowest efficiency of any solar-to-electric power. Because of its low bandgap, the p-type semiconductor CuO may improve light absorption. According to Figure 4.17 and Table 4.2, the DSSC using CuO biosynthesized nanoparticles had a solar-to-electric power conversion efficiency of 3.44%, an

open circuit voltage of 0.38 V, a short-circuit current of 11.1 mA/cm², a V_{mp} of 0.37, an I_{mp} of 9.64 mA/cm², and a fill factor of 0.85.

With a solar-to-electric power conversion efficiency of 6.4%, an open circuit voltage of 0.52 V, a short-circuit current of 13.5 mA/cm², a V_{mp} of 0.4, an I_{mp} of 40 mA/cm², and a fill factor of 0.57, the DSSC made with ZnO biosynthesized nanoparticles demonstrated the best performance in electron transport dominance, as shown in Table 4.2 and Figure 4.16. High electron mobility n-type semiconductor ZnO enhances charge transfer and lowers recombination. ZnO > CuO > Al₂O₃ > Control (Without NPs) is the order of efficiency. These findings demonstrate that, in comparison to the cell without nanoparticles, the addition of biosynthesized nanoparticles resulted in a significant rise in Voc. This implies that the voltage properties of the monolithic DSSCs are influenced by the presence of these nanoparticles.

However, when the DSSC is shorted, the current output is shown by the J_{sc} values of 13.5 mA/cm² to 4.9 mA/cm². In contrast to the Scell without nanoparticles, ZnO > CuO > Al₂O₃ notably exhibits higher J_{sc} values, indicating improved light absorption and electron generation. Additionally, the presence of zinc oxide, copper oxide, and aluminum oxide nanoparticles is indicated by higher V_{mp} and I_{mp} values, which indicate an improvement in power conversion efficiency. This implies that the counter electrode containing ZnO > CuO > Al₂O₃ nanoparticles is very useful for promoting the consumption and transmission of electrical energy that is produced. The efficiency of the fill-factor decreased from 0.57 to 0.29. The ability of a solar cell to use the electricity it generates is gauged by its fill factor. ZnO > CuO > Al₂O₃ nanoparticles have a percentage rise of 105.7 percent above the cell without nanoparticles in this instance, according to the percentage increase of the cells. The addition of ZnO > CuO > Al₂O₃ nanoparticles greatly increases the overall efficiency of the DSSCs, showing the best efficiency

among the studied compositions and exhibiting the synergistic benefits of mixing copper oxide, aluminum nanoparticles, and zinc oxide^{16,17, 18}.

The plasmonic effect of ZnO biosynthesized nanoparticles, which causes an electron to migrate quickly from ZnO biosynthesized nanoparticles to the TiO₂, may be responsible for the overall increased photovoltaic performance. Collective oscillations can be produced by the excitation of free electrons in metals by electrical properties of light. These oscillations may occur in a very small volume of ZnO biosynthesised nanoparticles, which strengthens the local field and increases the amount of light that strikes the particles. Consequently, the ZnO biosynthesised nanoparticles enhanced the dye-sensitized solar cell's ability to absorb light, hence boosting its efficiency. The effective use of ZnO biosynthesized nanoparticles also helped to further increase the effectiveness of the DSSC because of their increased dye adsorption. The ZnO biosynthesized nanoparticles increased efficiency by increasing the short-circuit current density, which was achieved by improving the dye absorption of titanium dioxide. Both the fill factor and the open-circuit voltage improved significantly. This outcome is consistent with earlier studies on artificial monolithic DSSCs^{16,17, 18}.

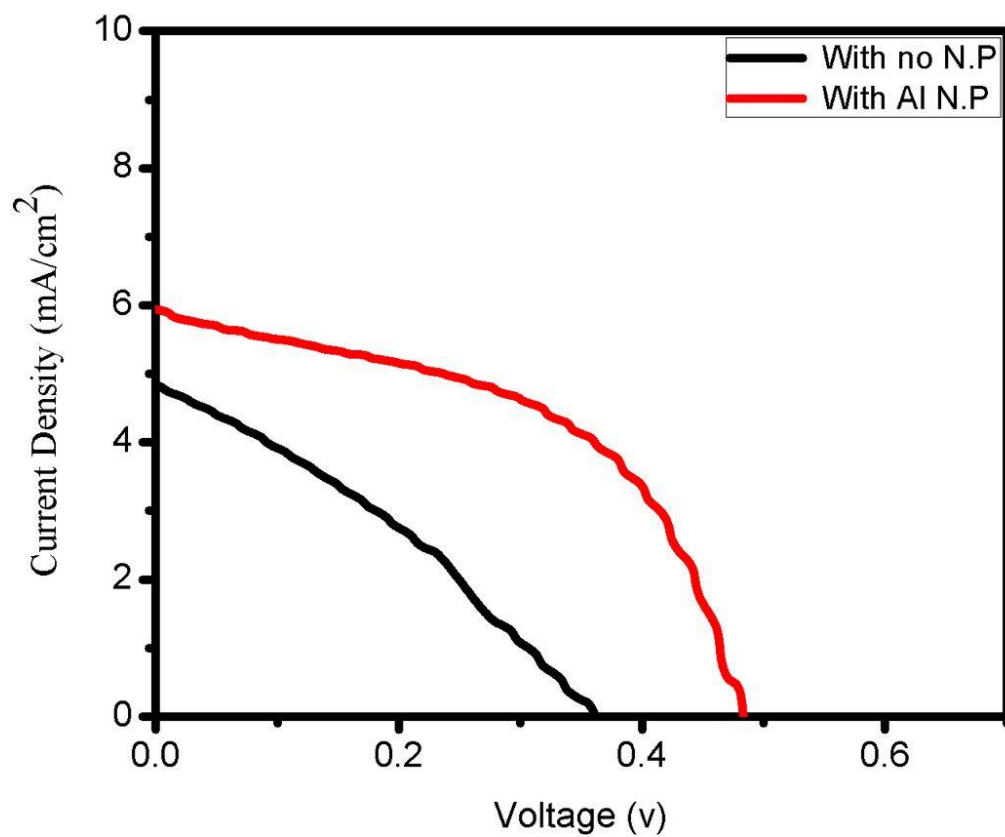


Figure 4.16: I-V Curves of DSSCs for Al_2O_3 Biosynthesized NP

Source: Author's Field Work, 2024

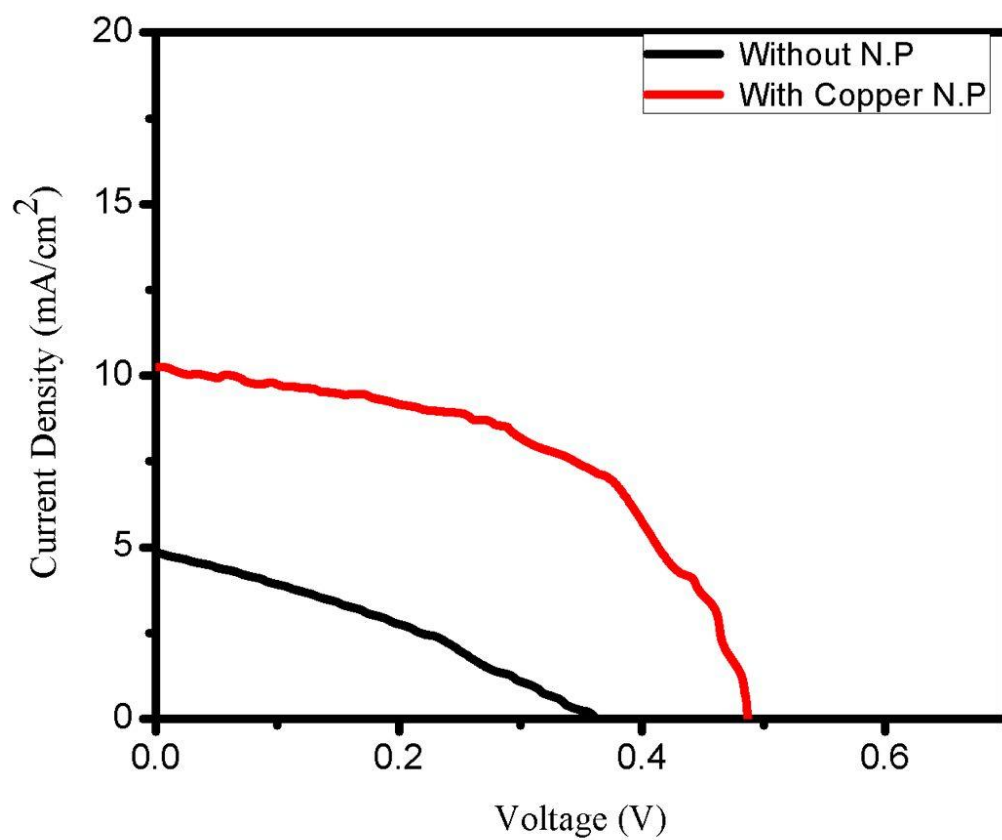


Figure 4.17: I-V Curves of DSSCs for CuO Biosynthesized NP

Source: Author's Field Work, 2024

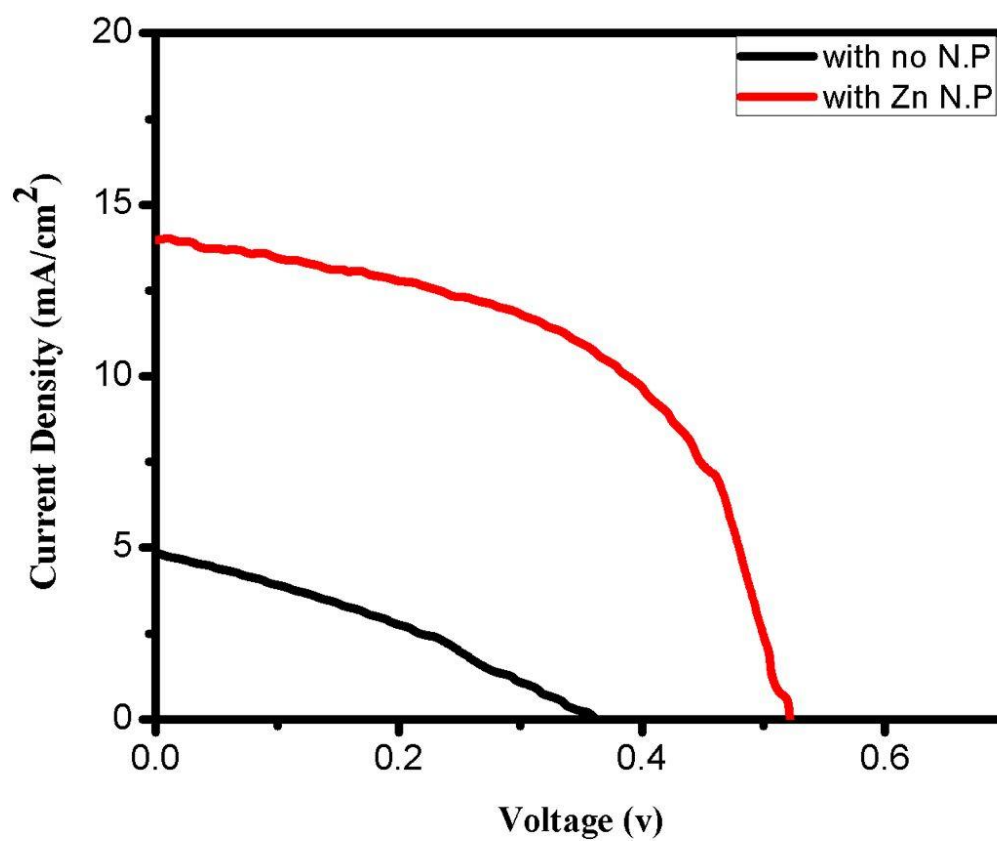


Figure 4.18: I-V Curves of DSSCs for ZnO Biosynthesized NP

Source: Author's Field Work, 2024

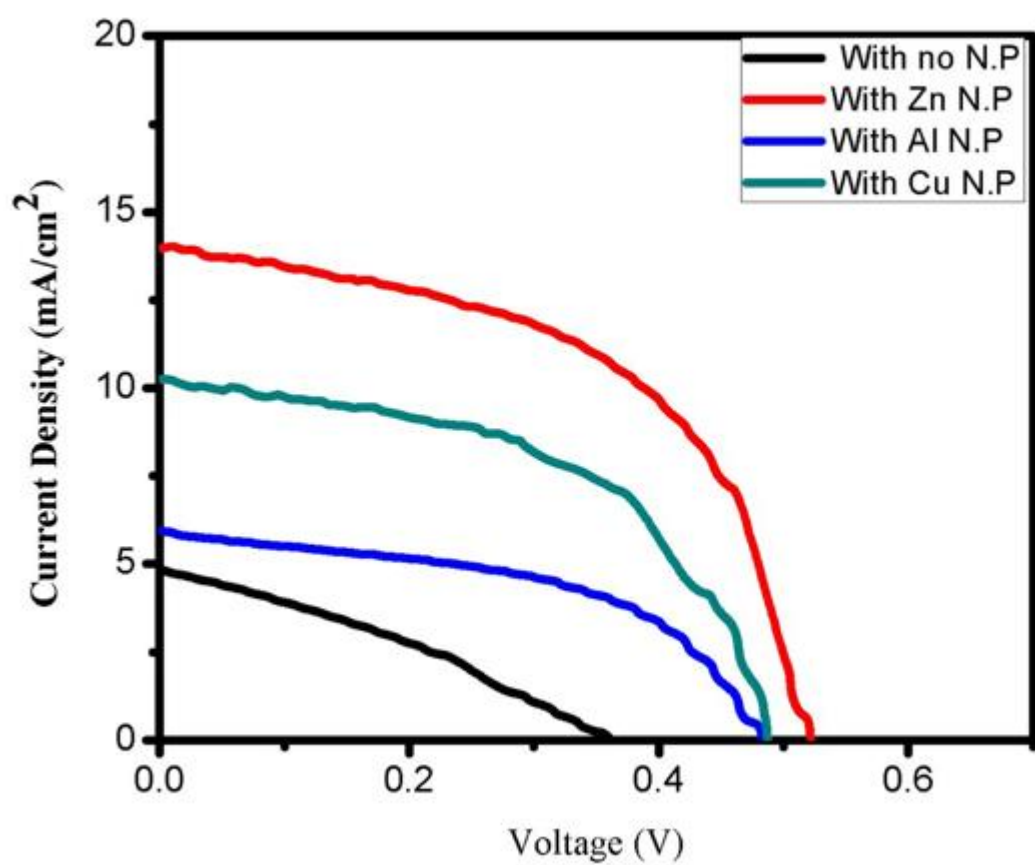


Figure 4.19: I-V Curves of DSSCs for without NP

Source: Author's Field Work, 2024

Table 4.2: Photovoltaic efficiency of dye-sensitized solar cells (DSSCs) made using nanoparticles of Without NP, Al₂O₃, CuO, and ZnO.

Nanoparticles	Voc (V)	Jsc (mA/cm ²)	Vmp (V)	Imp (mA/cm ²)	Fill factor	Efficiency (%)
Al ₂ O ₃	0.48	7.2	0.35	5.3	0.53	1.79
CuO	0.38	11.1	0.37	9.64	0.85	3.44
ZnO	0.52	13.5	0.4	40	0.57	6.4
Without NP	0.36	4.9	19.6	0.2	0.29	1.76

Source: Author's Field Work, 2025

4.3 Photodegradation of Neomycin Antibiotics over CuO and ZnO Nanoparticles

The photocatalytic efficacy is predominantly influenced by fluctuations in oxygen vacancy levels. The separation of electron-hole pairs is contingent upon the quantity of oxygen vacancies present. A significant benefit is that an increased number of oxygen vacancies facilitates rapid electron-hole recombination, thereby leading to a reduction in the photocatalytic activity of CuO and ZnO-NPs. A previous investigation indicates that the photocatalytic activity is modulated by the concentration of surface-level defects²⁰. An augmentation of surface defects correlates with a reduction in particle size, resulting in an elevated rate of charge carrier recombination, which ultimately enhances the photocatalytic activity. In the present investigation, biosynthesized CuO and ZnO-NPs exhibit diminished particle sizes, which corroborates their heightened photocatalytic activity. This phenomenon can be attributed to the superior efficiency in the separation of photogenerated charge carriers, enhanced light absorption, and an increased specific surface area.

Figures 4.20 and 4.21 illustrate the influence of the dosage of CuO and ZnO nanoparticles on the degradation of the neomycin (NEO) antibiotic.

The photocatalytic efficacy of CuO and ZnO nanoparticles was assessed concerning the degradation of NEO (365 nm) under UV light irradiation. Following 120 minutes of UV exposure, a degradation of 75% and 95% of NEO was observed with CuO and ZnO nanoparticles, respectively. The utilization of CuO nanoparticles revealed that as the reaction time for NEO extended from 0 to 120 minutes, the degradation percentage escalated from 38% to 75%, subsequently declining from 105 minutes to 120 minutes.

Upon the introduction of ZnO nanoparticles, a degradation of 95% of NEO antibiotics was achieved at 80 minutes, with a subsequent decline noted from 80 minutes to 120 minutes (Figure 4.22). The ZnO photocatalyst demonstrated superior effectiveness compared to the CuO photocatalyst in the degradation of the antibiotic neomycin. The findings regarding the photodegradation of NEO antibiotics utilizing ZnO NPs align with prior report²¹. The observed reduction in NEO concentration can be attributed to oxidation–reduction reactions occurring on the photocatalyst's surface and efficient electron–hole separation. The photocatalytic degradation efficiency of the synthesized photocatalysts concerning NEO, as established in this study and in related investigations, has been compiled in Table 4.2.

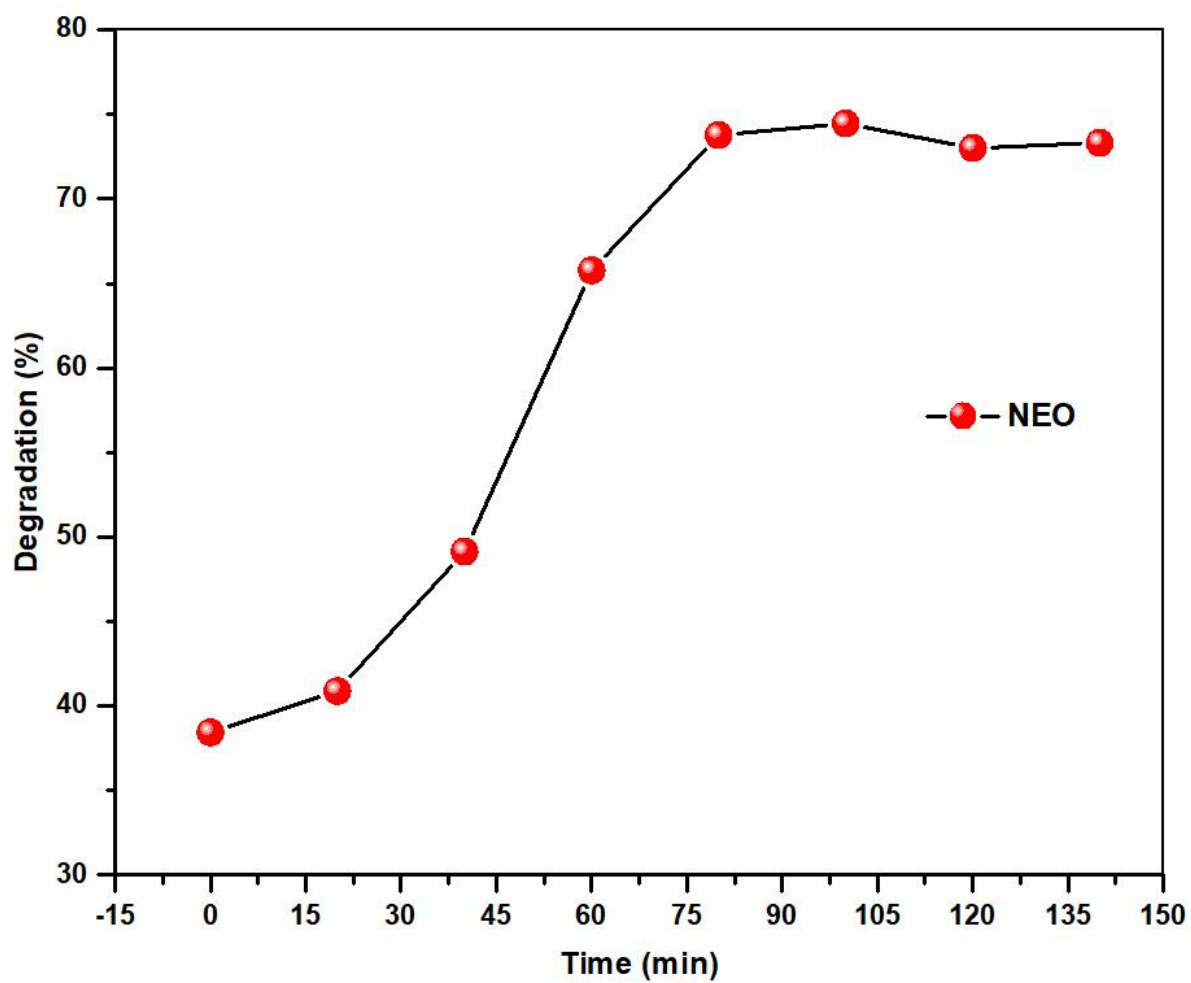


Figure 4.20: Photodegradation efficiency of Neomycin using Biosynthesized CuO

Source: Author's Field Work, 2025

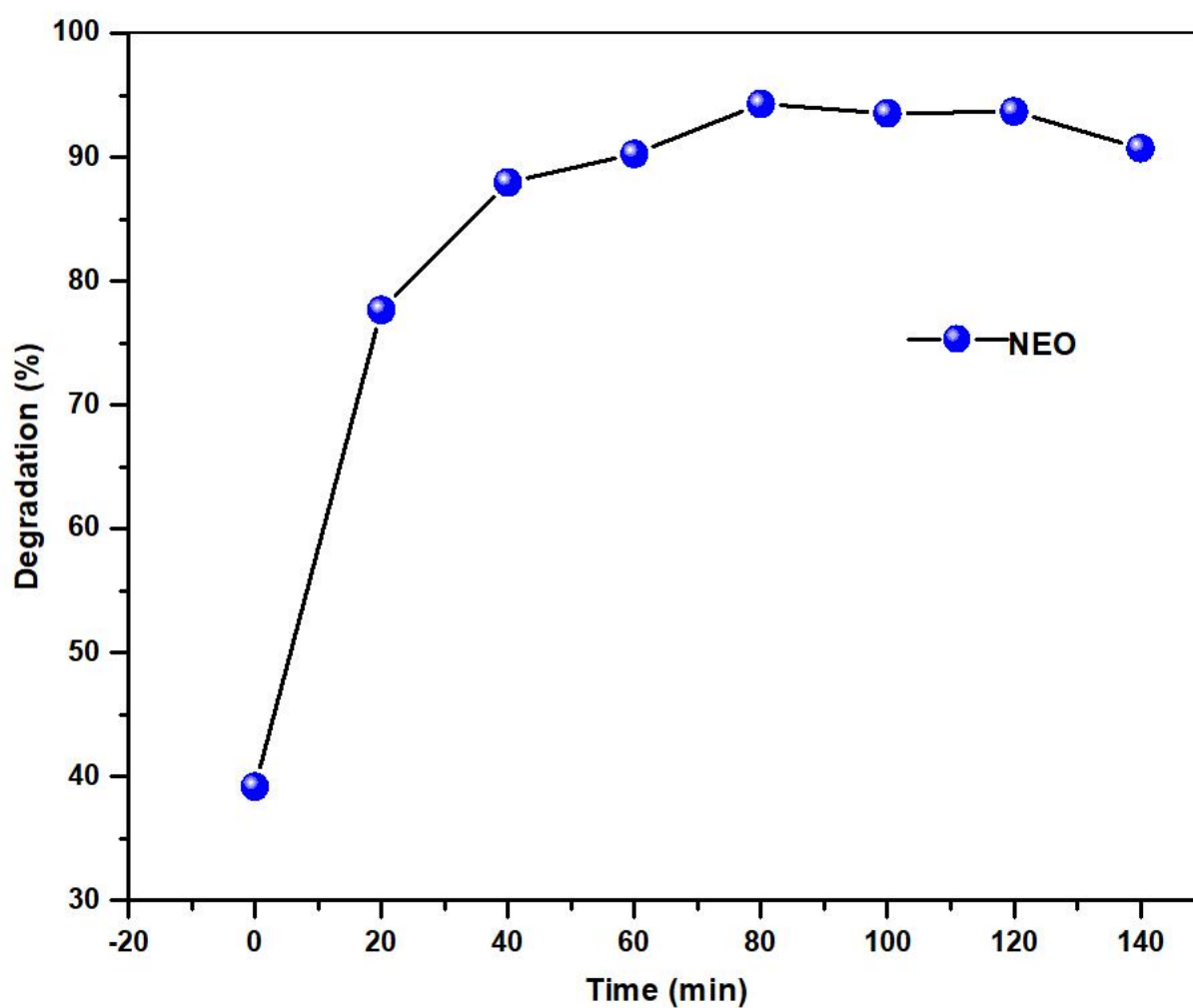


Figure 4.21: Photodegradation Efficiency of Neomycin using Biosynthesized ZnO

Source: Author's Field Work, 2025

Table 4.3: Comparison of ZnO-NPs and CuO Photocatalytic Activity Synthesized from Various Plant Extract Materials

Material used	Biological entity	Pollutant	Degradation efficiency (%)	Degradation time (min)	References
ZnO NPs	<i>Thymus vulgaris</i>	Tetracycline	95	30	22
CuO NPs	<i>Parthenium hysterophorus</i>	Rifampicin	98.4	8	23
CuO/Fe ₂ O ₃ NPs	<i>Psidium guajava</i>	Rhodamine B	88	80	24
Fe NPs	<i>Ficus hispida</i>	Neomycin	79.84	15	25
Co-ZnO NPs	<i>P. capillacea</i>	Ciprofloxacin	99	120	26
CuO NPs	<i>Syzygium malaccense</i>	Neomycin	75	105	Present study
ZnO NPs	<i>Syzygium malaccense</i>	Neomycin	95	80	Present study

Source: Author's Field Work, 2025

4.4 Degradation Kinetics Study

Kinetic analysis is essential for determining the rate of degradation. The experimental data of the first-order kinetic curves of NEO are shown in Figures 4.22 and 4.23. The applicability and validation of the first-order model were determined based on the values of the coefficient (R^2) and K . The kinetic reaction rate constant was calculated from the slope of the plot of $-\ln (C_t/C_0)$ versus experiment time (t). The K value was found for the CuO photocatalyst, with a value of 0.0072 min^{-1} and $R^2 = 0.83$. The results were consistent with a prior study that demonstrated that the first-order reaction rate constant was 0.0077 min^{-1} for the photodegradation of Oxytetracycline Dihydrate antibiotics using visible light and $\text{BTiO}_2\text{-ZnO}$ nanoparticles²⁶.

Figure 4.23 displays the results of a calculation of the photodegradation kinetics of NEO by biosynthesized ZnO-NPs. For the degradation of MB dye by produced CuO-NPs, the rate constant (K) is calculated using the pseudo-first-order rate equation. Plotting $\ln (C_0/C_t)$ against irradiation time yields a rate constant of 0.0072 min^{-1} . It is also found that the fitting correlation coefficient (R^2) is 0.83. At the end of the day, it is determined that the percentage of dye degradation increases as time increases and that the C_0/C_t decreases as time increases. The results indicate that the biosynthesized ZnO-NPs used in the leaf extract of *Syzygium malaccense* have superior photocatalytic activity on NEO antibiotic in comparison to CuO-NPs.

The electron and hole transfer that occurs in ZnO-NPs due to their distinct redox energy levels for their associated conduction and valence bands is the reason for their enhanced photocatalytic activity when compared to CuO-NPs. A longer lifespan for the charge carriers and improved interfacial charge transfer efficiency to adsorbed substrates are the results of effective charge

separation²⁷. By serving as electron acceptors and reducing the number of surface recombination sites, increased oxygen vacancies on the ZnO-NPs surface may have also helped to effectively degrade NEO. Additionally, oxygen vacancies can help the adsorbed O₂ absorb photo-induced electrons, producing superoxide radical anions at the same time, significantly improving the photocatalytic capabilities²⁷.

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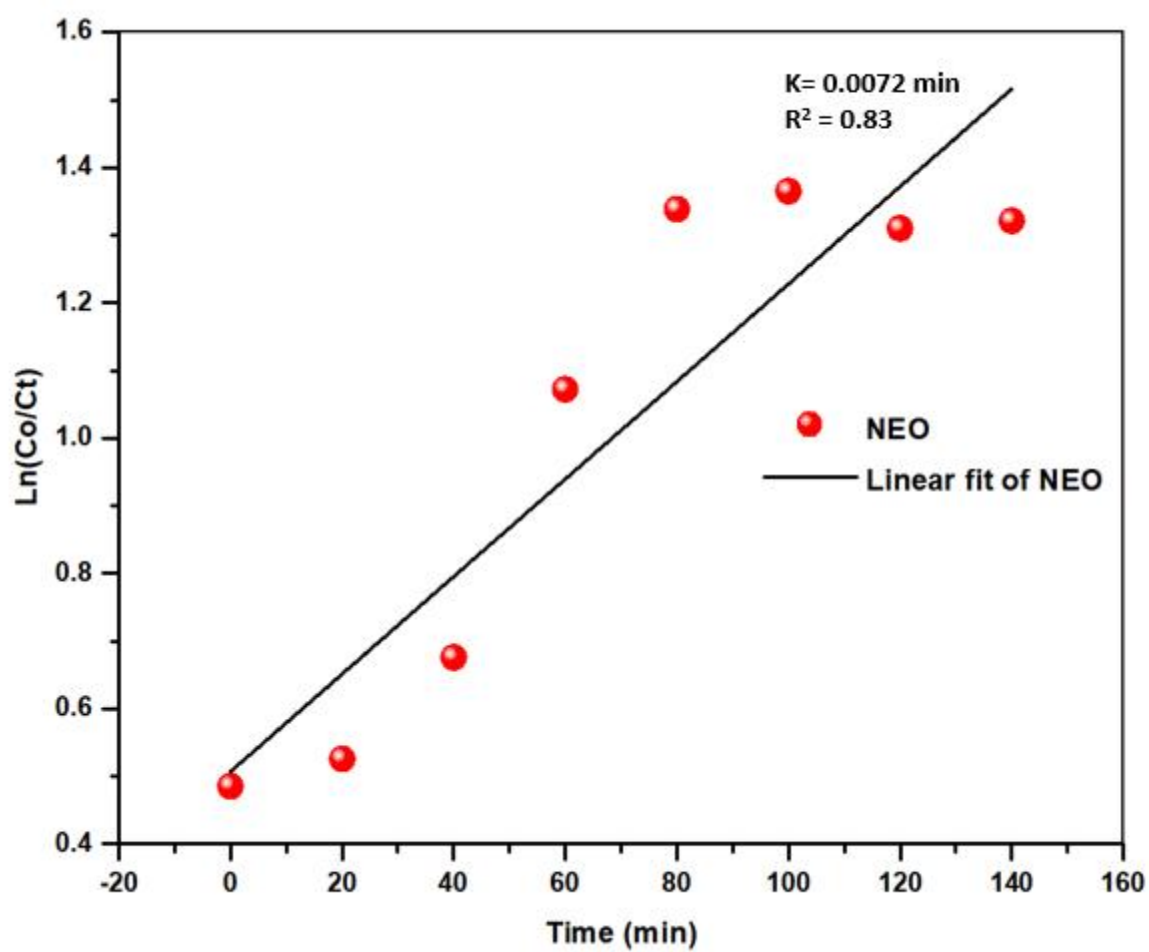


Figure 4.22: Kinetic study of photodegradation of NEO under optimum conditions using Biosynthesized CuO NPs.

Source: Author's Field Work, 2025

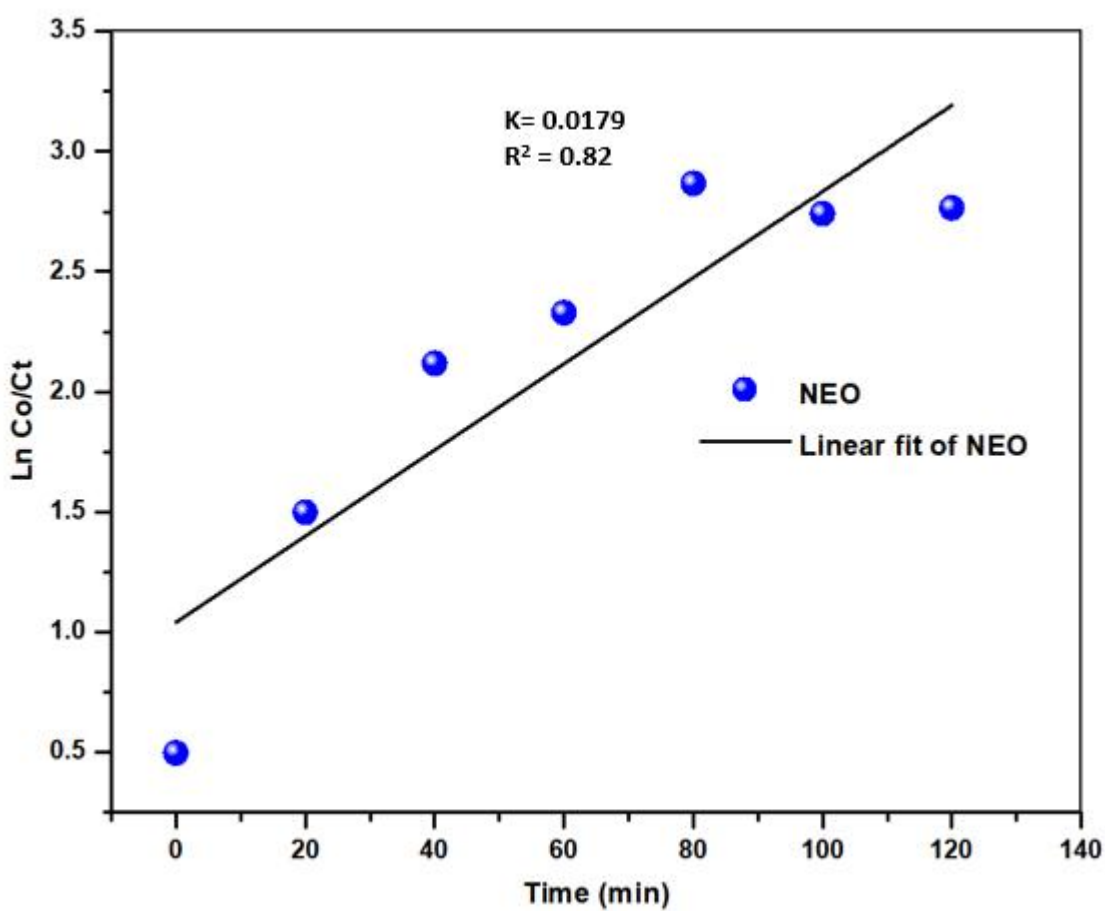


Figure 4.23: Kinetic study of photodegradation of NEO under optimum conditions using ZnO NPs

Source: Author's Field Work, 2025

Endnotes

1. M. Alqubati, S.O.M., Osman, S.A. Galil, M.A., Algrade, A. Mohammed Sultan, & A.M. Qaid. *Nonlinear effects of the biosynthesis temperature of ZnO nanoparticles on their structural, optical, and ultraviolet blocking parameters*. **Journal of Optics**, 53, 3, 2024, 2775-2792.
2. S. Thanaraj, A.N.K. Mitthun, P.G. Sravanthy, D.S. Carmelin, M. Surya, & M. Saravanan. *Green synthesis of aluminum oxide nanoparticles using clerodendrum phlomidis and their antibacterial, anti-inflammatory, and antioxidant activities*. **Cureus**, 16, 1, 2024.
3. C.B. Nettar, R.N. Bhowmik, & A.K. Sinha. *A comparative study of the lattice structure, optical band gap, electrical conductivity and polarization at different stages of the heat treatment of chemical routed Al(OH)₃*. **Ceramics International**, 48, 8, 2022, 10677-10687.
4. W.W. Andualem. *Green synthesis of cuo nanoparticles for the application of dye sensitized solar cell*. *Certified Journal 29 Andualem*. **World Journal of Pharmaceutical Research Wwww.Wjpr.Net** 9, 13, 2020, 30.
5. S.A. Akintelu, A.S. Folorunso, F.A. Folorunso, & A.K. Oyebamiji. *Green synthesis of copper oxide nanoparticles for biomedical application and environmental remediation*. **Heliyon**, 6, 7, 2020.
6. A. Rasheed, A.I. Ibrahim, & S. Reaad. *Synthesis and characterization of CuO nanoparticles for increase the efficiency of the photovoltaic cell*. **Egyptian Journal of Chemistry**, 66, 1, 2023, 49-53.
7. M.G. Batterjee, A. Nabi, M.R. Kamli, K.A. Alzahrani, E.Y. Danish, & M.A. Malik . *Green hydrothermal synthesis of zinc oxide nanoparticles for UV-light-induced photocatalytic degradation of ciprofloxacin antibiotic in an aqueous environment*. **Catalysts**, 12, 11, 2022, 1347.
8. M. Villen-Guzman, M.D.M. Cerrillo-Gonzalez, J. Paz-Garcia, J.M. Rodriguez-Maroto, & B. Arhoun. *VAL2O3rization of lemon peel waste as biosorbent for the simultaneous removal of nickel and cadmium from industrial effluents*. **Environ. Technol. Innov.** 2021, 21, 101380.
9. J.M. Santhoshkumar, S.V. Kumar, & S. Rajeshkumar. *Synthesis of zinc oxide nanoparticles using plant leaf extract against urinary tract infection pathogen*. **Resour.-Effic. Technol.** 2017, 3, 459–465.

10. J. Xia, H. Li, Z. Luo, H. Shi, K. Wang, H. Shu, & Y. Yan. *Microwave-assisted synthesis of flower-like and leaf-like CuO nanostructures via room-temperature ionic liquids*. **Journal of Physics and Chemistry of Solids**, 70, 11, 2009, 1461-1464.
11. S. Faisal, H. Jan, S.A. Shah, S. Shah, A. Khan, M.T. Akbar, M. Rizwan, F. Jan, N. Wajidullah & N. Akhtar. *Green synthesis of zinc oxide (ZnO) nanoparticles using aqueous fruit extracts of Myristica fragrans: Their characterizations and biological and environmental applications*. **ACS Omega**, 6, 2021, 9709–9722.
12. H. Chandra, P. Patel, P. Kumari, J.S. Jangwan, & S. Yadav. *Phyto-mediated synthesis of zinc oxide nanoparticles of Berberis aristata: Characterization, antioxidant activity and antibacterial activity with special reference to urinary tract pathogens*. **Materials Science and Engineering: C**, 102, 2019, 212-220.
13. H.B. Herbin, M. Aravind, M. Amalanathan, M.S.M. Mary, M.M. Lenin, C. Parvathiraja, & M.A. Islam. *Synthesis of silver nanoparticles using syzygium malaccense fruit extract and evaluation of their catalytic activity and antibacterial properties*. **Journal of Inorganic and Organometallic Polymers and Materials**, 32, 3, 2022, 1103-1115.
14. P. Pushparekha, B.K. Sarojini, & U. Vinoditha. *Effect of nano ZnO doping on structural, morphological and luminescent properties of pullulan films*. In **AIP Conference Proceedings**, 2020, 2244, 1.
15. A. Ahmed, M. Aqeel. & J. Alduhaidahawi. *Electrochemical synthesis of cuo and tio2 nanoparticles for dye-sensitized solar cells*. **Acta Chemica Iasi**, 31, 2, 2024 147–64.
16. J.K. Sharma, M.S. Akhtar, S. Ameen, P. Srivastava, & G. Singh. *Green synthesis of CuO nanoparticles with leaf extract of CA12O3tropis gigantea and its dye-sensitized solar cells applications*. **Journal of Alloys and Compounds**, 632, 2015, 321-325.
17. R. Shashanka, H. Esgin, V.M. Yilmaz, & Y. Caglar. *Fabrication and characterization of green synthesized ZnO nanoparticle based dye-sensitized solar cells*. **Journal of Science: Advanced Materials and Devices**, 5, 2, 2020, 185-191.
18. D. Ursu, N. Vaszilcsin, R. Bănica, & M. Miclau. *Effect of Al doping on performance of CuGaO 2 p-type dye-sensitized solar cells*. **Journal of Materials Engineering and Performance**, 25, 2016, 59-63.
19. Y.G. Alghamdi, B. Krishnakumar, M.A. Malik, & S. Alhayyani. *Design and preparation of biomass-derived activated carbon loaded TiO2 photocatalyst for photocatalytic degradation of reactive red 120 and ofloxacin*. **Polymers**, 14, 5, 2022, 880.

20. J. Malleshappa, H. Nagabhushana, S.C. Sharma, Y.S. Vidya, K.S. Anantharaju, S.C. Prashantha, B.D. Prasad, H.R. Naika, K. Lingaraju, & B.S. Surendra. *Leucas aspera mediated multifunctional CeO₂ nanoparticles: structural, photoluminescent, photocatalytic and antibacterial properties*. **Spectrochim Acta A**. 149, 2015, 452–462.
21. M.I. Din, F. Arshad, Z. Hussain, & M. Mukhtar. *Green adeptness in the synthesis and stabilization of copper nanoparticles: catalytic, antibacterial, cytotoxicity, and antioxidant activities*. **Nanoscale Res Lett**, 2017, 12, 1.
22. S.F. Alshahateet, S.A. Al-Trawneh, M. Er-Rajy, M. Zerrouk, K. Azzaoui, W.M. Al-Tawarh, & L. Rhazi. *Green synthesis of zinc oxide nanoparticles for tetracycline adsorption: experimental insights and DFT study*. **Plants**, 13, 23, 2024, 3386.
23. D.M. Nzilu, E.S. Madivoli, D.S. Makhanu, S.I. Wanakai, G.K. Kiprono, & P.G. Kareru. *Green synthesis of copper oxide nanoparticles and its efficiency in degradation of rifampicin antibiotic*. **Scientific reports**, 13, 1, 2023, 14030.
24. S. Kaushal, A. Kumar, H. Bains, & P.P. Singh. *Photocatalytic degradation of tetracycline antibiotic and organic dyes using biogenic synthesized CuO/Fe₂O₃ nanocomposite: pathways and mechanism insights*. **Environmental Science and Pollution Research**, 30, 13, 2023, 37092-37104.
25. S. Vijayaram, H. Razafindralambo, Y.Z. Sun, S. Vasantharaj, H. Ghafarifarsani, S.H. Hoseinifar, & M. Raeiszadeh. *Applications of green synthesized metal nanoparticles—a review*. **Biological Trace Element Research**, 202, 1, 2024, 360-386.
26. P. Sen, S.S. Soshi, & M.A. Gafur. *Photocatalytic degradation of oxytetracycline dihydrate from aqueous solution using nano ZnO and ZnO. xBaTiO₃ (x= 3%, 18%, 33% and 48%)*. **Materials Sciences and Applications**, 14, 12, 2023, 515-525.
27. L. Sawunyama, O. Oyewo, D.C. Onwudiwe, & S.S. Makgato. *Photocatalytic degradation of tetracycline using surface defective black TiO₂–ZnO heterojunction photocatalyst under visible light*. **Heliyon**, 9, 11, 2023.

Chapter Five

Conclusion

5.1 Summary of Findings

Three distinct varieties of environmentally sustainable, economically viable, and non-toxic nanoparticles Al_2O_3 , CuO , and ZnO were proficiently synthesized in the present study utilizing leaf extracts from *Syzygium malaccense* (Malay apple). The principal aim of this research is to fabricate and characterize Al_2O_3 , CuO , and ZnO nanoparticles prior to examining their catalytic properties. Additionally, the utilization of these nanomaterials as photanodes and spacers in dye-sensitized solar cells (DSSCs) was explored. Performance assessment of the DSSC was conducted through measurements of maximum voltage, maximum current, fill factor, open-circuit voltage, and short-circuit current. This investigation further demonstrated that the antibiotic neomycin can be efficiently eliminated from aqueous solutions when subjected to simulated ultraviolet light in the presence of Al_2O_3 , CuO , and ZnO nanoparticles. The efficacy of the removal process for the antibiotics was also significantly associated with kinetic analyses and contact duration. The synthesized nanoparticles underwent comprehensive characterization using Fourier-transform infrared spectroscopy (FTIR), ultraviolet-visible spectroscopy (UV-Vis), X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX).

The optical characteristics of Al_2O_3 nanoparticles were ascertained via Tauc's plot, yielding a band gap energy value of 2.09 eV alongside a maximum UV-Vis absorbance at 371.61 nm. The optical band gap energy for CuO nanoparticles was determined to be 2.05 eV, with their spectra exhibiting a well-defined, characteristic absorption peak at 370 nm. Moreover, the distinctive band of zinc oxide nanoparticles displayed a maximum absorbance peak value of 371 nm, while

a band gap energy of 3.23 eV was recorded. FTIR analysis indicated that the synthesized nanoparticles encompass various functional groups. The O-H, C-H, and C=O absorption bands (3600, 2700, and 1600 cm^{-1} respectively), along with the C-O, Al-O, Cu-O, and Zn-O bands (at approximately 400-800 cm^{-1}), exhibited differences among the three materials, as elucidated by the surface modification study of the biosynthesized nanoparticles Al_2O_3 , CuO, and ZnO. The detection of Al-O, Cu-O, and Zn-O characteristic bonds of the anatase structure at the same location is hypothesized to arise from the presence of copper and aluminum atoms, in addition to the FeO lattice structure. This observation supports the conclusion that the biosynthesized nanoparticles of ZnO, CuO, and Al_2O_3 were successfully synthesized.

The XRD analysis reveals that the synthesized nano materials are all crystalline, with sharp absorption bands. The SEM micrographs of Al_2O_3 , CuO, and ZnO NPs showed a consistent spherical shape, with average particle sizes of 27.50 nm, 11.01 nm, and 21.98 nm, respectively. Without any impurity peaks, the Al_2O_3 NP's EDX spectrum showed that the produced catalyst included the components aluminum (Al), oxygen (O), sulfur (S), and carbon (C). Al, O, S, and C have relative weight percentages of 10.68%, 76.07%, 8.47%, and 4.77%. The CuO NP's EDX spectrum showed that the produced nanoparticles included copper (Cu), oxygen (O), and sulfur (S) components without any contaminant peaks. Cu, O, and S have respective weight percentages of 33.25%, 57.24%, and 9.51%. The produced nanoparticles included zinc (Zn), oxygen (O), and sulfur (S) components without any impurity peaks, according to the ZnO NP's EDX spectrum in Figure 4.15. Cu, O, and S have relative weight percentages of 27.77%, 61.07%, and 11.16%. These findings unequivocally demonstrated the produced Al_2O_3 , CuO, and ZnO NPs' homogeneity and excellent purity. Monolithic DSSCs were developed using the

biosynthesized nanoparticles. The produced biosynthesized nanoparticles were then used to photodegrade the antibiotic (neomycin).

With an efficiency of 1.79%, an open circuit voltage of 0.48 V, a short-circuit current of 7.2 mA/cm², a V_{mp} of 0.35, an I_{mp} of 5.3 mA/cm², and a fill factor of 0.53, the solar-to-power conversion efficiency of DSSCs utilizing Al₂O₃ biogenic synthesized nanoparticles was demonstrated. A DSSC utilizing CuO biosynthesised nanoparticles recorded a 3.44% power conversion efficiency, an open circuit voltage of 0.38 V, a short-circuit current of 11.1 mA/cm², a V_{mp} of 0.37, an I_{mp} of 9.64 mA/cm², a fill factor of 0.85 and power conversion of 6.4%. The ZnO biosynthesized nanoparticle-based DSSC exhibited the best efficiency of solar-to-electric power conversion, with a fill factor of 0.57, an open circuit voltage of 0.52 V, a short-circuit current of 13.5 mA/cm², a V_{mp} of 0.4, and an I_{mp} of 40 mA/cm². ZnO > CuO > Al₂O₃ > Control (Without NPs) is the order of efficiency. This implies that the counter electrode containing ZnO > CuO > Al₂O₃ nanoparticles is very useful for promoting the consumption and transmission of electrical energy that is produced.

The photocatalytic performance of CuO and ZnO nanoparticles was studied towards NEO (365 nm) degradation under UV light irradiation. After 120 min of UV irradiation, 75% and 95% of NEO was degraded with CuO and ZnO nanoparticles respectively. Using CuO nanoparticle, as the time reaction of NEO increased from 0 to 120 min, the percent of degradation of NEO increased from 38% to 75% respectively, and it began to decline at 105 min to 120 min. After adding ZnO nanoparticle, 95% of NEO antibiotics was degraded at 80 min and it began to decline from 80 min to 120 min. ZnO photocatalyst proved more effective than CuO photocatalyst at degrading the antibiotic neomycin. The reduction in NEO concentration can be

attributed to oxidation–reduction reactions taking place on the surface of photocatalyst and efficient electron–hole splitting.

The kinetic reaction rate constant was measured from the slope of the plot of $-\ln (C_t/C_0)$ versus experiment time (t). The K value was found for the CuO photocatalyst which had the value of 0.0072 min^{-1} while $R^2 = 0.83$. The plot of $\ln (C_0/C_t)$ as a function of irradiation time produces the rate constant values 0.0072 min^{-1} . Furthermore, the fitting correlation coefficient (R^2) is determined to be 0.83. The *Syzygium malaccense* leaf extract using biosynthesized ZnO-NPs shows better photocatalytic activity on NEO antibiotic compared to CuO-NPs. The improved photocatalytic activity of ZnO-NPs compared to the CuO-NPs.

5.2 Conclusion

This research shows the environmentally friendly catalytic synthesis of aluminum oxide (Al_2O_3), copper oxide (CuO), and zinc oxide (ZnO) nanoparticles (NPs) employing the leaf extract of *Syzygium malaccense* (Malay apple). The use of biosynthesized NPs of Al_2O_3 , CuO, and ZnO as counter electrodes for dye-sensitized solar cells (DSSCs) enhanced the power efficiency, fill factor, open-circuit voltage, and short-circuit current density of the solar cell. The incorporation of the semiconductor in the order of $\text{ZnO} > \text{CuO} > \text{Al}_2\text{O}_3$ nanoparticles significantly improves the performance of DSSCs, thereby illustrating the synergistic advantages of integrating copper oxide, aluminum nanoparticles, and zinc oxide. Furthermore, the synthesized CuO and ZnO NPs displayed superior efficacy in the removal of neomycin from wastewater, achieving a maximum removal efficiency of 75% and 95%, respectively. The degradation kinetics of the neomycin antibiotic conform to the pseudo-first-order kinetic model. Consequently, the eco-friendly and economically viable green synthesis of CuO and ZnO NPs mediated by *Syzygium malaccense*

holds considerable promise for the degradation of antibiotics within wastewater treatment facilities, contributing to the mitigation of escalating water pollution issues. Serving as an effective and economical approach for the remediation of neomycin-contaminated wastewater, ZnO NPs have consistently proven to be the most promising biosynthesized nanoparticles, demonstrating significant potential for both antibiotic decomposition or degradation and the fabrication of DSSCs.

5.3 Recommendations

- i. Future research should focus on the usability of biosynthesized CuO and ZnO NPs in large-scale wastewater treatment and identifying actual degradation products and their implications on the ecosystem.
- ii. It is recommended that more study be conducted on other materials that maybe utilized to improve the catalytic behavior of carbon materials employed as DSSC counter electrodes. This might effectively expand the technology's applicability and cost-effectiveness.
- iii. Further studies should be conducted on recyclability of biosynthesized nanoparticles.

5.4 Contribution to Knowledge

The findings of this research provide a baseline for the investigations into the synthesis of Al₂O₃, CuO, and ZnO nanoparticles using *Syzygium malaccense* leaf extracts, as durable, eco-bening and cost effective approach for nanoparticle synthesis. Inspired by the principle of natural photosynthesis, dye-sensitized solar cells have become a credible alternative devices which serves as renewable and environmentally friendly energy generation. The adoption of the metal oxide as the photoanode solar cell fabrication improved efficiency of the DSSC. Furthermore, the quest to mitigate the menace of water pollution is at the forefront of public health

practioneers and enviromental scientist. In order to mitigate the hazards to human health and the environment challenges associated with drinking polluted water. This study provide a simple and effective means to degrade antibiotics from water/wastewater using the biogenic synthesized nanoparticles.

5.5 Suggested Areas for Further Studies

Lack of access to sophisticated equipment for material characterization like, Raman spectroscopy, high-resolution BET surface area measurements, High resolution Transmission Electron Microscopy (HR-TEM), and thermogravimetric analysis (TGA) hindered the comprehensive characterization of the synthesized nanoparticle materials. The thereapeutic properties of the nanomaterial should be assessed in order to determine their tendency to be used as probable drug or vehicle for drug delivery system.

Bibliography

Book

- Pandey, A.K., & Samykano, M. *Solar energy: direct and indirect methods to harvest usable energy, in Dye-sensitized solar cells*. Academic Press, Massachusetts, United States, 2022, 1-24.
- Tegegne, N.A., & Hone, F.G. *Solar cell technology: challenges and progress, in Electrode materials for energy storage and conversion*. CRC Press, Boca Raton, United states, 2020, 437-471.

Conference Proceedings

- Aung Kyaw, H.M., Yaacob, K.A., Mohd Noor, A.F., Matsuda, A., & Kawamura, G. *Effect of deposition time CdSe-TiO₂ nanocomposite film by electrophoretic deposition for quantum dot sensitized solar cell*. Materials Today: Proceedings, 17, 2019, 736-742.
- Pushparekha, P., Sarojini, B. K., & Vinoditha, U. *Effect of nano ZnO doping on structural, morphological and luminescent properties of pullulan films*. In AIP Conference Proceedings, 2020, 2244, 1.
- Runguphan, T., & Kitpichai, J. *Coaction of bio-sorption and bio-filtration for the remediation of domestic and agricultural wastewater contaminated with heavy metal*. IOP Conf. Ser. Mater. Sci. Eng. 965, 2020, 012010.
- Suman, P., Sharma, P., & Goyal, P. *Evolution of PV technology from conventional to nano-materials*. Materials Today: Proceeding, 28, 2020, 1593-1597.
- Thakar, M.A., Jha, S.S., Phasinam, K.R., Qureshi, Y., & Babu, V.H. *X ray diffraction analysis and evaluation of antioxidant activity of copper oxide nanoparticles synthesized from leaf extract of Cissus vitiginea*. Mater. Today Proc. 2021.

Journal

- Abdulah, H. I., Rheima, A. M., Hussain, D. H., & Abed, H. J. *Synthesis of Fe₂O₃ nanoparticles by photolysis method for novel dye-sensitized solar cell*. **Journal of Advanced Sciences and Nanotechnology**, 1, 1, 2022, 292022, 1–8.
- Aboelfetoh, E.F., Elabedien, M.E.Z., & Ebeid, E.Z.M. *Effective treatment of industrial wastewater applying SBA-15 mesoporous silica modified with graphene oxide and hematite nanoparticles*. **J. Environ. Chem. Eng.** 9, 2021, 104817.
- Agha, M., El-Kemary, M., Oraby, A.H., & Salim, E. *Efficient multilayers organic solar cells with hybrid interfacial layer-based P₃HT and CuO nanoparticles*. **Journal of Inorganic and Organometallic Polymers and Materials**, 34, 2, 2024, 557-564.
- Ahmadi, F., Zinatizadeh, A.A., Asadi, A., McKay, T., & S. Azizi, S. *Simultaneous carbon and nutrients removal and PHA production in a novel single air lift bioreactor treating an industrial wastewater*. **Environ. Technol. Innov.** 18, 2020, 100776.
- Ahmed, Ali A., & Aqeel M. Jreo Alduhaidahawi. *Electrochemical synthesis of CuO and TiO₂ nanoparticles for dye-sensitized solar cells*. **Acta Chemica Iasi**, 31, 2, 2024 147–64.
- Akhil, D., Lakshmi, D., Senthil Kumar, P., Vo, D.V.N., & Kartik, A. *Occurrence and removal of antibiotics from industrial wastewater*. **Environ. Chem. Lett.** 19, 2, 2021, 1477–1507.
- Akin, S. *Boosting the efficiency and stability of perovskite solar cells through facile molecular engineering approaches*. **Sol Energy**, 199, 2020, 136–142.
- Al-bahrani, M.R., Ahmad, W., Mehnane, H.F., Chen, Y., Cheng, Z., & Gao, Y. *Enhanced electrocatalytic activity by rGO/MWCNTs/NiO counter electrode for dye- sensitized solar cells*. **Nano-Micro Letters**, 7, 2015, 298-306.
- Alghamdi, Y.G., Krishnakumar, B., Malik, M.A., & Alhayyani, S. *Design and preparation of biomass-derived activated carbon loaded TiO₂ photocatalyst for photocatalytic degradation of reactive red 120 and ofloxacin*. **Polymers**, 14, 5, 2022, 880.
- Ali, J., Bibi, S., Jatoi, W.B., Tuzen, M., Jakhrani, M.A., Feng, X., & Saleh, T.A. *Green synthesized zinc oxide nanostructures and their applications in dye-sensitized solar cells and photocatalysis: A review*. **Materials Today Communications**, 2023, 106840.
- Alqubati, M., Osman, S. O. M., Galil, M. S. A., Algradee, M. A., Mohammed Sultan, A., & Qaid, A. M. *Nonlinear effects of the biosynthesis temperature of ZnO nanoparticles on their structural, optical, and ultraviolet blocking parameters*. **Journal of Optics**, 53, 3, 2024, 2775-2792.
- Alshahateet, S.F., Al-Trawneh, S.A., Er-Rajy, M., Zerrouk, M., Azzaoui, K., Al-Tawarh, W. M., & Rhazi, L. *Green synthesis of zinc oxide nanoparticles for tetracycline adsorption: experimental insights and DFT study*. **Plants**, 13, 23, 2024, 3386.

- Arumugam, B., Manaharan, T., Heng, C.K., Kuppusamy, U.R., & Palanisamy, U.D. *Antioxidant and antiglycemic potentials of a standardized extract of Syzygium malaccense*. **LWT-Food Sci. Technol.** 59, 2, 2014, 707–712.
- Batista, A.G., Mendonça, M.C., Soares, E.S., da Silva-Maia, J.K., Dionísio, A.P., Sartori, C.R., da Cruz-Höfling, M.A., & Júnior, M.R. *Syzygium malaccense fruit supplementation protects mice brain against high-fat diet impairment and improves cognitive functions*. **J. Funct. Foods**, 65, 2020, 103745.
- Batterjee, M. G., Nabi, A., Kamli, M. R., Alzahrani, K. A., Danish, E. Y., & Malik, M. A. *Green hydrothermal synthesis of zinc oxide nanoparticles for UV-light-induced photocatalytic degradation of ciprofloxacin antibiotic in an aqueous environment*. **Catalysts**, 12, 11, 2022, 1347.
- Begum, S.J., Pratibha, S., Rawat, J.M., Venugopal, D., Sahu, P., Gowda, A., & Jaremko, M. *Recent advances in green synthesis, characterization, and applications of bioactive metallic nanoparticles*. **Pharmaceuticals**, 15, 4, 2022, 455.
- Borousan, F., Yousefi, R., & Shabani, P. *Tuning the size of PbSe nanocubes for solar-cell applications*. **Mater Lett**, 268, 2020, 127590.
- Cao, D., Yin, H., Yu, X., Zhang, J., Jiao, Y., Zheng, W., Mi, B., & Gao, Z. *Role of modifying photoanodes by organic titanium on charge collection efficiency enhancement in dye-sensitized solar cells*. **Advanced Engineering Materials**, 22, 2019, 1901071.
- Chandra, H., Patel, D., Kumari, P., Jangwan, J. S., & Yadav, S. *Phyto-mediated synthesis of zinc oxide nanoparticles of Berberis aristata: Characterization, antioxidant activity and antibacterial activity with special reference to urinary tract pathogens*. **Materials Science and Engineering: C**, 102, 2019, 212-220.
- Chang, S., Yang, X., Sang, Y., & Liu, H. *Highly efficient photocatalysts and continuous-flow photocatalytic reactors for degradation of organic pollutants in wastewater*. **Chem Asian J** 11, 2016, 2352–2371.
- Deshpande, B., Agrawal, P., Yenkie, M., & Dhoble, S. *Prospective of nanotechnology in degradation of waste water: A new challenges*. **Nano-Struct. Nano-Objects**, 22, 2020, 100442.
- Di, J., Xia, J., Ji, M., Li, H., Xu, H., Li, H., & Chen, R. *The synergistic role of carbon quantum dots for the improved photocatalytic performance of Bi₂MoO₆*. **Nanoscale** 7, 2015, 11433–11443.
- Din, M.I., Arshad, F., Hussain, Z., & Mukhtar, M. *Green adeptness in the synthesis and stabilization of copper nanoparticles: catalytic, antibacterial, cytotoxicity, and antioxidant activities*. **Nanoscale Res Lett**, 2017, 12, 1.
- El-sayed, M.E.A. *Nanoadsorbents for Water and Wastewater Remediation*. **Sci. Total Environ.** 2020, 739, 139903.

- Faisal, S., Jan, H., Shah, S.A., Shah, S., Khan, A., Akbar, M.T., Rizwan, M., Jan, F., Wajidullah; Akhtar, N. *Green synthesis of zinc oxide (ZnO) nanoparticles using aqueous fruit extracts of Myristica fragrans: Their characterizations and biological and environmental applications*. **ACS Omega**, 6, 2021, 9709–9722.
- Gomathi, M., Sankar, A., Kannan, S., Shkir, M., & Reddy, V.R.M. *Tin selenide/carbon black nanocomposite-based high efficiency counter electrode for dye-sensitized solar cells (DSSCs)*. **Chemical Physics Letters**, 802, 2022, 139802.
- Guan, B., Yu, J., Guo, S., Yu, S., & Han, S. *Porous nickel doped titanium dioxide nanoparticles with improved visible light photocatalytic activity*. **Nanoscale Adv.** 2, 2020, 1352–1357.
- Guo, J., Li, Y., Hu, D., & Liu, H. *Preparation of transition-metal-doped ZnO nanophotocatalysts and their performance on photocatalytic degradation of antibiotic wastewater*. **Desalin. Water Treat.** 2014, 1–8.
- Hamidi, H., M. Zarrineh, A. Es-Haghi, & A. Ghasempour. *Rapid and sensitive determination of neomycin and kanamycin in measles, mumps, and rubella vaccine via high-performance liquid chromatography-tandem mass spectrometry using modified superparamagnetic Fe₃O₄ nanospheres*. **J Chromatogr A**, 1625, 2020, 461343.
- He, X., Kai, T., & Ding, P. *Heterojunction photocatalysts for degradation of the tetracycline antibiotic: a review*. **Environ. Chem. Lett.** 19, 6, 2021, 4563–4601.
- Herbin, H. B., Aravind, M., Amalanathan, M., Mary, M. S. M., Lenin, M. M., Parvathiraja, C., & Islam, M. A. *Synthesis of silver nanoparticles using syzygium malaccense fruit extract and evaluation of their catalytic activity and antibacterial properties*. **Journal of Inorganic and Organometallic Polymers and Materials**, 32, 3, 2022, 1103-1115.
- Huang, J., Li, D., Li, R., Zhang, Q., Chen, T., Liu, H., Liu, Y., Lv, W., & Liu, G. *An efficient metal-free phosphorus and oxygen co-doped g-C₃N₄ photocatalyst with enhanced visible light photocatalytic activity for the degradation of fluoroquinolone antibiotics*. **Chem. Eng. J.** 374, 2019, 242–253.
- Huang, Q.S., Wu, W., Wei, W., Song, L., Sun, J., & Ni, B.J.. *Highly-efficient Pb²⁺ removal from water by novel K₂W₄O₁₃ nanowires: performance, mechanisms and DFT calculation*. **Chem Eng J**, 381, 2020, 122632.
- Huang, Y., Wang, K., Guo, T., Li, J., Wu, X., & Zhang, G. *Construction of 2D/2D Bi₂Se₃/g-C₃N₄ nanocomposite with High interfacial charge separation and photo- heat conversion efficiency for selective photocatalytic CO₂ reduction*. **Appl. Catal. B Environ.** 277, 2020, 119232.
- Imran, M., Abutaleb, A., Ali, M. A., Ahamad, T., Ansari, A. R., Shariq, M., & Khan, A. *UV light enabled photocatalytic activity of α -Fe₂O₃ nanoparticles synthesized via phase transformation*. **Materials Letters**, 258, 2020, 126748.

- Jassby, D., Cath, T.Y., & H. Buisson, H. *The role of nanotechnology in industrial water treatment*. **Nat. Nanotechnol.** 13, 2018, 670–672.
- Jowitt, S.M., Mudd, G.M., & Thompson, J.F.H. *Future availability of non-renewable metal resources and the influence of environmental, social, and governance conflicts on metal production*. **Communications Earth & Environment**, 1, 2020, 13.
- Kadhum, H. A., Salih, W. M., & Rheima, A. M. *Improved PSi/c-Si and Ga/PSi/c-Si nanostructures dependent solar cell efficiency*. **Applied Physics A**, 126, 10, 2020, 1-5.
- Kalfa, A., Shapira, B., Shopin, A., Cohen, I., Avraham, E., & Aurbach, D. *Capacitive deionization for wastewater treatment: Opportunities and challenges*. **Chemosphere**, 241, 2020, 125003.
- Kamil, A. F., Abdullah, H. I., Rheima, A. M., & Mohammed, S. H. *Impact of Fe_2NiO_4 nanoparticles to increase efficiency of dye-sensitized solar cells*. **Materials Today: Proceedings**, 49, 2022, 2727-2732.
- Kamil, A. F., Abdullah, H. I., Rheima, A. M., Mohammed, S. H., Tumaa, S. J., & Abed, R. M. *Fabrication of Fe_2CuO_4 nanoparticles via photolysis technique for improved performance in dye-sensitized solar cells*. **Digest Journal of Nanomaterials & Biostructures (DJNB)**. 16, 4, 2021.
- Kamil, A. F., Abdullah, H., Rheima, A. M., & Mohammed, S. H. (2021). *Photochemical synthesized NiO nanoparticles based dye-sensitized solar cells: a comparative study on the counter electrodes and dye-sensitized concentrations*. **Journal of Ovonic Research**. 17, 3, 2020, 299-305.
- Kanimozhi, S., Prabu, K. M., Thambidurai, S., & Suresh, S. *Dye-sensitized solar cell performance and photocatalytic activity enhancement using binary zinc oxide-copper oxide nanocomposites prepared via co-precipitation route*. **Ceramics International**, 47, 21, 2021, 30234-30246.
- Kaushal, S., Kumar, A., Bains, H., & Singh, P.P. *Photocatalytic degradation of tetracycline antibiotic and organic dyes using biogenic synthesized $\text{CuO}/\text{Fe}_2\text{O}_3$ nanocomposite: pathways and mechanism insights*. **Environmental Science and Pollution Research**, 30, 13, 2023, 37092-37104.
- Kouhnavard, M., Ludin, N.A., Ghaffari, B.V., Ikeda, S., Sopian, K., & Miyake, M. *Hydrophilic carbon/ TiO_2 colloid composite: a potential counter electrode for dye-sensitized solar cells*. **Journal of Applied Electrochemistry**, 46, 2016, 259-266.
- Kovalakova, P., Cizmas, L., McDonald, T.J., Marsalek, B., Feng, M., & Sharma, V.K. *Occurrence and toxicity of antibiotics in the aquatic environment: A review*. **Chemosphere**, 251, 2020, 126351.

- Liang, Z., Yang, J., Zhou, C., Mo, Q., & Zhang, Y. *Carbon quantum dots modified BiOBr microspheres with enhanced visible light photocatalytic performance*. **Inorg. Chem. Commun.** 90, 2018, 97–100.
- Irazzaq, A.K., Bogнар, G., & Plesz, B. *Evaluation of different methods for solar cells/modules parameters extraction*. **Solar Energy**. 196, 2020, 183-195.
- Malleshappa, J., Nagabhushana, H., Sharma, S.C., Vidya, Y.S., Anan- tharaju, K.S., Prashantha, S.C., Prasad, B.D., Naika, H.R., Lingaraju, K., & Surendra, B.S. *Leucas aspera mediated multifunctional CeO₂ nanoparticles: structural, photoluminescent, photocatalytic and antibacterial properties*. **Spectrochim Acta A**. 149, 2015, 452–462.
- Medhi, R., Marquez, M.D., & Lee, T.R. *Visible-light-active doped metal oxide nanoparticles: review of their synthesis, properties, and applications*. **ACS Appl. Nano Mater.** 2020, 3, 6156–6185.
- Memari, M., & Memarian, N. *Designed structure of bilayer TiO₂–Nb₂O₅ photoanode for increasing the performance of dye-sensitized solar cells*. **Journal of Materials Science: Materials in Electronics**. 31, 2020, 2298-2307.
- Meng, J., Hu, X., Chen, P., Coffman, D.M., & Han, M. *The unequal contribution to global energy consumption Al₂O₃ in the supply chain*. **Journal of Environmental Management**. 268, 2020, 110701.
- Moon, M.M.A., Rahman, M., Hossain, J., & Ismail, A.B.M. *Comparative study of the second generation a-Si:H, CdTe, and CIGS thin-film solar cells*. **Advanced Materials Research**, 1154, 2019, 102-111.
- Mutezo, G., & Mulopo, J. *A review of Africa's transition from fossil fuels to renewable energy using circular economy principles*. **Renewable and Sustainable Energy Reviews**. 137, 2021, 110609.
- Naganthran, A., Verasoundarapandian, G., Khalid, F.E., Masarudin, M. J., Zulkharnain, A., Nawawi, N.M., & Ahmad S.A. *Synthesis, characterization and biomedical application of silver nanoparticles*. **Materials**, 15, 2, 2022, 427.
- Nettar, C. B., Bhowmik, R. N., & Sinha, A. K. *A comparative study of the lattice structure, optical band gap, electrical conductivity and polarization at different stages of the heat treatment of chemical routed Al(OH)₃*. **Ceramics International**, 48, 8, 2022, 10677-10687.
- Nogueira, A.C., Gomes, L.E., Ferencz, J.A.P., Rodrigues, J.E.F.S., Gonçalves, R.V., & Wender, H. *Improved visible light photoactivity of CuBi₂O₄/CuO heterojunctions for photodegradation of methylene blue and metronidazole*. **The Journal of Physical Chemistry C**, 123, 2019, 25680–25690.
- Nwaigwe, K., Mutabilwa, P., & Dintwa, E. *An overview of solar power (PV systems) integration into electricity grids*. **Materials Science for Energy Technologies**, 2, 2019, 629-633.

- Nzilu, D.M., Madivoli, E.S., Makhanu, D.S., Wanakai, S.I., Kiprono, G.K., & Kareru, P.G. *Green synthesis of copper oxide nanoparticles and its efficiency in degradation of rifampicin antibiotic*. **Scientific reports**, 13, 1, 2023, 14030.
- Oladipo, A.A., & Gazi, M. *Ternary $Ni_{0.5}Zn_{0.5}Fe_2O_4$ /carbon nanocomposite as counter electrode for natural dye-sensitized solar cells: Electro-photovoltaic characterizations*. **Journal of Photochemistry and Photobiology A: Chemistry**, 425, 2022, 113665.
- Olga, M., Jana, M., Anna, M., Irena, K., Jan, M., & Alena, Č. *Antimicrobial properties and applications of metal nanoparticles biosynthesized by green methods*. **Biotechnol Adv**, 2022, 107905.
- Oliveira, F.I., Gallão, M.I, Rodrigues, S., & Fernandes, FA.N. *Dehydration of Malay apple (*Syzygium malaccense* L.) using ultra- sound as pre-treatment*. **Food Bioprocess Technol.** 4, 4, 2011, 610–615.
- Pattarith K., & Areerob, Y. *Fabrication of Ag nanoparticles adhered on rGO based on both electrodes in dye-sensitized solar cells (DSSCs)*. **Renewables: Wind, Water, and Solar**, 2020, 7, 2020, 1-10.
- Qureshi, A.A., Javed, S., Asif Javed, H.M., Akram, A., Jamshaid, M.J., & Shaheen, A. *Strategic design of Cu/TiO₂-based photoanode and rGO-Fe₃O₄-based counter electrode for optimized plasmonic dye-sensitized solar cells*. **Optical Materials**, 2020, 109
- Rafique, S., Rashid, I., & R. Sharif, R. *Cost effective dye sensitized solar cell based on novel Cu polypyrrole multiwall carbon nanotubes nanocomposites counter electrode*. **Scientific Reports**, 11, 1, 2021, 14830.
- Rasheed, A., Ibrahim, A. I., & Reaad, S. *Synthesis and characterization of CuO nanoparticles for increase the efficiency of the photovoltaic cell*. **Egyptian Journal of Chemistry**, 66, 1, 2023, 49-53.
- Ren, M., Chen, J., Wang, P., Hou, J., Qian, J., Wang, C., & Ao, Y. *Construction of silver iodide/silver/Bismuth Tantalate Z-scheme photocatalyst for effective visible light degradation of organic pollutants*. **J. Colloid Interface Sci.** 532, 2018, 190–200.
- Santhoshkumar, J.M., Kumar, S.V., & Rajeshkumar, S. *Synthesis of zinc oxide nanoparticles using plant leaf extract against urinary tract infection pathogen*. **Resour.-Effic. Technol.** 2017, 3, 459–465.
- Sawant, J.P., & Kale, R.B. *CZTS counter electrode in dye-sensitized solar cell: enhancement in photo conversion efficiency with morphology of TiO₂ nanostructured thin films*. **Journal of Solid State Electrochemistry**, 24, 2020, 461-472.
- Sawunyama, L., Oyewo, O., Onwudiwe, D.C., & Makgato, S.S. *Photocatalytic degradation of tetracycline using surface defective black TiO₂-ZnO heterojunction photocatalyst under visible light*. **Heliyon**, 9, 11, 2023.

- Sen, P., Soshi, S. S., & Gafur, M. A. *Photocatalytic degradation of oxytetracycline dihydrate from aqueous solution using nano ZnO and ZnO. xBaTiO₃ (x= 3%, 18%, 33% and 48%). **Materials Sciences and Applications**, 14, 12, 2023, 515-525.*
- Serwecińska, L. *Antimicrobials and antibiotic-resistant bacteria: a risk to the environment and to public health. **Water***. 12, 12, 2020, 3313.
- Sharma, J. K., Akhtar, M. S., Ameen, S., Srivastava, P., & Singh, G. Green synthesis of CuO nanoparticles with leaf extract of *CA12O3tropis gigantea* and its dye-sensitized solar cells applications. **Journal of Alloys and Compounds**, 632, 2015, 321-325.
- Shashanka, R., Esgin, H., Yilmaz, V. M., & Caglar, Y. *Fabrication and characterization of green synthesized ZnO nanoparticle based dye-sensitized solar cells. **Journal of Science: Advanced Materials and Devices***, 5, 2, 2020, 185-191.
- Sher, F., Hanif, K., Iqbal, S.Z., & Imran, M. *Implications of advanced wastewater treatment: Electrocoagulation and electroflocculation of effluent discharged from a wastewater treatment plant. **J. Water Process Eng.*** 33, 2020, 101101.
- Thambidurai, S., Gowthaman, P., Venkatachalam, M., Suresh, S., & Kandasamy, M. *Morphology dependent photovoltaic performance of zinc oxide-cobalt oxide nanoparticle/nanorod composites synthesized by simple chemical co-precipitation method. **Journal of Alloys and Compounds***, 852, 2021, 156997.
- Thanaraj, S., Mitthun, A. N. K., Sravanthy, P. G., Carmelin, D. S., Surya, M., & Saravanan, M. *Green synthesis of aluminum oxide nanoparticles using clerodendrum phlomidis and their antibacterial, anti-inflammatory, and antioxidant activities. **Cureus***, 16, 1, 2024.
- Valadi, K., Gharibi, S., Taheri-Ledari, R., Akin, S., Maleki, A., & Shalan, A.E. *Metal oxide electron transport materials for perovskite solar cells: a review. **Environmental Chemistry Letters***, 19, 3, 2021, 2185-2207.
- Vijayaram, S., Razafindralambo, H., Sun, Y.Z., Vasantharaj, S., Ghafarifarsani, H., Hoseinifar, S.H., & Raeeszadeh, M. *Applications of green synthesized metal nanoparticles: a review. **Biological Trace Element Research***, 202, 1, 2024, 360-386.
- Vijayaram, S., Razafindralambo, H., Sun, Y.Z., Vasantharaj, S., Ghafarifarsani, H., Hoseinifar, S. H., & Raeeszadeh, M. *Applications of green synthesized metal nanoparticles—a review. **Biological Trace Element Research***, 202, 1, 2024, 360-386.
- Villen-Guzman, M., Cerrillo-Gonzalez, M.d.M., Paz-Garcia, J., Rodriguez-Maroto, J.M., & Arhoun, B. *VA12O3rization of lemon peel waste as biosorbent for the simultaneous removal of nickel and cadmium from industrial effluents. **Environ. Technol. Innov.*** 2021, 21, 101380.
- Wang, M., Jin, C., Li, Z., You, M., Zhang, Y., & Zhu, T. *The effects of bismuth (III) doping and ultrathin nanosheets construction on the photocatalytic performance of graphitic carbon nitride for antibiotic degradation. **J. Colloid Interface Sci.*** 533, 2019, 513–525.

- Xia, J., Li, H., Luo, Z., Shi, H., Wang, K., Shu, H., & Yan, Y. *Microwave-assisted synthesis of flower-like and leaf-like CuO nanostructures via room-temperature ionic liquids*. **Journal of Physics and Chemistry of Solids**, 70, 11, 2009, 1461-1464.
- Yadeta, T.F., & Imae, T. *Effect of carbon dot on photovoltaic performance of n-TiO₂/p-NiO and n-TiO₂/p-CuO heterojunctions in dye-sensitized solar cells*. **Applied Surface Science**, 2023, 157880.
- Yang, L., Wang, J., Zhang, Y., Zhou, B., Tan, P., & Pan, J. *Construction of S-scheme BiOCl/CdS composite for enhanced photocatalytic degradation of antibiotic*. **J. Mater. Sci. -Mater. El.** 33, 16, 2022, 13303–13315.
- Yang, X., Chen, Z., Zhao, W., Liu, C., Qian, X., Zhang, M., & Ok, Y. S. *Recent advances in photodegradation of antibiotic residues in water*. **Chemical Engineering Journal**, 405, 2021, 126806.
- Yildiz, Z.K., Atilgan, A., Atli, A., Ozel, K., Altinkaya, C., & Yildiz, A. *Enhancement of efficiency of natural and organic dye sensitized solar cells using thin film TiO₂ photoanodes fabricated by spin-coating*. **Journal of Photochemistry and Photobiology A: Chemistry**, 368, 2019, 23-29.
- Zahid, T., Arshed, N., Munir, M., & Hameed, K. *Role of energy consumption preferences on human development: a study of SAARC region*. **Economic Change and Restructuring**, 54, 2021, 121-144.
- Zatirostami, A. *Fabrication of dye-sensitized solar cells based on the composite TiO₂ nanoparticles/ZnO nanorods: investigating the role of photoanode porosity*. **Materials Today Communications**, 26, 2021, 102033.
- Zhang, Z., Zada, A., Cui, N., Liu, N., Liu, M., Yang, Y., Jiang, D., Jiang, J., & Liu, S. *Synthesis of Ag loaded ZnO/BiOCl with high photocatalytic performance for the removal of antibiotic pollutants*. **Crystals**, 11, 8, 2021, 981.
- Zhou, L., Zhang, W., Chen, L., Deng, H., & Wan, J. *A novel ternary visible-light-driven photocatalyst AgCl/Ag₃PO₄/g-C₃N₄: Synthesis, characterization, photocatalytic activity for antibiotic degradation and mechanism analysis*. **Catal. Commun.** 100, 2017, 191–195.

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B. Education Background

Educational Institutions Attended with Dates and Qualifications

- Lead City University, {**MSc. Industrial Chemistry**} 2022 – till date
- Landmark University, {**Industrial Chemistry**} 2013 – 2018
- Excellent Secondary School, Ilorin
(**Senior Secondary School Certificate**) 2007- 2013
- Yahweh Primary School, Ilorin, Kwara State
(**Primary school leaving certificate**) 2002 - 2007

C. Work Experience With Dates

- National Steel Raw Materials Exploration Agency 2025 - present
- Kwara State Government House 2021 - 2025

- Federal Institute of Industrial Research Oshodi (FIRRO) 2016 - 2017

D. Awards and Fellowship

- Certificate Of Participation In Unicef Peer Educators Training
- Certificate of Proficiency In the Use Of Microsoft Offices Packages
- Certificates of Participation In National Youth Peace Summit

E. Membership of Academic/Professional Bodies

Nil

F. Publications: Thesis and Dissertation

- Biogenic Synthesis of Zinc Oxide Nanoparticles Using *Syzygium malaccense* for Solar cell Application and photodegradation of Neomycin.

G. Major Conferences Attended with Dates

Nil

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The University Compliance Certification

This is to certify that this Thesis was written **Oluwole Elijah OGUNBIYI with matriculation number LCU/PG/005467** of the Department of Chemical Sciences, Faculty of Natural and Applied Sciences, Lead City University, Ibadan and it is in full compliance with the approved University format and style.

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