



**PHOTOCATALYTIC AND ANTIBACTERIAL PROPERTIES OF
Ag/ZnO/NC NANOCOMPOSITE**

by

KEBADIRETSE LEFATSHE

Reg. No: 14100843

BSc (Radiation and Health Physics, University of Botswana)

Department of Physics and Astronomy,

College of Science,

Botswana International University of Science and Technology

lefatshekebadiretse@rocketmail.com, (+267) 76035626

A Dissertation Submitted to the College of Science in Partial Fulfilment of the
Requirements for the Award of the Degree in Master of Science in Physics of Botswana
International University of Science and Technology

Supervisors: Dr Cosmas M. Muiva

Senior Lecturer, Department of Physics
and Astronomy,

College of Science, BIUST

muivac@biust.ac.bw, (+267) 4921566

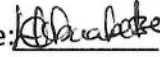
Dr Lemme P. Kebaabetswe

Lecturer, Department of Biological
Sciences & Biotechnology,

College of Science, BIUST

kebaabetswel@biust.ac.bw, (+267) 4921529

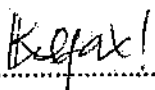
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CERTIFICATION

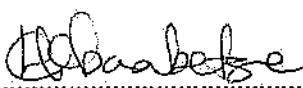
The undersigned certifies that he has read and hereby recommends for acceptance by the College of Science a dissertation titled: **PHOTOCATALYTIC AND ANTIBACTERIAL PROPERTIES OF Ag/ZnO/NC NANOCOMPOSITE**, in fulfillment of the requirements for the degree of Master of Science in Physics (*MSc Physics*) of the Botswana International University of Science and Technology.


.....

Dr. Cosmas M. Muiva

(Supervisor)

Date: 12th July 2017


.....

Dr. Lemme P. Kebaabetswe

(Co-supervisor)

Date: 12th July 2017

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DEDICATION

This research work is dedicated to my dad, mum, siblings, my future family and the future women scientists of Africa.

TABLE OF CONTENTS

DECLARATION AND COPYRIGHT	i
CERTIFICATION.....	ii
ACKNOWLEDGEMENTS	ii
DEDICATION	ii
TABLE OF CONTENTS.....	iii
LIST OF TABLES.....	v
LIST OF FIGURES.....	vi
LIST OF ABBREVIATIONS.....	vii
LIST OF PUBLICATIONS	viii
ABSTRACT	ix
CHAPTER 1: INTRODUCTION.....	1
1.0 Overview of Nanotechnology.....	1
1.1 Photocatalytic and Antibacterial Applications of Nanomaterials	2
1.2 Statement of the Problem.....	8
1.3 Aims and Objectives	9
1.4 Significance of Study.....	9
1.5 Dissertation Layout.....	10
CHAPTER 2: BACKGROUND INFORMATION AND LITERATURE REVIEW	12
2.0 Introduction.....	12
2.1 Photocatalytic Application of Semiconducting Metal Oxides	12
2.1.1 Background information of zinc oxide (ZnO).....	16
2.1.2 Synthesis of ZnO nanostructures.....	18
2.2. Antibacterial properties of Noble metals.....	21
2.2.1 Background information of silver (Ag).....	22
CHAPTER 3: EXPERIMENTAL PROCEDURE/ METHODOLOGY	26
3.0 Introduction.....	26
3.1. Materials and Methods	26

3.1.1 Preparation of nanocellulose.....	26
3.1.2 Preparation of ZnO nanostructures.....	29
3.1.3 Preparation of the ZnO/cellulose (ZnO/NC) nanocomposite	31
3.1.4. Preparation of silver-cellulose (Ag/NC) nanocomposite	31
3.1.5 Preparation of silver/zinc oxide/cellulose (Ag/ZnO/NC) nanocomposites	32
3.2 Characterisation and Instrumentation	33
3.2.1 Structural characterization	33
3.2.2 Optical characterization.....	37
3.3 Photocatalytic and Antibacterial Activity Assessment Procedures.....	40
3.3.1 Photocatalysis assessment procedure.....	40
3.3.2 Antibacterial assessment procedure	41
CHAPTER 4: RESULTS AND DISCUSSION	43
4.1 Structural and Morphological Characterization	43
4.1.1 X-ray powder diffractometry analysis	43
4.1.2. Fourier Transforms Infrared (FTIR) Spectroscopy	49
4.1.3 SEM and EDS results	52
4.2. Optical Characterization Results	56
4.2.1 Absorbance and optical band gap energy	56
4.3. Photocatalytic Activity Assessments	59
4.4 Antibacterial Assessment Results.....	69
CHAPTER 5: CONCLUSION AND RECOMMENDATIONS.....	77
5.1. Conclusion	77
5.2 Recommendations for Future Work	78
6.0 REFERENCES	79

LIST OF TABLES

Table 2.1: Summary of different properties of ZnO.....	17
Table 3.1: Preparation conditions; Ag and ZnO content for different Ag/ZnO/NC nanocomposite	32
Table 3.2: Operating parameters for the Bruker D8 Advance system used	34
Table 3.3: Operating parameters of the JEOL JSM 7100F FESEM used in this study	36
Table 3.4: Operating parameters of the used Perkin Elmer Spectrum Two ATR-FTIR spectrophotometer.....	38
Table 3.5: Operational parameters for the used Lambda 750 Perkin Elmer UV-Vis-NIR spectrophotometer.....	39
Table 4.1: Crystalline index of cellulosic fibres at different treatment stages	45
Table 4.2: Lattice parameters (a, b, c) constants (c/a) and unit volume of ZnO.	47
Table 4.3: Lattice parameters (a=b=c), constants (c/a) and unit volume of Ag.	48
Table 4.4: Optical band gaps of synthesised samples.....	59
Table 4.5: Percentages of MB degraded by different samples at 30 and 180 minutes	63
Table 4.6: Average zone of inhibition of different antibacterial agents against Gram positive (<i>S.aureus</i> and <i>B.subtilis</i>) and Gram negative (<i>E.coli.</i>).....	72

LIST OF FIGURES

Figure 2.1: Energy band structure of SMOs	14
Figure 2.2: Excitation process in semiconductor metals	14
Figure 2.3: Mechanism for SMO photocatalysis	15
Figure 2.4: Unit cell of (a) Rock salt, (b) Zinc Blende and (c) Wurtzite	17
Figure 3.1: Step by step extraction of cellulose	28
Figure 3.2: Flow chart showing the synthetic procedure for ZnO nanostructures	30
Figure 3.3: Different techniques for the characterisation of prepared nanomaterials.....	33
Figure 3.4: A picture of the Bruker D8 Advance XRD equipment used	35
Figure 3.5: A picture of the JEOL JSM 7100F FESEM equipment used in this study.....	37
Figure 3.6: A picture of the Perkin Elmer Spectrum Two ATR-FTIR spectrophotometer equipment used	39
Figure 3.7: A picture of the Lambda 750 Perkin Elmer UV-Vis-NIR spectrophotometer used.....	40
Figure 3.8: Chemical structure of methylene blue	40
Figure 4.1: XRD patterns of the samples as labelled in each diagram.....	44
Figure 4.2: FTIR spectrum of cellulose, ZnO, ZnO/NC, Ag, Ag/NC and Ag/ZnO/NC.....	51
Figure 4.3: SEM images of ZnO, cellulose, ZnO/NC and Ag/ZnO/NC at low and high magnification	54
Figure 4.4: Energy dispersive spectra of Ag/NC, ZnO/NC and Ag/ZnO/NC	55
Figure 4.5: Absorbance curves of ZnO, ZnO/NC, Ag, Ag/NC, Ag/ZnO/NC1, Ag/ZnO/NC2 and Ag/ZnO/NC3.....	57
Figure 4.6: A plot of (A/λ) against $(1/\lambda)$ for determining the optical band gap of ZnO, ZnO/NC, Ag/ZnO/NC1, Ag/ZnO/NC2 and Ag/ZnO/NC3	59
Figure 4.7: Time-dependent UV-Vis absorption spectra for degradation of MB using different photocatalysts as indicated on the graphs.	61
Figure 4.8: Plot of percentage degradation of MB as a function of time under sunlight irradiation photocatalysed by different samples.....	62
Figure 4.9: Relative absorbance of MB against irradiation time for Ag, Ag/NC (AC), ZnO, ZnO/NC (ZC), Ag/ZnO/NC1 (AZC1), Ag/ZnO/NC2 (AZC2) and Ag/ZnO/NC3 (AZC3).....	63
Figure 4.10: Kinetic plots for the decomposition of MB	68
Figure 4.11: Antibacterial zone of inhibition of cellulose, ZnO, ZnO/NC and Tetracycline (T) against <i>S.aureus</i> (A) and <i>E.coli</i> (B)	70
Figure 4.12 Antibacterial Activities of ZnO, ZnO/NC, Ag, Ag/NC, Ag/ZnO/NC1 (AZNC1), Ag/ZnO/NC2 (AZNC2) and Ag/ZnO/NC3 (AZNC3) and Tetracycline (T) against <i>E.coli</i> , <i>S.aureus</i> and <i>B.subtilis</i>	71
Figure 4.13 Growth inhibition plots of <i>E.coli</i> , <i>S.aureus</i> and <i>B.subtilis</i> as subjected to various nanostructures; Ag, Ag/NC, ZnO, ZnO/NC, Ag/ZnO/NC1 (AZNC1), Ag/ZnO/NC2 (AZNC2), Ag/ZnO/NC3 (AZNC3) and Tetracycline	74

LIST OF ABBREVIATIONS

e^-/h^+	Electron-hole pair
Ag	Silver
ZnO	Zinc Oxide
NC	Nanocellulose
Ag/NC	Silver/Nanocellulose
ZnO/NC	Zinc oxide/ nanocellulose
Ag/ZnO/NC	Silver/zinc oxide/nanocellulose
FWHM	Full Width at Half Maximum
FTIR	Fourier Transformer Infrared Spectroscopy
FESEM	Field Emission Scanning Electron Microscope
UV	Ultraviolet
XRD	X-Ray Diffraction
eV	Electron Volt
EDS	Energy Dispersive Spectroscopy
E_{gap}	Energy Band Gap
M	Molar
nm	Nanometer
min	Minutes
N	Newton
rpm	Revolutions per Minute
OPEFB	Oil Palm Empty Fruit Bunches
MB	Methylene Blue
WHO	World Health Organization
kWh/m^3	Kilowatt hour Per Cubic Meter
AOP	Advanced Oxidation Process

LIST OF PUBLICATIONS

Reviewed Publications from the Dissertation

1. **Kebadiretse Lefatshe**, Cosmas M. Muiva and Lemme P. Kebaabetswe, 'Extraction of nanocellulose and in-situ casting of ZnO/cellulose nanocomposite with enhanced photocatalytic and antibacterial activity' *Carbohydrate Polymers* 164 (2017), 301–308.

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Reviewed Conference Articles (Abstracts and Presentations)

2. **K. Lefatshe**, C.M. Muiva, L.P. Kebaabetswe. 'Investigation of ZnO nanostructures on cellulose polymer matrix.' Proceedings of the 54th annual conference of Microscopy Society of Southern Africa (MSSA), 5th- 9th December 2016. Broadwalk Centre, Port Elizabeth. Vol. 46, pg 45.

www.microscopy.co.za/nmmu-form/abstracts/abs-0045.pdf?version=1477650964

3. **K. Lefatshe**, C.M. Muiva, L.P. Kebaabetswe. 'Photocatalytic properties of Ag/ZnO/cellulose nanocomposite.' Accepted for presentation at the 1st Africa Energy Materials (AEM-2017) conference to be held at the CSIR International Convention Centre, Pretoria, South Africa on 28th - 31st March 2017.

ABSTRACT

Recently, organic and inorganic pollutants including heavy metals, effluents, dyes, and bacteria have been removed from wastewater and other environmental settings using nanomaterials. Combining two or more nanomaterials to form nanocomposites offers improved and tailored properties for these applications. Metal-polymer nanocomposites exhibit elevated optical, electrical, thermal and mechanical properties, which make them interesting candidates for the manufacturing of functional devices as well as other industrial applications. In this study, Ag/ZnO/cellulose nanocomposite was synthesised through in-situ solution casting method which offers a good adhesion and dispersity of nanostructured materials. The morphological properties of the synthesized nanostructures were studied from scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) measurements. X-ray diffractometer (XRD) patterns were recorded to reveal the structural properties of the samples. The optical absorbance was measured using a UV-Vis-NIR spectrophotometer and used to determine the energy band gap (E_g). From SEM analysis, nanodiscs-like structures were observed for ZnO while nanospheres and nanosheets were observed for Ag and cellulose, respectively. EDS confirmed the presence of only Zn, O, Ag and C. XRD analysis pointed to cellulose monoclinic type-1. Peaks corresponding to typical hexagonal wurtzite structure for ZnO and also to face-centred-cubic Ag structure were identified. Photodecomposition of aqueous methylene blue (MB) under direct sunlight irradiation was monitored to study the photocatalytic activity of the nanocomposite. About 92% of MB was degraded in the presence of Ag/ZnO/cellulose nanocomposite. The antibacterial activity of the prepared samples was investigated against three pathogenic bacteria species; Gram negative *Escherichia coli*, Gram positive *Staphylococcus aureus* and Gram positive, spore forming *Bacillus subtilis*. The prepared nanocomposite exhibited strong activity against the growth of all the bacterial species though in different quantified measures.

CHAPTER 1: INTRODUCTION

1.0 Overview of Nanotechnology

Changing standards of living has brought challenges within the science and technology community. Over the past decades, there has been an increased need in the development and manufacturing of materials and technology to meet the growing human demand. Efforts are now being made to improve the imperfections of old materials and technologies as well as tailoring them into required standards. The development of materials at a very small scale known as the “nanoscale” is been recognized as a fast, cheaper, economic and environmentally friendly promising innovative technology.

Ever since the first inspiring lecture on the promising future of discovery and importance of nanomaterials by an American physicist called Richard Feynman in 1959, this field is massively growing and evolving to be a key solution to detriments encountered with old technologies [1]. Nanotechnology has been referred to as the enabling or refining technology as it aids in improving other already existing technologies. The engineering, manipulation, exploitation and application of nanomaterials is collectively known as nanotechnology. In 2002 the number of nanoproducts in the global market was estimated to be about 200. Within six years this number quadrupled. Lux Research, an independent research forum, estimated that there will be about 2.6 trillion manufactured goods in 2014. The critical role of nanotechnology in our everyday lives lies in the obligatory need to overcome community necessities and needs through alternative options, which are much reliable, cost-efficient and offers improved performance.

Nano-scaled materials are the building blocks of nanoscience. They have at least one dimension scaled from 1 to 100 nm [2]. Nanomaterials can be classified according to dimension i.e. whether there are one dimensional (1D), two-dimensional (2D) or three dimensional (3D). As compared to bulk-sized materials, nanomaterials have distinguishable properties owing to their unchallenged dimensions. The nano-dimensions

of these materials have contributed to unconquerable properties, including larger specific area, large fraction of surface atoms, high surface energy, spatial confinement as well as other exclusive size-dependent properties. Different nanomaterials ranging from both organic and inorganic materials for example metals, fillers and polymers have been investigated for their different properties and applications.

Metal based nanomaterials, including noble metals and metal oxides have attained escalating growth in materials research due to their much reported properties and applications [3-4]. Metallic nanomaterials have been reported to possess increased and exclusive functionality, mechanical, UV radiation shielding, conductivity and optical properties [5]. Recently, there is more interest on the catalytic and antimicrobial properties of metallic nanomaterials.

1.1 Photocatalytic and Antibacterial Applications of Nanomaterials

The vast growth of industrialization in both developing and well developed countries has ultimately led to an escalating release of toxic and harmful organic pollutants to the environment which causes environmental problems such as water and air pollution. Different sectors of industries release different kinds of organic pollutants including dyes, aromatic compounds, detergents, heavy metals, manufacturing waste, pesticides, acids, fuels and drugs which can directly or indirectly be discharged into water bodies. Organic pollutants have multifaceted chemical structures, which makes them environmentally unfriendly because they persist over a long time without being broken down to less harmful substances. Past efforts to assist in degrading organic pollutants have been developed and have proved to be futile. Many of these technologies have proved to be unfriendly to the environment due to high energy consumption [6]. High pressure and temperature are normally required for the use of these methods hence resulting in consumption of excessive amount of energy and leading to high operation costs [7]. For example, during water purification using the reverse osmosis technique, hydrostatic pressure that surpasses osmotic pressure has to be applied and this requires about 6.1 - 14.3 kWh/m³ per leachate depending on the type of system used [8]. Non-renewable

sources of energy have been exploited to meet this high demand; however, the dwindling of fossil fuels deposits poses a significant global challenge. It has been reported that the demand for energy is anticipated to increase by 50% by the year 2025. This calls for the global nation to identify alternative energy saving measures. In addition to these detriments, the equipment used is expensive, and other costs from using these old technologies arise from waste disposal. It is so costly to dispose the charcoal waste from the use of the activated carbon method for wastewater treatment. Due to the chemical instability of the contaminants, these technologies have demonstrated to be ineffective as they fail to achieve complete demineralization of pollutants and can lead to creation of a more concentrated pollutant-containing phase.

Although the ecosystem is not complete without microorganisms, their presence may negatively affect the environment they living in. They are known to be agents of disease; hence their excess accumulation, multiplication and proliferation in the environmental systems raise a concern. As people are becoming more civilized and hygienic standard becoming too stringent, the control of pathogenic microorganisms is one of the issues not to be overlooked. Microbes are an alarming cause of diseases and infections. The discovery of antibiotics such as streptomycin, methicillin, vancomycin and penicillin came as a promising alternative for the treatment of bacterial infections and diseases. Unfortunately some bacterial strains have developed resistance against such antibiotics [9]. The centre for disease control and prevention (CDCP), reports that two in a hundred people carry the multidrug-resistant *Staphylococcus aureus* [10]. This strain of bacteria is resistant against many antibiotics as sulphonamide, penicillin, methicillin, and vancomycin. *Staphylococcus aureus* is one common type of bacteria which causes pneumonia infection. The report further states that the number of infections from this bacteria increased from 127,000 to 278,000 annually between the years 1999 and 2005 due to drug resistance, [10]. An alarming emergence and spread of diseases and infections caused by antibiotic resistant bacteria is a serious threat to global public health and requires action for prevention measures across all sectors and societies.

The development of strong and innovative agents that can without perimeter inhibit bacterial growth at the same time showing no cytotoxic effects on humans and the

environment is an imperative task [11]. Due to their antimicrobial activity, metallic nanomaterials have been recognized as a possible solution to curb the public health catastrophe of antibiotics resistance and re-emergence of infections. The microbial action of these nanomaterials is attributed to their morphology and dimension. The smaller dimensions of nanomaterials allow them to enter living cells and partake in antimicrobial mechanisms. The antifungal, antibacterial and antiviral properties of noble metals against a wide range of microorganisms are reported [12-13], and have resulted in range of environmental remediation applications including air disinfection, water treatment, surface disinfections and their impregnation in biomedical devices. In particular, the development and application of silver based agents are drawing increasing attention for their potential antimicrobial properties due the scarcity and high cost of other noble metals [14].

Ever since the emergence of advanced oxygen processes (AOPs), nanotechnology is also a promising strategy to overcome the issue of pollutants removal as several metallic elements have been investigated for their ability to decompose both organic and inorganic pollutants [15]. Upon irradiation of wide band semiconductors by photons with a higher energy, photocatalytic degradation of pollutants is induced because of their sufficient ability for reduction and oxidation (redox) processes.

Even though nanotechnology is a promising tool in environmental remediation the toxicological aspects are not be ruled out, hence it is necessary to fabricate environmental friendly materials to avoid posing a new risk to the environment. Excessive intake of TiO_2 has been reported to induce pulmonary inflammation and other harm to human tissues [16]. An increased use of metallic silver can lead to its escalated toxic release in the environment. High exposure of silver can lead to a condition known as argyria [17-18].

Due to high reactivity of some metallic nanomaterials, surface leaching can occur and thus limiting their antimicrobial applications. For instance, when used for wastewater treatment, the leached metallic nanomaterials can end up being digested by humans in an unknown quantity, can move to the sediment where it poses hazards to the aquatic

biota or can combine with other compounds leading to more complex pollutants [19]. In some applications it is necessary to embed metallic nanostructures on support materials to allow for an extended release of ions for microbial action is a very important aspect for possible antimicrobial applications. For example, for air disinfection it is essential to integrate Ag on filters. The antibacterial effectiveness of silver has been reported to be short lived, thus need to keep changing the materials at intervals. The generation of stable and efficient silver hosted nanostructures offers an advanced perspective to mitigate these drawbacks.

The effective utilization of electron-hole pairs is a key factor for rapid degradation of pollutants during a photocatalytic reaction. However; most SMOs suffer from rapid electron-hole recombination effect, which is the most critical limitation of semiconductor metal oxides in the field of photocatalysis. After formation of electron-hole pair in the valence and conduction bands there is a possibility of them to recombine if a scavenger for electron-hole pair is not available. Charge separation and recombination are two ever-competitive processes during photocatalysis. Recombination normally happens when the photoexcited electron reverts back to the created hole in the valence band, instead of reacting with absorbed species to produce ROSs [20].

With abundant free and inexhaustible solar energy throughout the year in Botswana, using sunlight as a source of illumination for the photocatalytic reaction will be a great and sustainable step towards reducing the high energy consumption calamity. This means it is desirable that the photocatalyst material have the ability to absorb in the visible light region. However, most SMO's are unable to absorb and utilize the solar energy that is abundant in the ecosystem. Higher photon absorption is noted in the UV region as compared to the visible region. The solar spectrum contains about less than 3-5 % of UV and 45-50% of visible light.

Controlling the morphology and structure of respective materials can be implemented to modify their properties. This can be achieved either through immobilization of metallic nanostructures. A larger surface area, smaller size and surface activity can be achieved by dispersing metallic nanostructures on large surface support systems. Fabrication of

heterostructure through addition of an impurity; either another metallic or non-metallic component to the existing structure can be also adopted to improve the antibacterial and photocatalytic properties. Taking advantage of synergetic effect between a noble metal and a semiconductor metal oxide, coupling noble metals with semiconductor metal oxides modifies both the antibacterial and photocatalytic activities. Several metal oxides have been studied for their photocatalytic and antibacterial properties. Among them, ZnO has been used for the treatment of textiles and it has proved to be non-toxic to human cells [21]. ZnO displays antibacterial property to some extent in the absence of light in neutral pH environments, hence making it the best semiconductor with good antibacterial property [22-23]. It can be incorporated with Ag to modify Ag's antibacterial activity.

The incorporation of two or more nanomaterials yields what is known as a nanocomposite. Nanocomposite engineering has been regarded as an innovative approach to generate materials whose properties are one way or another favoring in comparison to those of the discrete components. Polymer nanocomposites, thin film nanocomposites, ceramic nanocomposites, mixed metallic nanocomposites have been generated materials to improve the effectiveness of the individual materials. Even though different nanocomposites have been investigated for different properties and applications; polymer-based nanocomposites have withstanding advantages. The expansion of polymer nanocomposites is hastily emerging as a very attractive multidisciplinary route in scientific and industrial interests to upgrade and diversify properties and applications of metallic nanostructures.

Polymers can be used as reaction sites to control the growth of metallic nanomaterials thus altering their properties. Polymers also offer long-term stability and outstanding optical, catalytic, and electrical properties [24]. Recently, metallic-polymer nanocomposites have attracted a deal of attention because of their enhanced interesting properties which results in possible applications in the fields of catalysis, electronics, photonics, biotechnology [25]. Cellulose, starch, gelatin, alginate, chitosan, collagen, polyvinyl alcohol, polyvinyl pyrrolidone, poly ethylene glycol are some of the polymers that have been used to disperse metallic nanostructures in order to modify their

photocatalytic and antibacterial properties. Even though studies mostly reports the use of synthetic polymers for fabrication of polymer nanocomposites natural polymers are exceptionally environmentally and economically advantageous over synthetic polymers due to their low cost and biodegradability.

Cellulose is the most abundant natural polymer and because of its renewability, low cost, non-toxicity, biodegradability and biocompatibility [26] it will be ideal to use it for dispersing metallic nanostructures to enhance their photocatalytic and antibacterial activity. Furthermore, it is known to have low thermal expansion, high surface area, high aspect ratio, high strength, and optical properties which have resulted to its application as multifunctional agents in various fields [27]. The applications of cellulose include biosensors, drug delivery and also manufacture of reinforced nanocomposites.

Natural fibers including pineapple, banana, wood, wheat straws, rice straws, oil palm, and kenaf fibers are some of the sources of cellulose. Animals and bacteria are also sources of cellulose. Oil palm fruit bunches (OPEFB) is a vast available source of cellulose. Together with lignin, hemicellulose, pectin and ash, cellulose makes up the constituents of oil palm empty fruit bunch lignocellulosic material, which is considered a potential low cost and yet renewable source of cellulose. Pretreatment of cellulosic biomass is necessary to break and separate the hemicelluloses and lignin at the same time increasing the accessibility and proportion of cellulose [28].

Cellulose consists of linear homopolysaccharide composed of β -D glucopyranose units linked together by β -1-4-linkages [27, 29]. The chains of cellulose also possess a large number of hydroxyl ions and thus making them a good environment for the growth of metallic nanostructures. Cellulose can be used as a green support system for the immobilization of metallic nanostructures in the development of a new environmentally friendly system for photocatalytic and antibacterial applications which includes large scale wastewater treatment.

Different methods have been used for the synthesis of polymer nanocomposites. These methods can either be in-situ or ex-situ. In-situ synthesis approach is a simple method

that allows the nanoparticles to be synthesized inside the polymer matrices. In this method suitable precursors are used to generate materials of interest in the polymeric solution. In-situ synthesis gives good adhesion of nanostructures onto the matrix and can also be used to control the growth of the nanostructures [24]. A good spatial distribution is also maintained at the same time preventing nanostructures from agglomerating into clusters. Chemically oriented synthetic approaches such as spin coating, lithography; lamination, electro-spinning and solution casting are used for in-situ fabrication of nanocomposites.

In our work, we present a very simple, low cost yet scalable in situ nanocomposite synthesis, combining the photocatalytic and antibacterial properties of Ag and ZnO for an effective dual function material.

1.2 Statement of the Problem

Metallic nanomaterials have been widely investigated for their photocatalytic and antibacterial applications. Photoactive metal oxide ZnO is the most promising solution for degradation of pollutants and environmental remediation. In addition Ag has been widely studied for its well documented antibacterial activity against both Gram positive and Gram negative bacteria. However; the use of ZnO and Ag for respective applications has certain limitations. It has been reported that application of ZnO for complete photocatalytic degradation of organic pollutants has been limited by rapid electron-hole recombination effect. Furthermore, a lower number of surface reactive sites for photon absorption have also been reported to result in reduced activities. With abundant free and inexhaustible solar energy throughout the year in Botswana, using sunlight as a source of illumination for the photocatalytic reaction will be a great and sustainable step towards reducing the high energy consumption calamity. However, most SMO's are unable to absorb and utilize the solar energy that is abundant in the ecosystem. Higher photon absorption is noted in the UV region as compared to the visible region. On the other hand, the utilization of Ag for antibacterial applications has been limited by partial and unstable antimicrobial action and also toxicity to the environment due to a high rate of Ag ions release to the environment. For any technology it is important to assess the

environmental impact on continued application. The release of synthetic non-biodegradable polymers in the environment is bound to raise issues of contamination. There is need for promotion of more environmentally-friendly materials.

1.3 Aims and Objectives

The main purpose of this work was to synthesize a novel nanocomposite which possesses both excellent antibacterial and photocatalytic properties. In this research, the nanocomposite of interest is based on the noble metal silver (Ag), the semiconducting metal oxide zinc oxide (ZnO) all dispersed on cellulose polymer matrix. This will be accomplished chronologically through the following objectives;

- ✚ Extraction of cellulose from oil palm empty fruit bunches (OPEFB).
- ✚ Low cost synthesis of Ag/ZnO/NC nanocomposite through in-situ solution casting method.
- ✚ Investigation of the photocatalytic activity of Ag/ZnO/NC nanocomposite against methylene blue (MB) dye.
- ✚ Evaluation of the antibacterial activity of Ag/ZnO/NC nanocomposite against Gram positive *Staphylococcus aureus*, Gram positive spore-forming *Bacillus subtilis* and Gram negative *Escherichia coli*.

1.4 Significance of Study

The manoeuvring of nanomaterials is vital in establishing new philosophies, skills and approaches hence leading to breakthroughs in great scientific problems. A novel concept to synthesize an environmentally friendly nanocomposite with excellent antibacterial and photocatalytic activity is proposed. Few attempts have been made on synergistic combining two or more nanomaterials for dual purpose applications. Approaches have been implemented to separately leverage the antibacterial and photocatalytic properties. Immobilizing semiconductors or noble metals on polymer support materials can help to achieve an increase in their active surface area and also develop a controlled

time-release mechanism of Ag ions to form a long time protective barrier against microbes [17]. Polymers also control the growth of nanostructures thus minimizing agglomeration of SMO nanostructures which may arise during growth of these nanostructures or upon interaction with a pollutant. Coagulation/agglomeration affects the reactivity of photocatalysts as it reduces the amount of light reaching the SMOs active sites. In addition, the use of more potent natural cellulose polymer can mitigate costs and environmental issues associated with synthetic polymers. The unique advantages and properties of the ZnO, Ag and cellulose polymer can be collectively combined together to fabricate a novel and multi-functional nanocomposite with outstanding anticipated applications. Each of these components has a unique designed function, and thus will contribute impressively for sustainable, economic and environmentally friendly applications. Hybridization of ZnO and Ag to leverage the advantages of both materials can effectively impede electron-hole recombination during photocatalytic process; and also result in a combination of two mechanisms for both photocatalysis and antibacterial activity while significantly minimizing the release of potentially toxic ions. This work could provide a new insight into the fabrication and properties of Ag/ZnO-cellulose based nanocomposites and facilitate their application in environmental protection issues.

1.5 Dissertation Layout

This dissertation is divided into five (5) main chapters.

Chapter 1 is the introduction that gives a brief insight on the subject at hand. It also outlines the significance and motivation of this study as well as aims and objectives that will be tackled.

Chapter 2 contains in-depth background information on the nanomaterials of interest, i.e. silver, ZnO, cellulose and the nanocomposite. The structures and properties of these materials are discussed in full details. Also the photocatalytic and antibacterial application of nanomaterials will be discussed in this chapter. Finally, this chapter gives a review on the work that has already been done by other researchers in relation to this area, highlighting their findings and detriments.

Chapter 3 is an elaborative section on the synthesis, characterization techniques and assessments procedures.

Chapter 4 presents results and findings for all work done. Results attained on the characterization, antibacterial and photocatalytic assessments and underlying discussions are clearly underlined.

Chapter 5 is a brief summary of what has been done or achieved in this project. Recommendations on future research directions are also given in this chapter.

The references for the whole dissertation are given at the end of the dissertation.

CHAPTER 2: BACKGROUND INFORMATION AND LITERATURE REVIEW

2.0 Introduction

Of recent, the application of nanotechnology in different industries is a highly interesting subject. This chapter reviews the properties of Ag and ZnO nanomaterials. There are a large number of publications on Ag and ZnO as bare nanostructures for their respective applications. A depth review on the antibacterial and photocatalytic applications of these materials is provided. ZnO has been explored for the removal of dyes and other organic pollutants because of its high photocatalytic activity, while Ag has mostly been utilized for biological treatment as it is reported to possess antibacterial activity against a wide of pathogens including the thermophiles and basophiles. Modification of nanomaterials structures and morphologies through the generation of polymeric nanocomposites is a great achievement. Taking into account the synergic contribution of different types of nanomaterials, the antibacterial and photocatalytic application of nanocomposites are explored.

2.1 Photocatalytic Application of Semiconducting Metal Oxides

The concept of advanced oxidation processes (AOP) is an extensively and hastily growing technology and has been adopted for both waste water and contaminated air purification [30]. AOPs are based on production of reactive species that oxidises a broad range of pollutants in a short time interval. Photocatalysis, ozonation, photo-Fenton oxidation and Fenton are some of the developed outstanding AOPs. The process of photocatalysis involves the acceleration of a photoreaction in the presence of a catalyst. It is a photon-activated or driven process. Photocatalysis is an environmentally friendly process which induces the removal of heavy metals including mercury and lead, and also the destruction of organic and inorganic compounds (cyanide, ammonia, nitrates, mineral acids, pesticides and dyes). Other applications of photocatalysis are photodynamic therapy, energy conversion and environmental purification. In addition,

photocatalysis has also been applied in construction, and in biomedical applications such as cancer treatment, tooth whitening and antimicrobial inhibition.

Photocatalytic degradation occurs primarily on the surface of the metal oxide. A photocatalyst is able to produce chemical transformations of reaction participants through absorption of light quanta and yet remain unchanged during the reaction. Even after cyclic uses, the structure of a good photocatalyst should not be altered. A large number of studies have reported the use of metal containing compounds e.g. metal sulphides and oxides for photocatalysis applications [31-33].

The use of semiconductor metal oxides for photocatalytic wastewater treatment is known as heterogeneous photocatalysis. Hetero means two or more. Two phases are involved in the heterogeneous photocatalysis process; the solid phase photocatalyst and the liquid phase of contaminated water. Upon interaction with light in the surface of a pollutant, the absorbed light induces semiconductors to generate reactive oxygen species (ROSs). Atomic oxygen (O), singlet oxygen (O_2), hydrogen peroxide (H_2O_2) and hydroxyl radicals ($OH^\cdot$) are the most commonly photocatalytic generated ROSs. Other than the above mentioned species for AOP; fluorine, chlorine, iodine and permanganate can also indulge in photocatalysis.

Electrons in an atom are quantized into discrete energy levels and given quantum numbers n , l and m . When electrons are filled into their respective energy levels, they obey Pauli's exclusion principle that states that no two electrons of the same energies can occupy the same space. This therefore means that if two atoms are in close proximity, their energy level will be split into two. If many atoms are in close proximity, discrete energy levels are replaced with bands of energy states, which are separated by gaps between the bands as shown in Figure 2.1. The energy difference between the valence band and the conduction band, which is the space in between them, is known as the 'band gap'. The electrons that occupy a valence band that is a totally filled band do not have any net velocity and hence there is no current conductivity amongst them. Normally a valence band is fully occupied while the conduction is either empty or not fully filled.

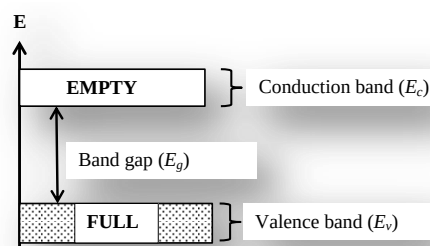


Figure 2.1: Energy band structure of SMOs

Upon irradiation by photons with an equal or greater energy, electrons on the valence band of a photocatalyst gain enough energy and are excited to a greater energy state, which is the conduction band. As an electron migrates to the conduction band, a hole is also formed in the valence band as shown in Figure 2.2.

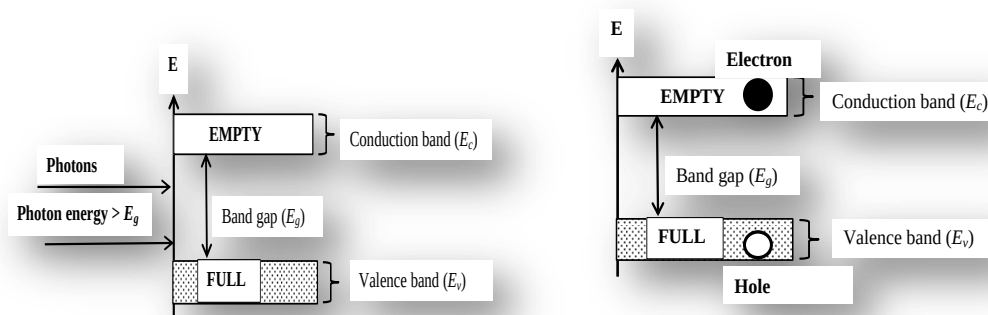


Figure 2.2: Excitation process in semiconductor metals

The electron carries its normal negative charge, whilst the resultant hole has a positive charge. Unlike charges will always attract each other. If charge separation is maintained, the electron and hole may migrate to the surface of the catalyst where they separately participate in redox (reduction and oxidation) reactions with adsorbed species. In most cases the absorbed species are water and oxygen. Holes vacancies may react with the absorbed water molecules or hydroxyl ions (OH^-) to produce the hydroxyl radical ($\text{OH}^\bullet$). Free electrons maybe picked up by oxygen to generate superoxide radical anions (O_2^-) as shown in Figure 2.3 [34]. As mentioned earlier both $\text{OH}^\bullet$ and O_2^- are reactive oxygen species that partake in the degradation of the pollutants to harmless materials. This is the basic mechanism of SMO photocatalysis. Other than participating in redox reactions,

metal oxides can either act as electron donor or acceptor upon coming in contact with pollutants.

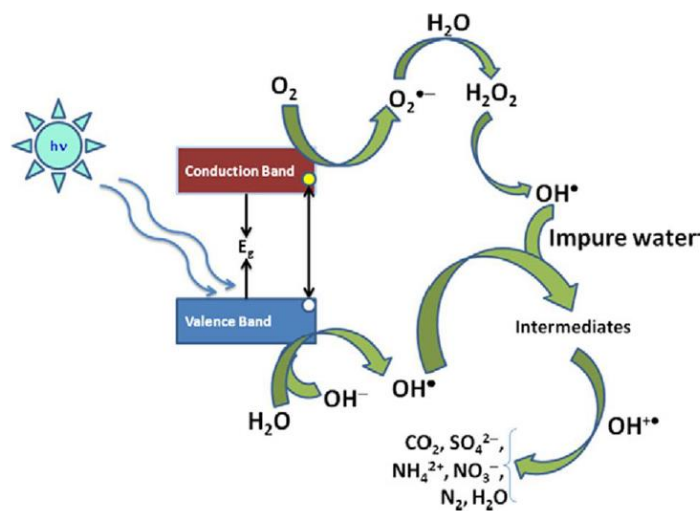


Figure 2.3: Mechanism for SMO photocatalysis, [34]

Apart from remaining unchanged even after cyclic uses, a best photocatalyst should also possess great stability towards photocorrosion and photoactivity, and be able to go through photoexcitation under both visible and ultraviolet light irradiation. Low cost, low toxicity and also biological and chemical inertness are some of the properties of a good photocatalytic material. Excellent morphology and large surface area are the key factors to be considered when choosing the best photocatalysts. Semiconductor metal oxides are used as photocatalysts because of their resistance to poisoning and deactivation. Several studies have been reported on degradation of different pollutants through use of tin oxide (SnO_2), zinc oxide (ZnO), germanium dioxide (GeO_2), magnesium oxide (MgO), antimony trioxide (Sb_2O_3), tungsten trioxide (WO_3), titanium oxide (TiO_2), copper (I) oxide (Cu_2O), indium oxide (In_2O_3), niobium pentoxide (Nb_2O_5), zirconium oxide (ZrO_2), iron (III) oxide (Fe_2O_3) and vanadium (V) oxide (V_2O_5) [31-32, 35]. The photocatalytic ability of ZnO and TiO_2 are the most extensively studied. This owes to their wide band gap, good activity, inexpensiveness and extended photo-stability.

The first SMO photocatalyst to be discovered was TiO_2 in 1972 by Fujishima and Honda, for the photochemical splitting of water into hydrogen and oxygen and ever since then its

applications as a photocatalyst have tremendously grown [6, 36-41]. Even though more than a thousand publications on the photocatalytic efficiency of TiO_2 have been reported, there are some drawbacks which come in line with its utilisation. The inability of TiO_2 to utilize abundant solar irradiation is a challenge. Several attempts to sensitize TiO_2 for the much longer visible range absorption have been implemented; however its photocatalytic activity still remains low even after its surface modification [6]. According to Ibhadon and Fitzpatrick [6], during photocatalysis TiO_2 not only destroy pollutants but also the organic matrix in which it is embedded on. Owing to these discredits which limit the utilization of TiO_2 , ZnO has been reported to be a suitable alternative to replace TiO_2 as a photocatalyst.

ZnO is a developing and more promising semiconductor for photocatalysis of organic pollutants. Its wide band gap is analogous to that of TiO_2 . It absorbs a larger fraction of the solar spectrum compared to TiO_2 [42], and thus can utilize the abundant free and inexhaustible solar energy irradiation for photocatalytic process. The non-toxicity nature of ZnO is another reason why it out rules TiO_2 [43]. ZnO nanostructures have also been reported to exhibit higher photocatalytic activities as compared to TiO_2 nanostructures for the degradation of different organic pollutants regardless of the environmental status due to its elevated generation of hydrogen peroxide, its high reaction rate and also because it has a high number of active sites with high reactivity [44-46]. A good knowledge on ZnO background will provide an insight in understanding its photocatalytic properties.

2.1.1 Background information of zinc oxide (ZnO)

Zinc oxide (ZnO), one of the most interesting and promising candidate in nanotechnology is a thermally stable compound that belongs to the family of transition metal oxides. ZnO is known as an II-VI semiconductor material because it is made of Zn and O belonging to group II and VI of the periodic table respectively. It is a semiconductor with three known different crystal structures; hexagonal wurtzite, cubic zinc-blende blend and a rarely-observed cubic rock-salt all shown in Figure 2.4. Of these three, the most common form is the hexagonal wurtzite as it is the most thermodynamically stable under ambient

conditions. The much appraised wide applications of ZnO are one way or the other influenced by the physical and chemical properties listed in Table 2.1.

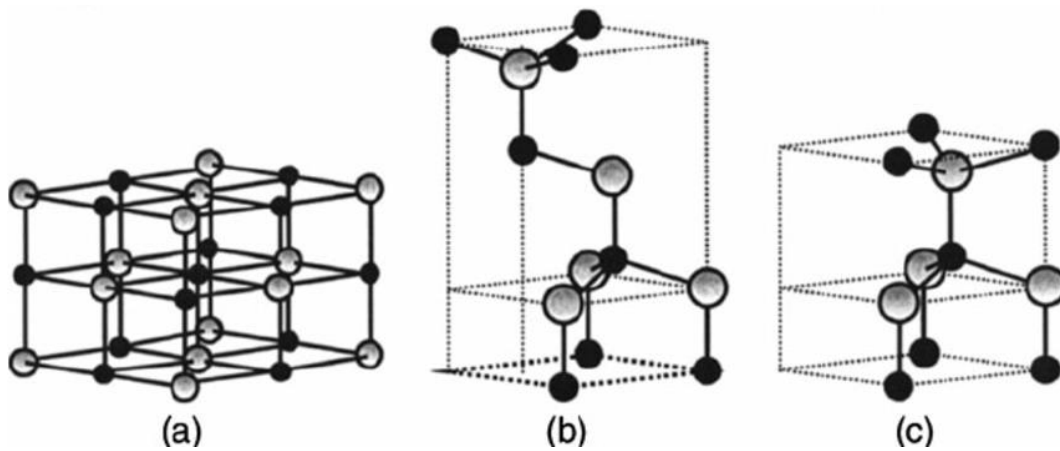


Figure 2.4: Unit cell of (a) Rock salt, (b) Zinc Blende and (c) Wurtzite [47]

Table 2.1: Summary of different properties of ZnO

Property	Value	References
Energy band Gap	3.3 -3.4 eV	[48-51]
Exciton binding energy	60 MeV	[48,50]
Hole effective mass (m_0)	0.59	[52]
Electron effective mass(m_0)	0.24-0.30	[48,52]
Specific gravity	5.5/5.7	[52]
Refractive Index	2.0041, 2.008	[48]
Thermal conductivity	0.6	[48,53]
Melting point	1975 °C	[52,54]
Boiling point	2360 °C	[55]
Volume	23.8	[52]
Density	5.605 g/cm ³	[52]
Solubility in water	0.0004%	[52]
Lattice parameter a	0.3248-0.3250 nm	[50,53]
Lattice parameter c	0.5204-0.5208 nm	[50,53]
Hardness	~5 GPa	[52-53]

ZnO has ventured as one of the most essential candidate in the modern nanoscience. It has a larger exciton energy which is about more than two times the room-temperature thermal energy. Because of this energy, ZnO has astonishing electrical, optical transparency in the visible region, electron mobility, piezoelectricity, strong room-

temperature luminescence, UV absorption, high refractive index, high thermal conductivity, chemical stability and biocompatibility. It also possesses antimicrobial activity against a wide range of microorganisms ranging from bacteria to viruses and fungi. Due to its attractive properties ZnO has a vast range of applications such as gas sensing devices, solar cells, lasing and light emitting diodes, antibacterial agents, catalysts, electronic devices, UV-absorbers and display screens [56].

2.1.2 Synthesis of ZnO nanostructures

The structural, morphological properties and applications of different nanostructures are dependent highly on their synthetic routes. Different morphologies of ZnO have been synthesized using biological, chemical and physical approaches. Sol-gel [57-58], hydrothermal, [59-61], co-deposition [57], precipitation, combustion, spray pyrolysis [62-63], thermal decomposition [64-65], microwave assisted synthesis [66] are some of the methods that have been engaged to synthesize different ZnO nanostructures of various shapes ranging from nanoflowers [35,67], nanorods [43,59,64,68], nanopencils [61], nanowires [69], nanospheres [70-71], nanobelts [60], nanosausages [63], nanodiscs [72-73] etc. Different morphologies of ZnO exhibit different properties including different photocatalytic activities.

Large surface area for more active sites, suitable band width for efficient absorption and conversion of visible light to photogenerated electron-hole pairs, smaller grain size, are some of the best favorable characteristics for a photocatalyst in pursuit of achieving merit photocatalysis [74]. In addition, photocatalysis requires surface trapping of electrons and holes to retard recombination, non-toxicity, biological and chemical inertness of a photocatalyst. TiO_2 has been reported to have high rate of electron/hole pair recombination as compared ZnO. This however does not rule out ZnO as an exception to this challenge. Similar to other photoactive metal oxides, a rapid recombination of the positive charged hole and the negative charged electron, limits the application of ZnO in photocatalysis. Devotion to design SMOs with desirable photocatalytic efficiencies is an on-going process. Modification of the physicochemical properties of ZnO, its particle size, pore topology, surface area, and crystallinity can alter its photocatalytic performance.

Selective surface modification through doping, forming heterostructure composites with other semiconductors or other metals, and anchoring the photocatalyst onto large surface area materials are the most common approaches that have been employed to modify the photocatalytic activity of ZnO. Some of these approaches have been reported to amend its energy band gap resulting in sensitization in the visible light region. Other than surface area, surface defects also play an important part in photocatalysis. This could be achieved by introducing some impurities of foreign material to the photocatalyst. Coupling two or more semiconductors enhances the photocatalysis performance by enhancing charge separation [75]. These semiconductors can either be used as dopants or to make composites. In most cases these semiconductors have different band structures. Combined SMOs heterostructure including; ZnO/TiO₂, [76-80], ZnO/SnO₂, [75, 81-82], TiO₂/WO₃, [83-84] and SnO₂/TiO₂ [85-86] have been reported to possess high photocatalytic performance as compared to each pristine photocatalyst component. Apart from retarding recombination, coupled semiconductors also have the ability to absorb light in the visible light region leading to an increased excitation rate of electrons from lower-energy orbitals to higher-energy orbitals. Short band gap semiconductors like CdS, WO₃ and Fe₂O₃ are used for doping large band gap semiconductors.

Anandan *et al* [87], studied the photocatalytic activity of TiO₂/WO₃ composite which was synthesised through an ultrasound assisted method. The photocatalytic activity of the composite was tested by investigating the degradation of wastewater contaminated with methylene blue. The solution was irradiated under visible light illumination. It was found that TiO₂/WO₃ composite exhibited enhanced photocatalytic performance as compare to pure TiO₂ under equivalent conditions, hence it can be said that WO₃ successfully enhanced the photocatalytic activity of TiO₂.

In their work Karunakaran *et al* [80], deposited ZnO on TiO₂ to fabricate a heterostructure ZnO/TiO₂ nanocomposite via modified ammonia-evaporation- induced synthetic procedure. The photocatalytic assessment of the synthesised composite was tested against methylene blue (MB), sunset yellow (SY) and Rhodamine B (RB) dyes as pollutants models. The band gap of the composite and pure TiO₂ was determined and it was concluded that ZnO shifted the band gap of TiO₂ towards the visible region. The

photocatalytic activity of ZnO/TiO₂ nanocomposite was greater than that of pure TiO₂ against MB and RB; however pure TiO₂ showed better activity against SY as compared to ZnO/TiO₂.

Doping of SMOs involves introduction of a small percentage of impurities on their surface for the purpose of modifying the selected properties without formation of new phases or structures. The approach induces charge separation hence reducing electron recombination hence. Both metals and non-metals can be used for doping SMOs. Metal doping induces localized states between the valence band and the conduction band. Mid-gap states could be utilized to temporarily trap photogenerated electron-hole pair and thus somehow decrease the rate of recombination. Erbium (Er), tin (Sn), aluminium (Al) and Antimony (Sb) have been used as dopants to improve the photocatalytic ability of ZnO [44, 62]. Carbon(C), sulphur (S) and nitrogen (N) are some of the non-metals that have been used to modify the photocatalytic property of photocatalysts.

Transition metals including silver (Ag), nickel (Ni), gold (Au), platinum (Pt), Copper (Cu), molybdenum (Mo), cobalt (Co) and chromium (Cr) have previously been used for modifying semiconductor metal oxides in order to improve their photocatalytic activity. SMO-noble metal composites offer improved functionality. Many transition metals and their compounds are reported to be catalytic as they absorb visible light due to their surface plasmon resonance (SPR) effect [88]. When introduced on the surface of metal oxides, Ag can act as scavengers or rather as a sink to trap electrons thus delaying e^-/h^+ pair recombination [89].

Upon addition of Ag on to ZnO, surface crystal defects and oxygen vacancies are induced. Silver is a large work function material. Depositing a large work function metal on the surface of SMOs efficiently hampers the recombination process. This has been explained to be due to the formation of a barrier at the metal-semiconductor boundary. The barrier is known as the “Schottky barrier”. Addition of Ag to ZnO alters the opto-electric properties of ZnO which in turn affects its photocatalytic activity. As mentioned earlier, ZnO is a native type (n-type) semiconductor metal oxide. It has been reported that doping with or introducing Ag can transform it to a p-type material [90].

The photocatalytic process is dependent on the surface area, thus photocatalysis can be said to be a surface based mechanism. A larger surface area proportionally leads to an increase in photocatalytic performance thus increasing the surface area of a photocatalyst increases its photocatalytic activity. Dispersing SMO on large surface polymers was adopted to increase their active surface area hence leading to an enhanced activity [91]. Polymers also control the growth of nanostructures thus minimizing agglomeration of SMO nanostructures which may arise during growth of these nanostructures or upon interaction with a pollutant. Coagulation/agglomeration affects the reactivity of photocatalysts as it reduces the amount of light reaching the SMOs active sites. Polymers can also be used to deposit nanomaterials in order to achieve a higher surface area/volume aspect ratio. Polymers nanocomposites also result in high abrasion, better transparency, increased chemical stability and also help in immobilizing the photocatalyst. Polymer composites are reported to be advantageous because of their excellent recyclability and stability for potential applications in environmental remediation. Different metallic nanoparticles have been dispersed on cellulose for antibacterial and photocatalytic uses [68, 92-96]. Due to its long chain of negatively charged hydroxyl groups, strong interactions are formed between metal ions and cellulose matrix.

2.2. Antibacterial properties of Noble metals

Both inorganic and organic nanomaterials have been reported to possess antimicrobial activities. Amongst inorganic nanomaterials, antimicrobial activities of transitional metals and semiconducting metal oxides have been tested against a wide range of pathogens. This owes to their selectivity, durability, stability and resistance against harsh environments including heat, high temperatures and pressure [97]. Silver (Ag), copper (Cu), gold (Au), platinum (Pt), and palladium (Pd) have been studied for their antimicrobial activity. The historical discovery of silver as an antimicrobial agent dates back in ancient times. In the 1800's silver was used to treat ulcers and also administered to new born babies to prevent eye infections. Nevertheless it was later discarded upon the discovery of penicillin antibiotic. There is a resurgence of silver in antimicrobial applications as it is resurfacing to be the most captivating metal and exhibiting great

activity against a wide range of microorganisms when utilized on its own or as a compound.

The broad antimicrobial property of silver is well known; its antifungal [13], antibacterial [98-99], antiviral [100-103] and antiplatelet [104] effects have been reported. A comprehensive understanding of Ag nanostructures from physical and chemical properties, synthesis processes, applications and toxicity to the environment is important.

2.2.1 Background information of silver (Ag)

Silver is a naturally occurring yet rare element. It possesses the highest electrical and thermal conductivity as compared to all metals [105]. Ag compounds have a range of applications that include catalysis, electronics, biosensors, filters, therapeutics, biomolecular detection and diagnostics. Nano-scale Ag has been reported to possess greater antimicrobial activity as compared to bulk size Ag. Because of this property Ag nanoparticles play a huge role in the biomedical field.

The antimicrobial application of nano-silver ranges from coating-based usages (e.g. surface coating for neurological shunts, endotracheal tubes and venous catheters), disinfection of medical devices, treatments of nosocomial infections, treatment of wounds and burns, textiles coatings, paints, plastics manufacturing, cosmetics, water purification and a number of other environmental applications. Catheters and surgical masks are some of the medical devices that have been impregnated with nanosilver for improved antibacterial activity [106-107]. Ag has also been applied as a dressing for both first degree and second degree wounds. Using Ag nanoparticles on wounds improve the healing process as Ag nanoparticles retard the bacterial growth on the wound [108-109].

To develop Ag nanostructures of novel and distinguished morphologies and properties a number of various physical, chemical and biological synthetic routes are available. These includes reduction in solutions, chemical reduction; using polysaccharides [110], sonochemical, thermal decomposition [111], radiation assisted [99], micro emulsion, laser ablation, magnetron sputtering, microwave assisted, electrochemical [112], and

photochemical reduction to fabricate silver nanotubes [113], nanocubes [114-116], nanorods [117-118], nanowires [117, 119-120] and nanosheets [121-122].

Ag nanostructures have been investigated for their antibacterial action against a wide range of both Gram positive and Gram negative bacteria. Good activities were reported against some spores that have been previously labeled as multi-resistant. Amirulhusni *et al* [123], investigated the antibacterial activity of Ag against a multi resistant *Pseudomonas aeruginosa*, a gram negative bacterium. It was found that Ag nanoparticles exhibited significant effect against the *P.aeruginosa* even though it has previously been ruled susceptible to antibiotics. It is essential to know the antibacterial mechanisms of antibacterial agents. Ag and other metallic nanostructures inhibit the proliferation of bacterial through different mechanisms some of which are shown in Figure 2.6.

Antibacterial activities of TiO₂, Al₂O₃, SiO₂, ZnO, CeO₂, MgO, ZrO₂, NiO, Co₃O₄, CdO, CuO and CaO nanostructures are found in literature because of their ability to inhibit the growth of prokaryotic cells and also induce death in eukaryotic cells [11, 124-135]. Comparative studies have also shown ZnO nanostructures to display excellent bactericidal and bacteriostatic potential more than other SMOs [136-139]. Due to its antibacterial property of ZnO, applications in food packaging and textiles have been reported.

Recently, studies on the combined antibacterial effect of semiconductor metal oxides and Ag nanostructures against a wide of bacterial strains are reported. A wide spectrum of Ag-metal oxides including Ag-TiO₂ [140], Ag-SiO₂ [141], Ag-Fe₃O₄, Ag-CuO, and Ag-Al₂O₃ are found to exhibit excellent activities against both Gram positive and Gram negative bacteria. Zhang *et al*, [140] recently achieved potent antibacterial activity against *E.coli* through a one pot-synthesis of Ag nanostructures immobilized on TiO₂ support.

Ag nanostructures can be modified for better efficiency to facilitate their applications in different fields including biomedical applications. Embedding silver nanostructures on larger surface supports to control their antibacterial effectiveness is reported. These support materials do not only increase their surface-volume ratio but also improves other properties like the mechanical strength. Thin films, glass substrates have in the past

been used to embed silver nanostructures in order to control their leaching effect. Ag nanostructures on chitosan, [143-145], starch [146], polyvinyl alcohol (PVA), [147], polyaniline (PANI) [148], carbon fibers and nano tubes [149], polycarbonate (PC) [99], polypropylene (PP) [150] and alginate [151] are reported. It is thus interesting to study the properties of Ag on cellulose polymer matrix.

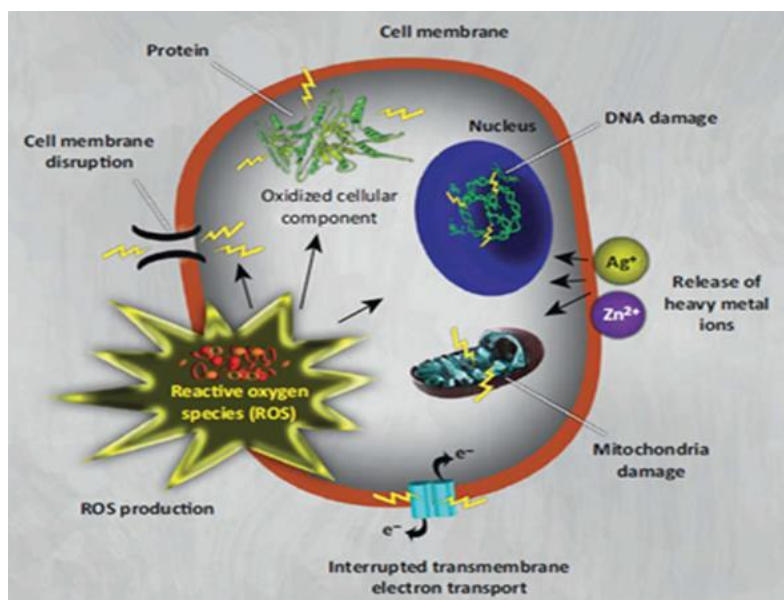


Figure 2.6: Proposed antibacterial mechanism of metallic nanostructures [142]

Besides, it is important to enhance the antimicrobial activity of Ag which can be achieved through different approaches. Hwan *et al* [141] reports the antibacterial activity of Ag-SiO₂ nanocomposite. The inhibitory effects of Ag-SiO₂ nanocomposite was investigated through monitoring inhibitory effects against different microorganisms which includes three Gram negative bacterial strains; *E. cloacae*, *P.aeruginosa*, *E.coli*, one Gram positive strain; *S.aureus*, yeast and fungus strains. Ag-SiO₂ showed excellent inhibitory effects to all tested specimen. According to Hwan *et al*, [141] SiO₂ controls the dispersion of Ag nanostructures, avoiding agglomeration and thus an elevated contact of Ag with bacterial cell. Table 2.2 presents a summary of some of the approaches that have been implemented for efficient antibacterial and photocatalytic activity of ZnO and Ag either through incorporation on polymer matrix of addition of another metallic nanostructure.

The next chapter gives an overview on the materials and methods used to fabricate, characterize and assess Ag/ZnO/cellulose nanocomposite

Table 2.2: A brief summary of some of the surface modified Ag and ZnO for photocatalysis and antibacterial applications.

Study	Material and method	Results
Dhanavel <i>et al</i> [152]	ZnO-chitosan composite through chemical precipitation method.	High photocatalytic activity as compared to bare ZnO as about 80% of methylene blue was degraded in 4 hours under UV irradiation in the presence of ZnO-chitosan composite
Ye <i>et al</i> [153]	ZnO in-situ dispersed on cellulose matrix through combined solvothermal and electrospinning methods	A dramatic increase in the photocatalytic activity of ZnO when dispersed on cellulose matrix. ZnO/cellulose nanocomposite recycled and re-tested it again obtaining a higher activity.
Lu <i>et al</i> [154]	Ag-ZnO nanocomposite through one-pot hydrothermal method	Ag/ZnO showed potential applications in photodegradation of organic dyes pollutants and destruction of bacteria.
Yin <i>et al</i> [155]	Ag/ZnO/activated carbon nanocomposite through powder sol method	Hybridization of Ag, ZnO and activated carbon significantly improved the photocatalytic efficiency of ZnO against methyl orange
Pant <i>et al</i> , [156]	Ag/TiO ₂ -nylon nanocomposite mats through combined photo-reduction and electrospinning methods	Superior photocatalytic against methylene blue and antimicrobial activities against <i>Escherichia coli</i> .
Hwan <i>et al</i> [141]	Ag-Polystyrene composite through chemical reduction method	Significant antibacterial activity against Gram positive <i>S.aureus</i> and Gram negative <i>E.coli</i> , <i>Klebsiella pneumoniae</i> , and <i>Salmonella</i>
Kim <i>et al</i> [157]	Ag-SiO ₂ nanocomposite through the Stober method	Higher activities detected against Gram positive bacteria, yeast and fungi

CHAPTER 3: EXPERIMENTAL PROCEDURE/ METHODOLOGY

3.0 Introduction

Different methods ranging from biological, chemical and physical approaches as mentioned in chapter 2 have been used for the synthesis of different nanomaterials. With the aim of shifting to much eco-friendly technologies, green composites have gained interest. This chapter gives an overview on the materials, methods and procedures used for the preparation of Ag/ZnO/Cellulose nanocomposite and other test samples. It also describes the techniques used for characterisation of the samples and finally the photocatalytic and antibacterial activity assessment procedures are described in the chapter.

3.1. Materials and Methods

All chemicals used in this work are of high analytical grade and obtained from Sigma-Aldrich and hence no further purification was done.

3.1.1 Preparation of nanocellulose

Different approaches have been used to extract cellulose from different sources. In this project a combined alkaline-acid hydrolysis treatment procedure is reported for the extraction of cellulose from oil palm empty fruit bunches (OPEFB).

Reagents used in this work include;

- ✚ Oil palm empty fruit bunches (locally collected, Palapye Botswana)
- ✚ Ethanol (Sigma Aldrich, Germany, 99.99% purity)
- ✚ De-ionized water (collected from DI plant, Department of Chemistry & Forensic Sciences)
- ✚ Sodium hydroxide pellets (Sigma Aldrich, Germany 99.99% purity)

- ✚ Sodium hypochlorite (Sigma Aldrich, Germany 10 % w/v)
- ✚ Hydrochloric acid (Sigma Aldrich, Germany, 40 % w/v)

The cellulose biomass extract was obtained from the oil palm empty fruit bunches (OPEFB) around Palapye village. Firstly the OPEFB (shown in Figure 3.1) were washed with distilled water to remove dust and other unknown impurities. These fruit bunches were cut open and the inner part (seed) thrown away. The outer coverings were then mechanically milled. The resulting powder was then sieved to obtain the finest particles. The particles were soaked in ethanol for 24 hours in order to remove wax and other impurities which may have been left from washing with distilled water. The soaking in ethanol was repeated two more times this time at an interval of 2 hours.

To isolate cellulose fibres, previously reported procedures were adopted to remove non-cellulosic components in OPEFB [92, 158-160]. The obtained biomass was treated in an alkaline media by soaking in 4 % w/v of sodium hydroxide at elevated temperatures of 90 °C for 2 hours. Alkaline treatment plays a significant role in the removal of most of the alkali soluble, non-cellulosic cementing material (hemicellulose and lignin). It also overcomes the problems of lack of good interfacial adhesion; low melting point and poor wettability [161]. After alkaline treatment the biomass was filtered and treated through a step known as acid hydrolysis in 30 % w/w hydrochloric acid, at a temperature of 45 °C for an hour. Acid hydrolysis helps in digestion of the residual hemicellulose. Bleaching was carried out using 3.5 wt. % of sodium hypochlorite. The bleaching process was repeated three times until the fibres were white. It has been reported that apart from improving the physical appearance of fibres, bleaching helps in improvement of mechanical properties due to the enhanced fibre/matrix interfacial adhesion [162]. The cellulose was then harvested by filtration, washed three times with de-ionized water and allowed to dry in air for 48 hours. Figure 3.1 illustrates the whole cellulose extraction process.

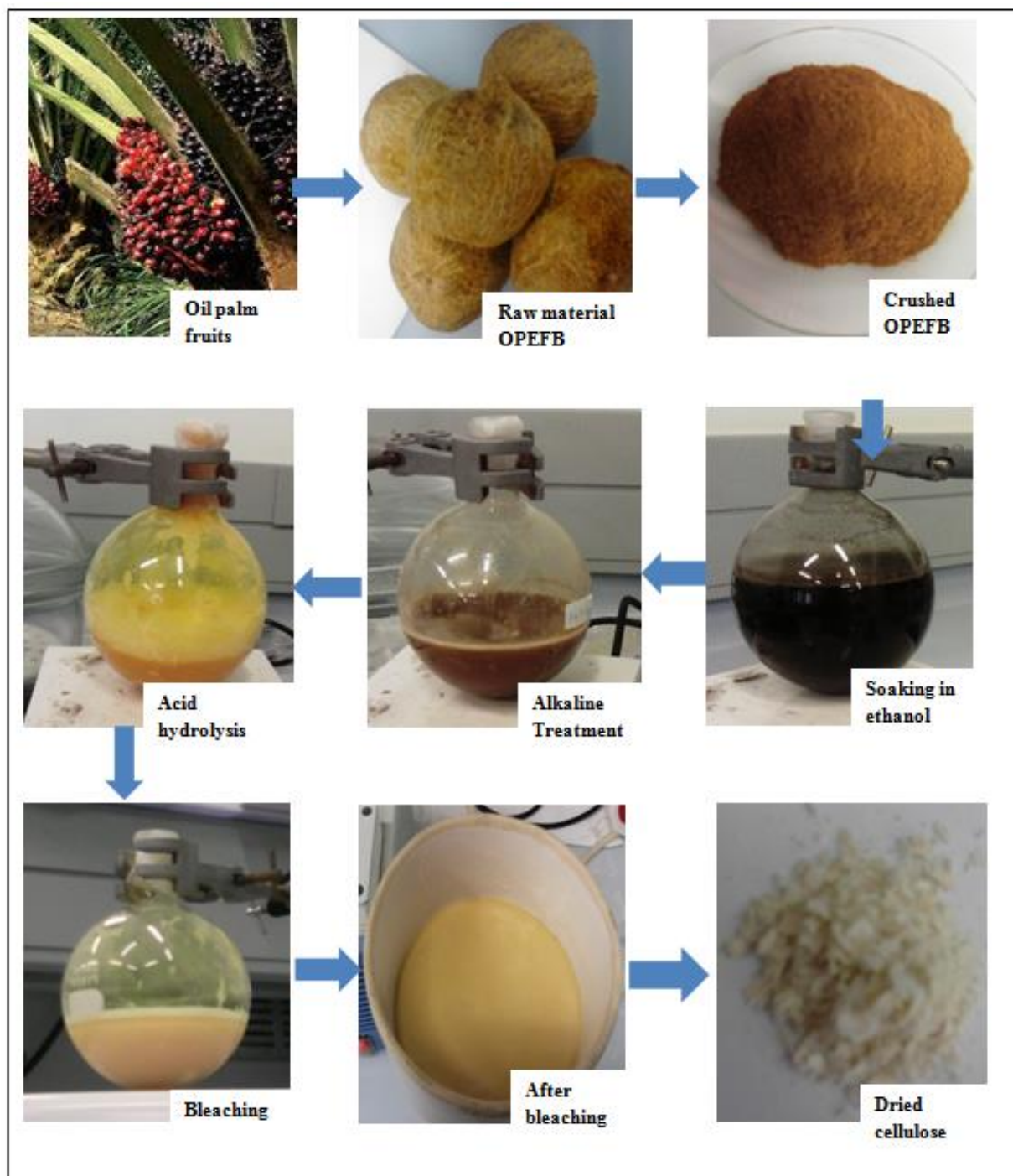


Figure 3.1: Step by step extraction of cellulose

3.1.2 Preparation of ZnO nanostructures

In this work a simple, fast and high yield efficient wet-chemical method was used to synthesis ZnO nanostructures.

Reagents used in this work include;

- ✚ Zinc nitrate hexahydrate salt (Sigma Aldrich, Germany 99.99 % purity)
- ✚ Sodium hydroxide pellets (Sigma Aldrich, Germany 99.99% purity)
- ✚ De-ionized water (collected from DI plant, Department of Chemistry & Forensic Sciences)

Zinc oxide nanoparticles were synthesized by wet chemical reduction method using zinc nitrate hexahydrate as the Zn source. 100 ml of each of 1.0 M NaOH and 0.5 M Zn (NO₃)₂·6H₂O solutions were prepared. The molar ratios were chosen to allow the conversion of all of the Zn (NO₃)₂·6H₂O. The following calculations were carried for the preparation of 1.0 M NaOH and 0.5 M of Zn (NO₃)₂·6H₂O respectively;

Preparation Zn (NO₃)₂·6H₂O aqueous solution

Molar mass: 297.41668 g/mol

Desired final volume: 100 mL.

Desired concentration: 0.5 M

Mass = 14.8708 g

Preparation of NaOH aqueous solution

Molar mass: 39.99 g/mol

Desired final volume: 100 mL.

Desired concentration: 1.0 M

Mass = 3.9997 g

The procedure for the preparation of ZnO nanostructures is described by flow chart in Figure 3.2.

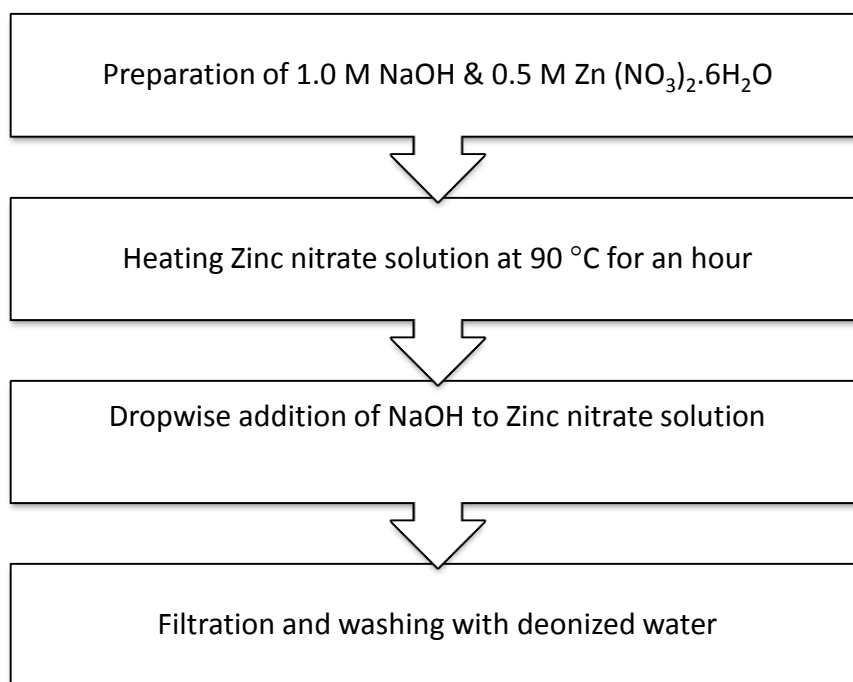
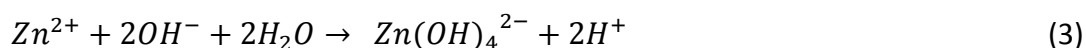
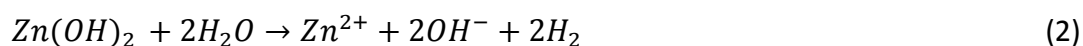
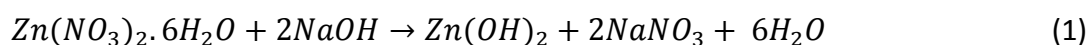


Figure 3.2: Flow chart showing the synthetic procedure for ZnO nanostructures

The prepared zinc nitrate solution was heated at 90 °C under constant magnetic stirring for an hour. The sodium containing solution was added drop wise to the zinc nitrate solution for 30 minutes, still maintaining the same temperature of 90 °C. A white precipitate was observed. After 3 hours the white precipitate was harvested by filtration using a Whatman No.1 filter paper. The harvested precipitate was washed three times with de-ionized water to remove access reagents and unwanted by products. The precipitate was left overnight to dry and then oven dried at 65 °C for 8 hours. Equations 1- 4 describe the reactions for the formation of ZnO.



3.1.3 Preparation of the ZnO/cellulose (ZnO/NC) nanocomposite

In-situ solution casting technique was used for preparing ZnO/NC by using the cellulose extracted from section 3.1.1. Same conditions as in the preparation of ZnO nanostructures were maintained.

Reagents used for the synthesis of ZnO/NC composite include;

- + Zinc nitrate hexahydrate salt (Sigma Aldrich, Germany, 99.99 % purity)
- + De-ionized water (collected from DI plant, Department of Chemistry & Forensic Sciences)
- + Sodium hydroxide pellets (Sigma Aldrich, Germany, 99.99 % purity)
- + Extracted cellulose (From section 3.1.1)

An equal content of cellulose and ZnO was used for the preparation of ZnO/NC composite. An appropriate amount of the previously extracted cellulose was suspended in de-ionized water. 0.5 M solution $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was prepared and added to the cellulose suspension. This solution was then kept under magnetic stirring at 90 °C for an hour. 1.0 M solution of NaOH was then prepared and added drop wise to the cellulose-nitrate solution while maintaining same conditions (constant magnetic stirring at 90 °C). Formation of a white precipitate was observed when adding the sodium hydroxide solution. The solution was left under constant stirring and temperature for 3 hours after which the precipitate was harvested by filtration and washed with de-ionized water three times to remove by-products. The precipitate was then left over night to air-dry, followed by heating in an oven at 65 °C for several hours. The main role of dispersing ZnO on the cellulose polymer is to overcome the problem of agglomeration thus increasing surface area to volume ratio and also the increasing the number of exposed active sites for light absorption.

3.1.4. Preparation of silver-cellulose (Ag/NC) nanocomposite

Reagents used in this work include;

- ✚ Silver nanoparticles (Sigma Aldrich, Germany)
- ✚ De-ionized water- (collected from DI plant, Department of Chemistry & Forensic Sciences)
- ✚ Extracted cellulose (from section 3.1.1)

An equal content of cellulose and Ag was also used for the preparation of Ag/NC composite. About 1g of the previously extracted cellulose was suspended in de-ionized water. The same amount (1g) of silver nanoparticles was added to the cellulose mixture. The mixture was vigorously stirred for several hours to obtain a homogeneous mixture and to allow the Ag nanoparticles attach to the cellulose molecules, followed by filtration. The obtained filtrate was washed with de-ionized water three times to remove by-products. The precipitate was then left over night to air-dry followed by drying in an oven.

3.1.5 Preparation of silver/zinc oxide/cellulose (Ag/ZnO/NC) nanocomposites

Three different Ag/ZnO/NC nanocomposites with different silver and ZnO contents were synthesized. The amount of cellulose used across all nanocomposites was constant, however the amount of silver and ZnO were varied. The ratio of Ag and ZnO used are shown in Table 3.1.

Table 3.1: Preparation conditions; Ag and ZnO content for different Ag/ZnO/NC nanocomposite

Sample	Ag	ZnO	ZnO/Ag
Ag/ZnO/NC1	0.75	0.25	0.33
Ag/ZnO/NC2	0.50	0.50	1.00
Ag/ZnO/NC3	0.25	0.75	3.00

Other than different Ag and ZnO ratios, preparation conditions were kept constant as the preparation of other samples (ZnO, ZnO/NC and Ag/NC). For these three different Ag/ZnO/NC composites, first the appropriate mass of cellulose was dispersed into 100 ml

of distilled water. 0.5 M solution of zinc nitrate hexahydrate was prepared and added to the cellulose suspension after which the mixture was kept under static magnetic stirring at 60 °C for an hour. A corresponding mass of silver nanopowders was added and the whole mixture vigorously stirred for another hour. 1.0 M of sodium hydroxide solution was prepared and added drop wise to the cellulose/zinc nitrate/Ag suspension. The mixture was left under continuous magnetic stirring for another 5 hours, after which the precipitate was harvested through filtration and washed several times with de-ionized water to remove excess reactants. The precipitate was finally left overnight to dry and heated in an oven at 120 °C for 8 hours to convert all zinc and hydroxyl ions to zinc oxide.

3.2 Characterisation and Instrumentation

Different experimental techniques were used to characterize the synthesised materials. The structural, optical and surface morphology of the samples were investigated. This section describes different characterization techniques used in this work, which are given in Figure 3.3.

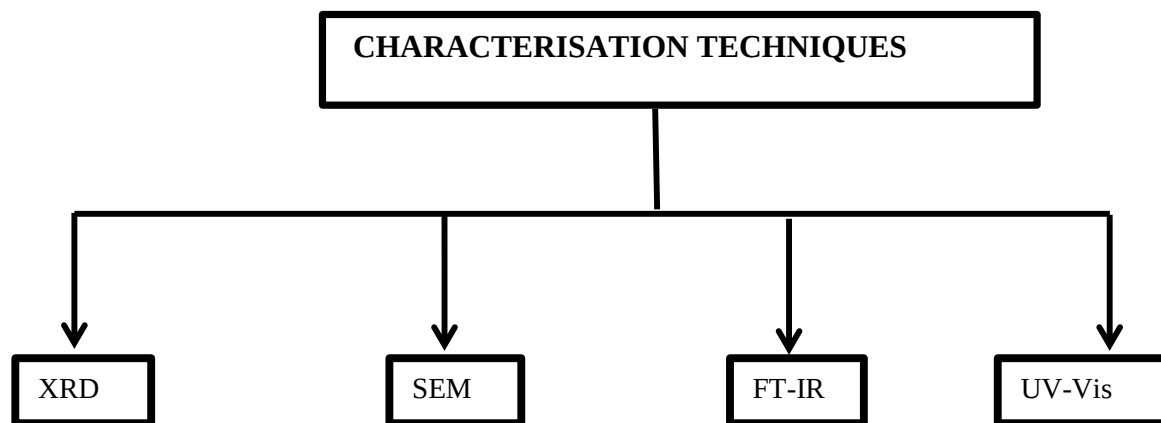


Figure 3.3: Different techniques for the characterisation of prepared nanomaterials.

3.2.1 Structural characterization

3.2.1.1 X-Ray diffraction patterns

To determine the structural and crystalline properties of the samples, X-ray diffraction patterns were obtained using a Bruker D8 Advance X-ray diffractometer shown in Figure 3.4. This diffractometer is fitted with a Lynx detector, equipped with a monochromatic K_{α} radiation source of being copper with wavelength 0.15406 nm. The operating parameters for XRD measurements are summarized in Table 3.2.

Table 3.2: Operating parameters for the Bruker D8 Advance system used

Operating parameter	Value
Accelerating voltage	40 kV
Current	40mA
Scanning step	0.05°
Scanning rate	2 s/step, (1.5°/min)
Scan type	Coupled two theta/theta
Scan mode	Continuous PSD fast

An XRD houses a cathode ray tube which generates X-rays that are filtered to produce monochromatic radiation. The rays are collimated towards the sample, which upon interaction with the sample produces constructive interference and a diffracted ray which obeys Bragg's law stated in equation 5;

$$n\lambda = 2d\sin\theta \quad (5)$$

Where;

n is the integer 1,2,3.....(usually 1)

λ is the wavelength of the electromagnetic radiation used (in Å)

θ is the angle of diffraction (in degrees)

d is the lattice spacing in the sample (spacing between atomic layers)

The diffracted X-rays are then detected, processed and counted. Eva XRD software was used for analysis of the recorded patterns.



Figure 3.4: A picture of the Bruker D8 Advance XRD equipment used

3.2.1.2 Field emission scanning electron microscopy (FESEM)

A JEOL JSM 7100F field emission scanning electron microscope (FESEM) (Figure 3.5) was used to study surface morphology of the samples. The technique uses electron beams to scan the surfaces of samples and give resultant images at high resolution. Basic components of the FESEM include the cathode ray tube; the lens system, electron gun, and electron collector. A beam of electrons with significant amount of kinetic energy is produced through thermionic emission from an electron gun fitted with a tungsten filament cathode. The electron beam is then accelerated on a vertical path through the microscope tube, which is held within a vacuum. The beam travels through electromagnetic fields and lenses, focusing the beam down towards the sample. The energy carried by accelerated electrons is dissipated as a variety of signals produced by interactions between the sample and electrons. These include backscattered electrons,

secondary electrons (that produce SEM images); diffracted backscattered electrons (which are normally used to determine the crystal structures and orientations of materials), photons (which are characteristic X-rays used for elemental analysis and continuous X-rays), visible light and heat are also produced. The JEOL JSM 7100F FESEM is equipped with an energy dispersive spectrometer (EDS) for elemental and chemical composition analysis. EDS was used for detailed analysis on the composition of all constituents of the sample. Operating parameters of the FESEM and EDS equipment used are given in Table 3.3.

Table 3.3: Operating parameters of the JEOL JSM 7100F FESEM used in this study

Operating Parameters	Value
Accelerating Voltage	10-15 kV
Working distance (W.D)	10 mm
Probe current	2-6 mA

Sample preparation is necessary before using SEM. It helps to avoid the charging of samples. All dry samples were coated with a thin layer of a conductive material to avoid charge buildup. The samples were mounted on an SEM sample holder known as a stub and coated with carbon graphite using a sputter coater.



Figure 3.5: A picture of the JEOL JSM 7100F FESEM equipment used in this study

3.2.2 Optical characterization

3.2.2.1 *Fourier transform infrared spectroscopy (FTIR)*

The FTIR technique as the name implies, uses low energy infrared radiation (IR) for qualitative and quantitative analysis of a sample and components making up that sample; either be organic or inorganic samples. Generally IR radiation is produced by a black body source which is simply an inert solid that upon being heated electrically stimulates thermal emission of radiation in the infrared region of the electromagnetic spectrum. A silicon carbide rod also known as a Globar is a widely known black body source. When IR is generated from the source, it is passed through the sample and reaches the detector. However; not all the generated radiation reaches the detector, part of it is transmitted while the other is absorbed by the sample.

Because of different molecules and functional groups making up each different sample, the sample only absorbs resonant frequency that is specific to its structure. For this reason each sample produces its own different infrared spectrum, with different absorption bands at different wavenumbers corresponding to the absorbed resonant frequency. Knowing the functional groups of a material is an important fundamental aspect in FTIR analysis. A Perkin Elmer Spectrum Two ATR-FTIR model spectrophotometer (made in USA) shown in Figure 3.6 was used to investigate functional groups of the samples in the mid IR region. Operating parameters of the FTIR spectrometer are given in Table 3.4.

Table 3.4: Operating parameters of the used Perkin Elmer Spectrum Two ATR-FTIR spectrophotometer

Operating Parameters	Value
Wavenumber range	4000-400 cm^{-1}
Spectral resolution	4 cm^{-1}
Number of scans	32

3.2.2.2 UV-VIS-NIR spectrometry

UV-Vis Spectroscopy also known as the absorption spectroscopy is a technique which involves the use of higher energy radiation in the UV (200-400 nm) and visible (400-700 nm) range of the electromagnetic spectrum for sample characterisation. This radiation somehow causes organic molecules to undergo electronic transitions, as valence electrons are excited from a lower energy to a higher energy molecular orbital.

Basically, the spectrophotometer sends white light to the monochromator which transmits specific wavelengths. The selected wavelength of light reaches the sample; part of it is absorbed while the remaining photons are detected by the detector. A Lambda 750 Perkin Elmer UV-Vis-NIR spectrophotometer shown in Figure 3.7 was used to measure the absorbance and transmittance of the samples. Table 3.5 represents operating parameters used for all measurements.



Figure 3.6: A picture of the Perkin Elmer Spectrum Two ATR-FTIR spectrophotometer equipment used

Table 3.5: Operational parameters for the used Lambda 750 Perkin Elmer UV-Vis-NIR spectrophotometer

Operating parameter	Value
Wavelength range	290-900 nm
Data interval	1 nm



Figure 3.7: A picture of the Lambda 750 Perkin Elmer UV-Vis-NIR spectrophotometer used

3.3 Photocatalytic and Antibacterial Activity Assessment Procedures

3.3.1 Photocatalysis assessment procedure

The photocatalytic efficiencies of the samples were investigated through monitoring the degradation of aqueous methylene blue dye as a probe model compound, [color index. number 52015; molar mass 319.86 g/mol, wavelength maximum 665 nm, chemical formula ($C_{16}H_{18}ClN_3S$)] and chemical structure shown in Figure 3.8.

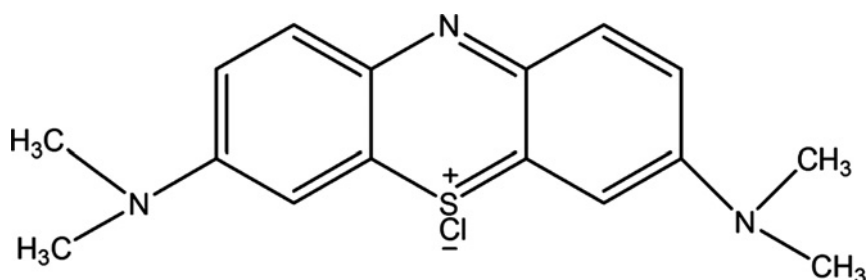


Figure 3.8: Chemical structure of methylene blue [163]

About 75 mg of the synthesized nanopowders were separately dispersed into 150 mL of freshly prepared methylene blue aqueous solution to get a concentration 0.004 mg/mL. The mixture was magnetically stirred in the dark for an hour to establish the adsorption-desorption equilibrium and stabilise. Irradiation was carried out in an open space using visible light from the sun as a source of radiation. All photocatalytic experiments were carried out at the same time, under similar conditions. After irradiation for 30, 60, 90, 120, 150 and 180 minutes, 3 mL of the mixture was collected and centrifuged at 1300 rpm for 20 minutes to allow small particulates of the photocatalyst to settle at the bottom. The degradation was monitored by measuring the absorbance amount using a double beam UV–Vis spectrophotometer (Perkin Elmer Lambda 750, described in section 3.22) in the wavelength range of 500 to 800 nm.

3.3.2 Antibacterial assessment procedure

Agar well diffusion method [164] also known as zone of inhibition method was adopted to assess the antibacterial properties of the prepared samples. Gram positive *Staphylococcus aureus* and Gram negative *Escherichia coli* bacterial species were used as model bacteria. Another Gram positive, a spore forming bacteria known as *Bacillus subtilis* was also used to test the antibacterial activities of the samples.

Nutrient agar (NA) medium was used as an enriched medium for the growth of fresh pathogenic species. About 1.6g of the ready-made nutrient agar powder was dissolved in 100 ml of distilled water to prepare the NA. The prepared medium was then sterilized in an autoclave at 121 °C for 60 minutes and later poured into sterile petri dishes to solidify. Two of petri dishes were used for each bacterial strain.

0.1 ml (100 µl) of freshly grown culture of the bacterial species was pipetted from the nutrient broth into the respective labeled agar-containing petri dishes and smeared using an aseptically cleaned sterile glass rod. The plates were kept at room temperature in a laminar/fume hood for about 5 minutes to dry. Eight wells of 7 mm diameter were made using a sterile well cutter in all the plates, making sure there is equal distance apart

between them and that they were not closer to the wall of the Petri dishes so as to allow maximum diffusion.

0.05 g of each sample was used to make a paste using de-ionized water. The paste was then loaded into the respective labeled well. Tetracycline was used as standard antibacterial agent. It is known to be a broad spectrum antibiotic as it inhibits both Gram negative and positive microorganisms. An equal amount of tetracycline was also loaded into its respective labeled well. The plates were allowed to stand for an hour to allow for proper absorption of the samples into the surrounding medium, after which they were incubated for 24 hours at 37 °C and observed for zone of bacterial growth inhibition around the wells. The size of the zone (including the diameter of the well) was measured to the nearest millimeter using a ruler at two cross-sectional points and the average was taken as the diameter of inhibition zone. The whole procedure was conducted out in a sterile environment. Autoclaving, flame and ethanol were used to sterilize the equipment and surroundings. Three replicate tests were carried out in the same conditions for each bacterial species.

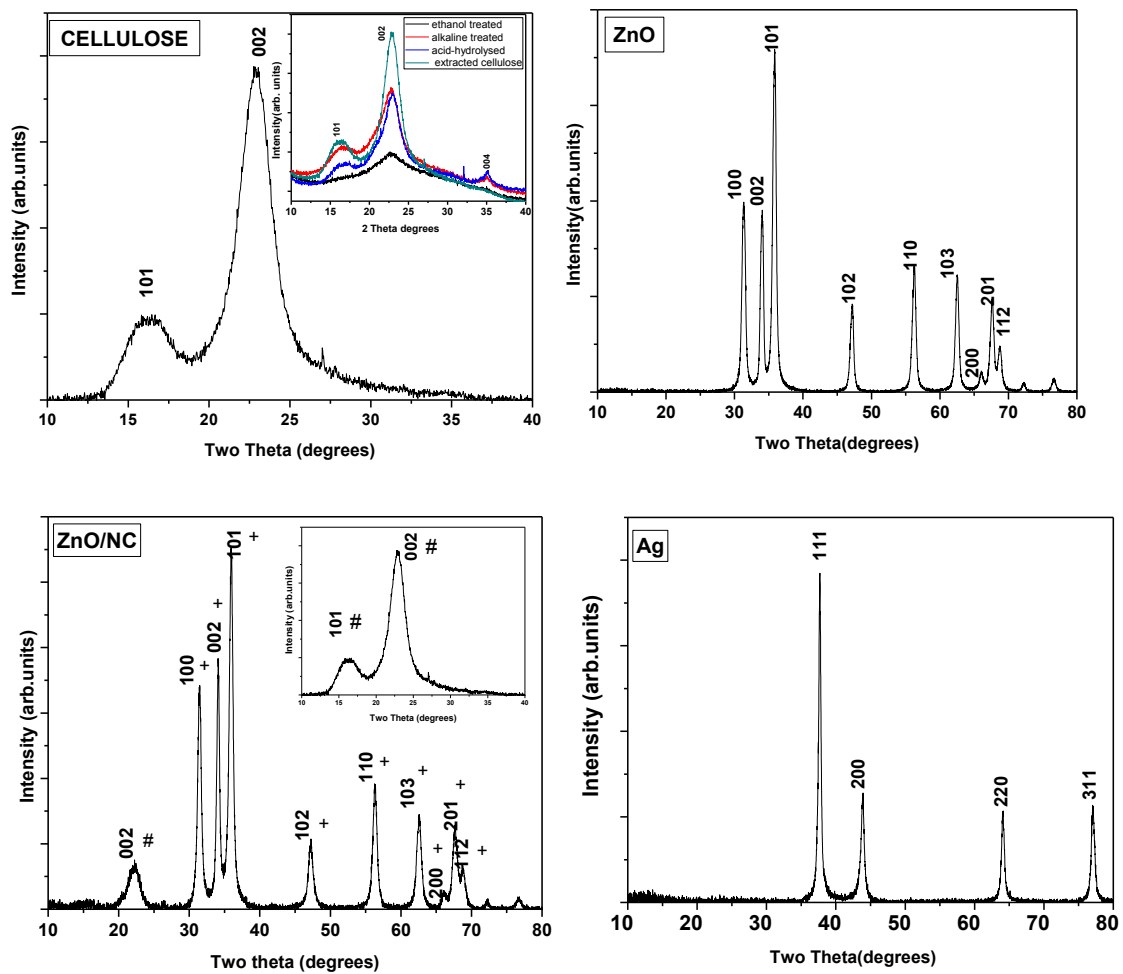
The next chapter presents the results obtained on the morphological, structural and optical characteristics of the synthesised samples. As stated, a field emission scanning electron microscope equipped with energy dispersive spectrometer was used for morphological and elemental analysis, X-ray diffraction for structural analysis and FTIR and UV-Vis-NIR for optical characterisation, respectively. It also reports the photocatalytic activity of samples against degradation of methylene blue and lastly the antibacterial assessments of the prepared samples against some bacterial species.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Structural and Morphological Characterization

4.1.1 X-ray powder diffractometry analysis

The phase purity and composition of the samples were examined through X-ray diffraction measurements taken from different 2θ range per sample. The XRD diffractographs of cellulose, Ag, ZnO, Ag/cellulose (Ag/NC), ZnO/cellulose (ZnO/NC) and Ag/ZnO/Cellulose (Ag/ZnO/NC) are illustrated in Figure 4.1.



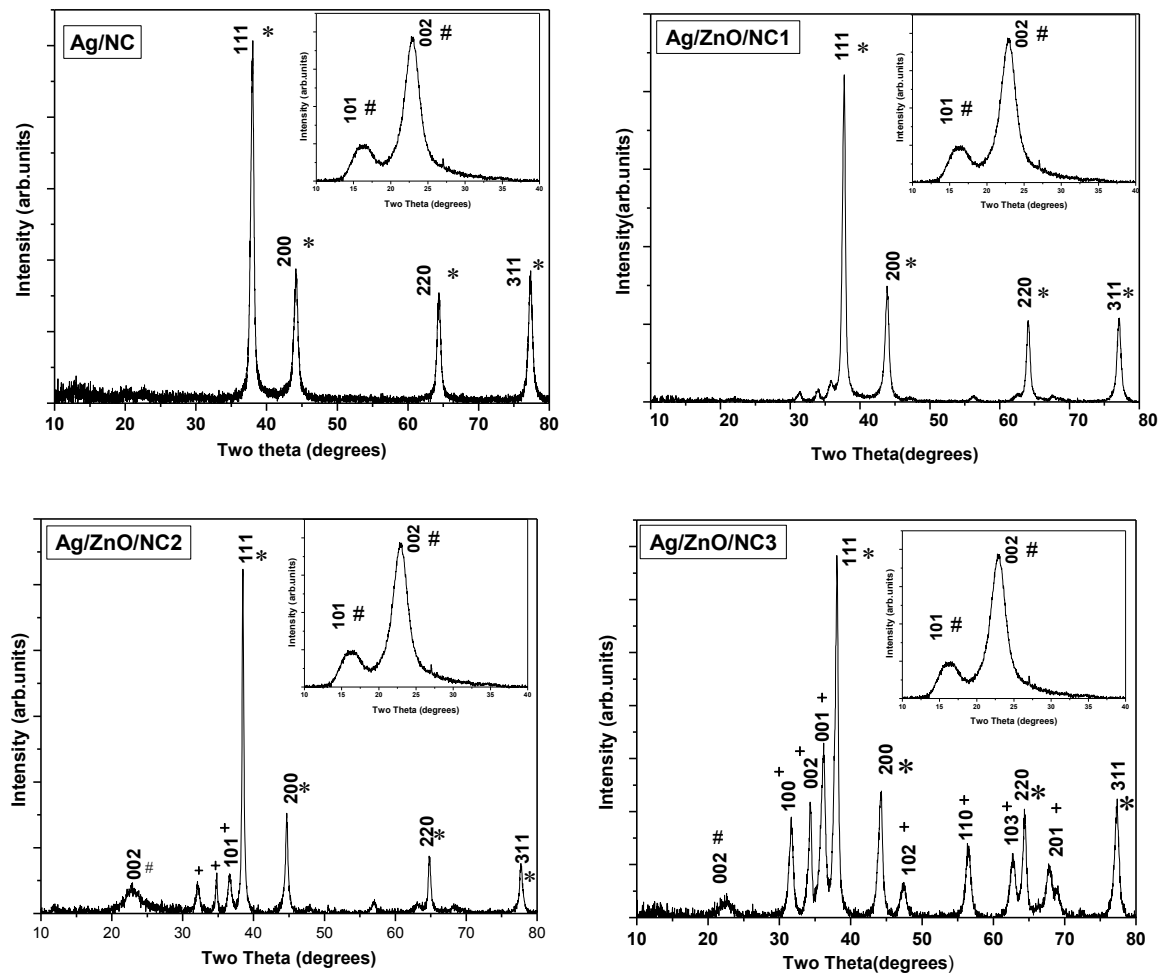


Figure 4.1: XRD patterns of the samples as labelled in each diagram {(#) indicates cellulose peaks and (*) indicates ZnO peaks and (+) indicates Ag peaks in the composite}

From XRD analysis, the main characteristic peaks of the extracted cellulose were observed at $2\theta = 16.28$ and 22.96° as shown in Figure 4.1. These peaks were attributed to the (101) and (002) planes, respectively. Two types of cellulose are reported in literature, cellulose type I and cellulose type II. For this experiment the observed peaks pointed to cellulose I monoclinic structure, and were all indexed to the 2013 COD database of ID number COD 4114994. XRD measurements were also done for all the treatment stages of the OPEFB (shown as an insert in cellulose diffractograph), and from this XRD spectra the percentage crystalline index (% C.I) for each stage was calculated using the amorphous subtraction method described by equation 5; [165].

$$\%C.I = \frac{I_{002} - I_{am}}{I_{am}} * 100 \quad (5)$$

Where I_{002} is the maximum intensity of the principal peak (002) lattice diffraction and I_{am} is the intensity of diffraction attributed to amorphous cellulose, which is the valley between peak (101) and (002).

From the calculated data, it can be deduced that each treatment step affected the crystallinity of the material. The results of the calculated % C.I.'s are tabulated in Table 4.1. Treatment of the fibres increased their % C.I. The C.I. was found to have increased from 35.7 % to 62.6 % after the removal of lignin and hemicelluloses as indicated in Table 4.1. This increase in % C.I. indicates an improvement in the structure of the cellulose. The physical and mechanical properties of cellulose are influenced by its crystalline structure. Crystalline index is one important parameter of cellulose crystal structure. Pre-treatment of fibres increases their crystalline index as the ratio of crystalline to amorphous regions is increased hence this affects the accessibility of cellulose molecules, increases dimensional stability, increases surface roughness, and also decreases the swelling of the polymer [158].

Table 4.1: Crystalline index of cellulosic fibres at different treatment stages

Treatment stage	I_{am}	I_{002}	(%)C.I
Ethanol treatment	2557	3975	35.7 %
Alkaline treatment	4036	7092	43.3 %
Acid hydrolysis	3245	6951	53.3 %
Final cellulose extract	3725	10098	62.6 %

An XRD profile of ZnO synthesized through wet chemical method. The observed significant XRD peaks of ZnO at $2\theta = 31.30, 33.96, 35.74, 47.26, 56.35, 62.78, 66.32, 67.43, 68.99, 72.53$ and 76.52° correspond to the (100), (002), (101), (102), (110), (103), (200), (201) and (112) peaks respectively. All the observed ZnO peaks resemble those previously reported in literature, [58, 62, 166-169]. No secondary phase was detected as the pattern showed a single-phase nature. High peak intensity was observed for ZnO, indicating the crystalline nature of the synthesized ZnO nanostructures. The observed peaks match a wurtzite hexagonal crystallographic lattice and are consistent with the 2013 COD database of ID number COD 2300112.

As revealed in Figure 4.1, the XRD profile of ZnO-cellulose (ZnO/NC) nanocomposite displays two phase structures corresponding to cellulose (#) and ZnO (+). A reflection at 2θ of 22.22° was attributed to the (002) crystal lattice of cellulose. All ZnO and cellulose peaks that were observed for pristine samples were also displayed in the nanocomposite. It can be deduced from these profile that the presence of ZnO has not altered the crystal structure of the cellulose matrix, and that ZnO nanostructures have crystallised well in the cellulose polymeric matrix as no significant new peaks or any peak shift were observed. ZnO and cellulose peaks were in the same 2θ positions as in individual materials; however there were some changes in the intensities of the peak. The intensities of both the cellulose and ZnO peaks decreased in the nanocomposite, due to the dispersal of the materials. The width of the peaks also narrowed, indicating an increase in crystallinity.

To determine the crystallographic planes in the unit cell, Miller indices (hkl) of the samples were used. Since different materials exhibit different crystal structures, different lattice geometry equations are used for calculating the lattice parameters (a, b and c) of each structure. The calculated lattice parameters can be employed to determine the volume of a unit cell structure.

The observed structure of ZnO was a hexagonal structure. Equation 6 is used to calculate the lattice parameters of a material with a hexagonal cell structure.

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + l^2}{a^2} \right) + \frac{l^2}{c^2} \quad (6)$$

The unit volume of ZnO in each sample containing ZnO was calculated using equation 7;

$$V = \frac{\sqrt{3}a^2c}{2} \quad (7)$$

The calculated lattice parameters, lattice constants, unit volume and reference COD values of ZnO in all samples containing ZnO are presented in Table 4.2.

Table 4.2: Lattice parameters (a, b, c) constants (c/a) and unit volume of ZnO.

Parameters	Values (nm)					
	ZnO	ZnO/NC	Ag/ZnO/NC1	Ag/ZnO/NC2	Ag/ZnO/NC3	COD 2300112
a=b (nm)	0.3240	0.3246	0.3247	0.3246	0.3249	0.3249
c (nm)	0.5205	0.5209	0.5205	0.5204	0.5200	0.5205
c/a	1.6064	1.6045	1.6032	1.6031	1.6004	1.6020
Volume(nm ³)	0.0473	0.0475	0.0475	0.0475	0.0475	0.0476

XRD pattern of Ag in Figure 4.1 shows its crystalline structure. About four significant peaks of high intensities were displayed at $2\theta = 37.50, 43.93, 63.88$ and 76.97° , which were ascribed as the (111), (200), (220) and (311) planes, respectively. All observed reflection correspond to neat silver metal. No spurious peaks indicating impurities were observed as all peaks agree to those that have been previously reported [170-173]. All Miller indices of the Bragg reflections were index to the standard 2013 COD database of ID number 1100136. From XRD crystallographic analysis, it was found that the Ag displayed a face-centered-cubic structure.

The Ag nanospheres dispersed well in the cellulose matrix as evidenced by peaks for both the Ag and cellulose in the Ag/NC nanocomposite as shown in Figure 4.1. No new peaks were observed. Cellulose peaks were identified in the composite but were dwarfed decreased as the Ag peaks intensified because of the high crystallinity nature of Ag. There was a slight shifting of the peaks positions to higher 2θ angles and also reduction in the intensity of the peaks as compared to in pristine samples. These two changes are associated with reaction between Ag and cellulose.

The crystalline nature of Ag exhibits a cubic crystal structure. The lattice parameters of silver were calculated using equation 8 and presented in Table 4.3.

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad (8)$$

For a cubic cell lattice parameter $a=b=c$, hence the unit cell volume calculated by equation 9:

$$V = abc \text{ or } V = a^3 \quad (9)$$

Table 4.3: Lattice parameters (a=b=c), constants (c/a) and unit volume of Ag.

Parameters	Values					
	Ag	Ag/NC	Ag/ZnO/NC1	Ag/ZnO/NC2	Ag/ZnO/NC3	COD
						1100136
a=b=c (nm)	0.4036	0.4068	0.4066	0.4078	0.4072	0.4086
c/a	1	1	1	1	1	1
Volume (nm ³)	0.06574	0.06732	0.06722	0.06782	0.06752	0.06822

The crystallographic analysis showed that all Ag/ZnO/NC composites showed three sets of peaks corresponding to Ag, ZnO and cellulose peaks. The Ag and ZnO peaks in the composites were indexed to the face-centred-cubic and hexagonal wurtzite crystal structures, respectively. No impurity peaks were observed. However, there was a slight peak shifting to higher angle values, which may be due to Ag-ZnO defects or indication of the metal nanoparticles stabilising well in the polymer matrix [174]. All the three Ag/ZnO/NC composites show the peaks at almost same angle positions. This shows that varying the ZnO: Ag content ratio has not affected the components structure. Peak broadening was observed for both the Ag and ZnO peaks as the ZnO/Ag content ratio changed.

A slight uneven increase in the value of the calculated lattice parameters was observed. The increase in lattice parameters indicates the stretching of unit cells. Shama *et al* [175], reported that adsorption of polymer molecular chains on the surface of ZnO nanostructures causes an increase in lattice parameters; thus increasing the volume of the unit cell of ZnO. The crystallite sizes of all components (Ag, ZnO and cellulose) were calculated using the most intense peak for every sample. The (111), (101), and (002) peaks are the most intense peaks for Ag, ZnO and cellulose, respectively. The calculations were done using the Debye- Scherer's equation [176]:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (10)$$

Where D is the crystalline size, λ is the X-ray wavelength (1.5406 Å for Cu K α radiation), β is the observed angular width at half maximum intensity of the peak (FWHM) and θ is the Bragg diffraction angle corresponding to that most intense peak for the sample.

The calculated crystallite sizes of Ag, ZnO and cellulose in bare samples and composites are summarised in Table 4.4.

Table 4.4: The calculated crystallite size from XRD measurements

	Particle Size (nm)							
	Ag	ZnO	NC	Ag/NC	ZnO/NC	Ag/ZnO/NC1	Ag/ZnO/NC2	Ag/ZnO/NC3
Ag	25	—	—	16	—	19	23	20
ZnO	—	30	—	—	20	18	18	16
NC	—	—	4	4	4	4	4	4

As shown in Table 4.4 dispersing nanoparticles in polymer reduces its particle size. This decrease is reported to result in improved size dependent properties that includes; electrical, magnetic, photocatalytic, mechanical, thermal and antibacterial properties.

4.1.2. Fourier Transforms Infrared (FTIR) Spectroscopy

The characteristic functional groups of all samples were investigated using FTIR spectroscopy in a region of 4000-400 cm^{-1} . The plotted spectra of cellulose, Ag, ZnO, Ag/NC, ZnO/NC and Ag/ZnO/NC nanopowders respectively are given in Figure 4.2. A broad peak is observed at region 3650 - 3030 cm^{-1} for all spectra due to the stretching of the hydroxyl (O-H) group arising from water adsorption [177-178]. Comparing the spectra of the metal/cellulose nanocomposites with that of cellulose, there is a slight change at the position or wavenumber of the intense peak at this region. The peaks have slightly moved to either a higher or lower wavenumber. This indicates that there is an interaction between the metal nanoparticles and the cellulose matrix thus causing a slight shift in the position of the functional group. Some peak shifting due to the interaction of metal nanoparticles with polymer matrix has been reported in literature [174].

Other common intense absorption bands were observed at around 1000-1050 cm^{-1} and around 2800 cm^{-1} . These bands are observed in cellulose and all composites of cellulose (ZnO/NC, Ag/NC and Ag/ZnO/NC) and are attributed to the pyranose ring ether band and the stretching of the C-H group of cellulose, respectively. A slight wavenumber shifting of the pyranose ether band from 1050 of cellulose to 1030, 1053 and 1051 cm^{-1} upon formation of ZnO/NC, Ag/NC and Ag/ZnO/NC composites, respectively was observed. The shifting of this peak is also due to the strong interaction between cellulose and the metal nanoparticles (ZnO and Ag). Another intense peak ascribed to the stretching of C-O is displayed at 1026 and 1022 cm^{-1} for the composite and cellulose respectively.

Metal oxides normally show their significant absorption bands in the fingerprint region. The fingerprint region contains a complex series of absorptions overlapping each other due to inter atomic vibrations. This region falls in the wavenumbers of below 1000 cm^{-1} . Comparing the spectra of ZnO, ZnO/NC and Ag/ZnO/NC to that of cellulose, they are some absorption shoulders between 700 and 442 cm^{-1} that are displayed. These bands are attributed to the distinct stretching mode of the metal oxide ZnO (ν -ZnO) [65].

Addition of silver nanoparticles to cellulose and ZnO/NC nanocomposite led to a shift of the characteristic H_2O scissoring mode found at 1630 peak to lower wavenumbers. The shifting is as a result of silver nanoparticles stabilizing well on the surface of both the ZnO and cellulose nanostructures. The observed absorption peaks for ZnO, cellulose and Ag align well with those previously reported in literature [179]. However, slight differences in the intensity of the peaks and little variations in the wavenumber positions were noted due to the different conditions maintained when synthesising this samples which may be different to those used in literature.

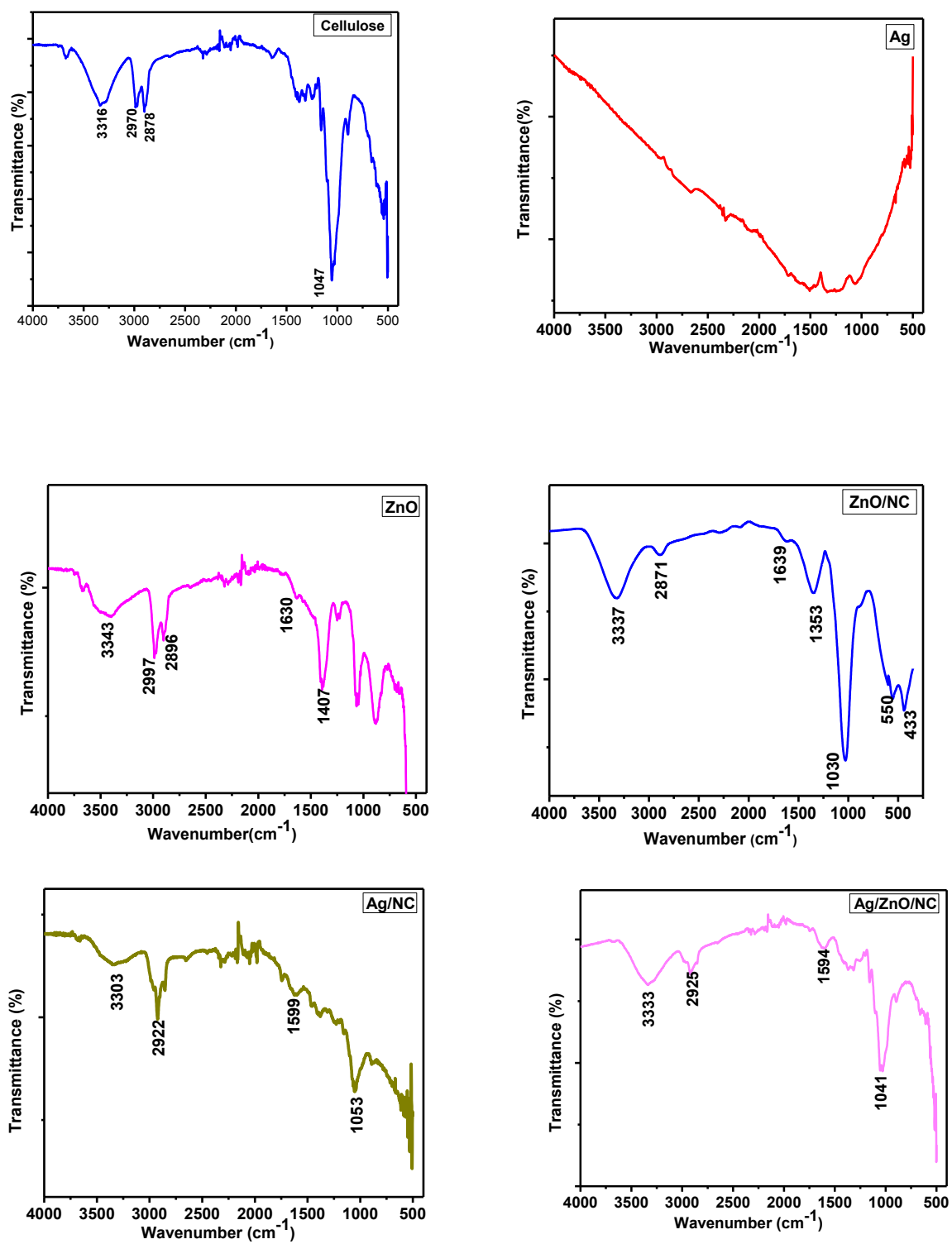
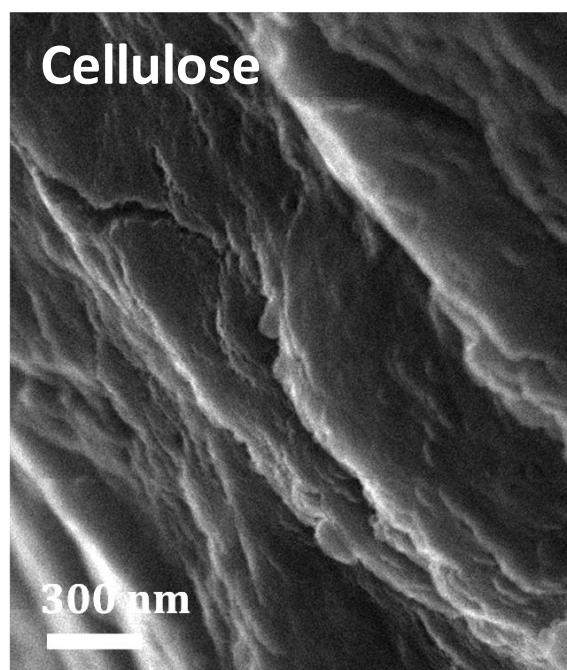
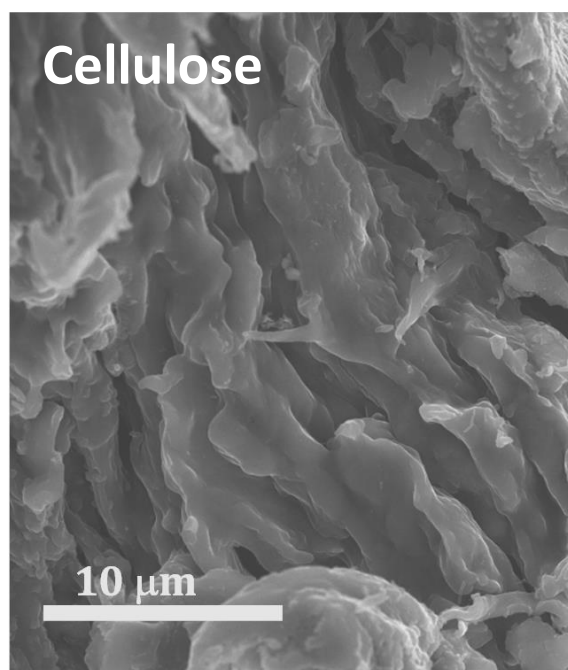
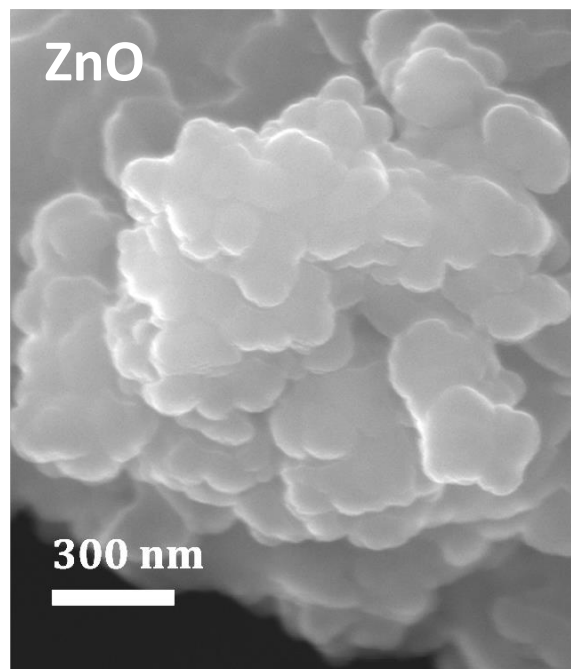
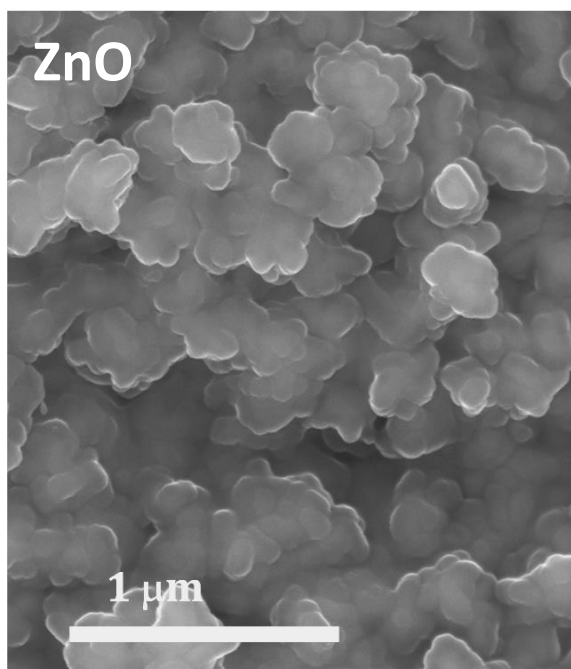


Figure 4.2: FTIR spectrum of cellulose, ZnO, ZnO/NC, Ag, Ag/NC and Ag/ZnO/NC

4.1.3 SEM and EDS results

The surface morphology of the samples was examined from SEM analysis. The micrographs of the samples are given in Figure 4.3. Cellulose exhibited hierarchical sheet-like structures. The average thickness of the nanocellulose was estimated to be 16 nm. The SEM image of bare ZnO displayed irregular disc-like shaped structures as shown in Figure 4.3. The ZnO structures agglomerated to form cloud-like clusters. Upon being dispersed on cellulose matrix, the shape of ZnO nanostructures remained unchanged, same disc-like ZnO nanostructures were observed. Spherical nanostructures were observed for Ag. Both Ag and ZnO nanostructures were well dispersed on the cellulose matrix. In-situ solution casting of metallic nanoparticles on polymeric surfaces overcomes their aggregation and increases their dispersibility. Introducing Ag into ZnO/NC did not alter the morphology of either cellulose, ZnO or Ag. The presence of Ag nanospheres was observed in the interface of ZnO in the composite.

The chemical composition of the samples was determined by the use of energy dispersive spectroscopy (EDS). The spectrum of the samples is given by Figure 4.4. The spectra showed the presence of Ag, Zn, O and C at the respective corresponding energy levels. The peaks of both Ag and Zn were detected in the Ag/ZnO/NC nanocomposite. This confirms that all the necessary metallic nanostructures were present in the nanocomposite.



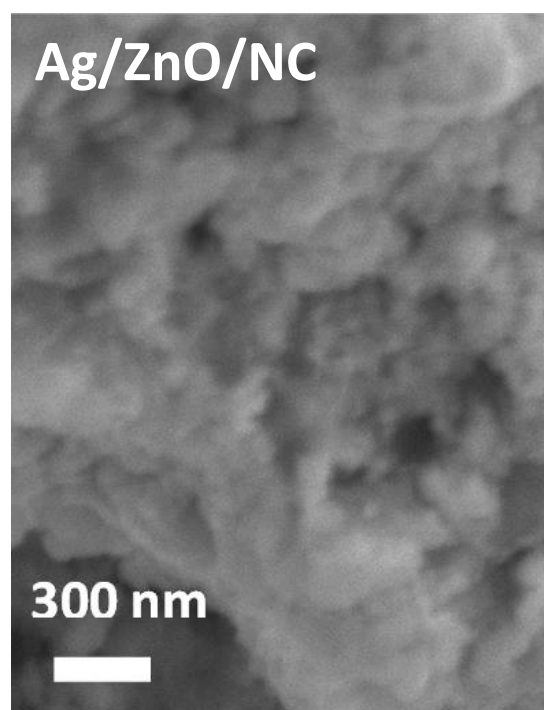
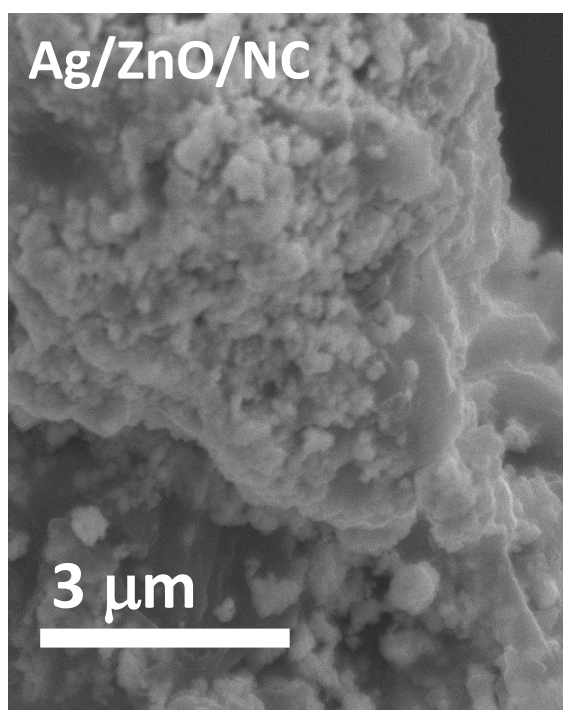
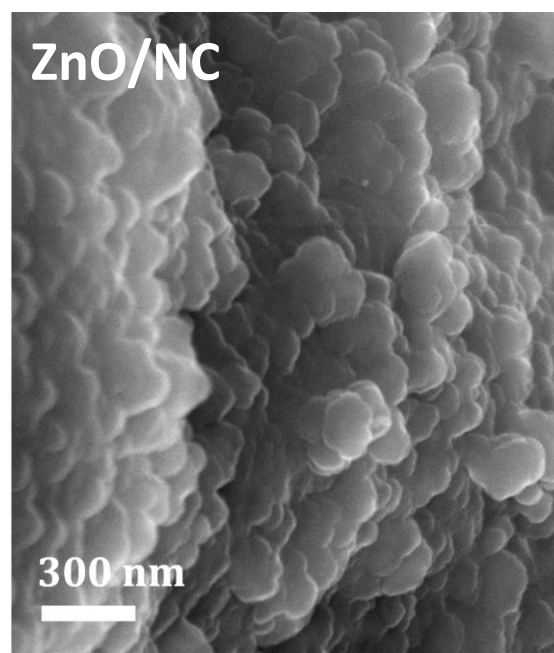
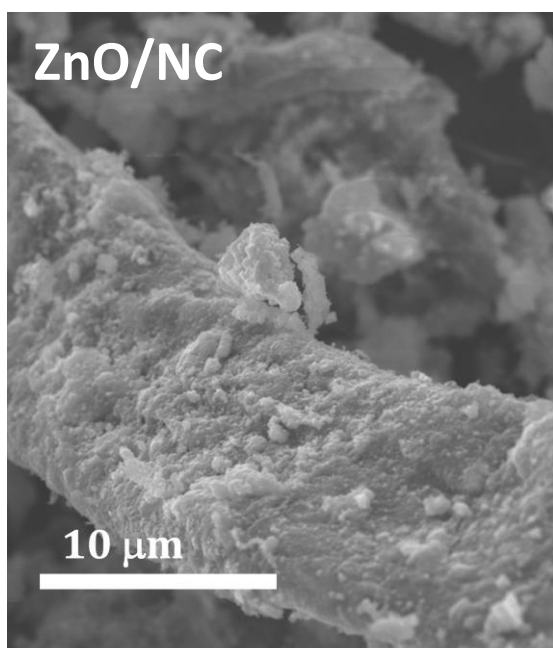


Figure 4.3: SEM images of ZnO, cellulose, ZnO/NC and Ag/ZnO/NC at low and high magnification

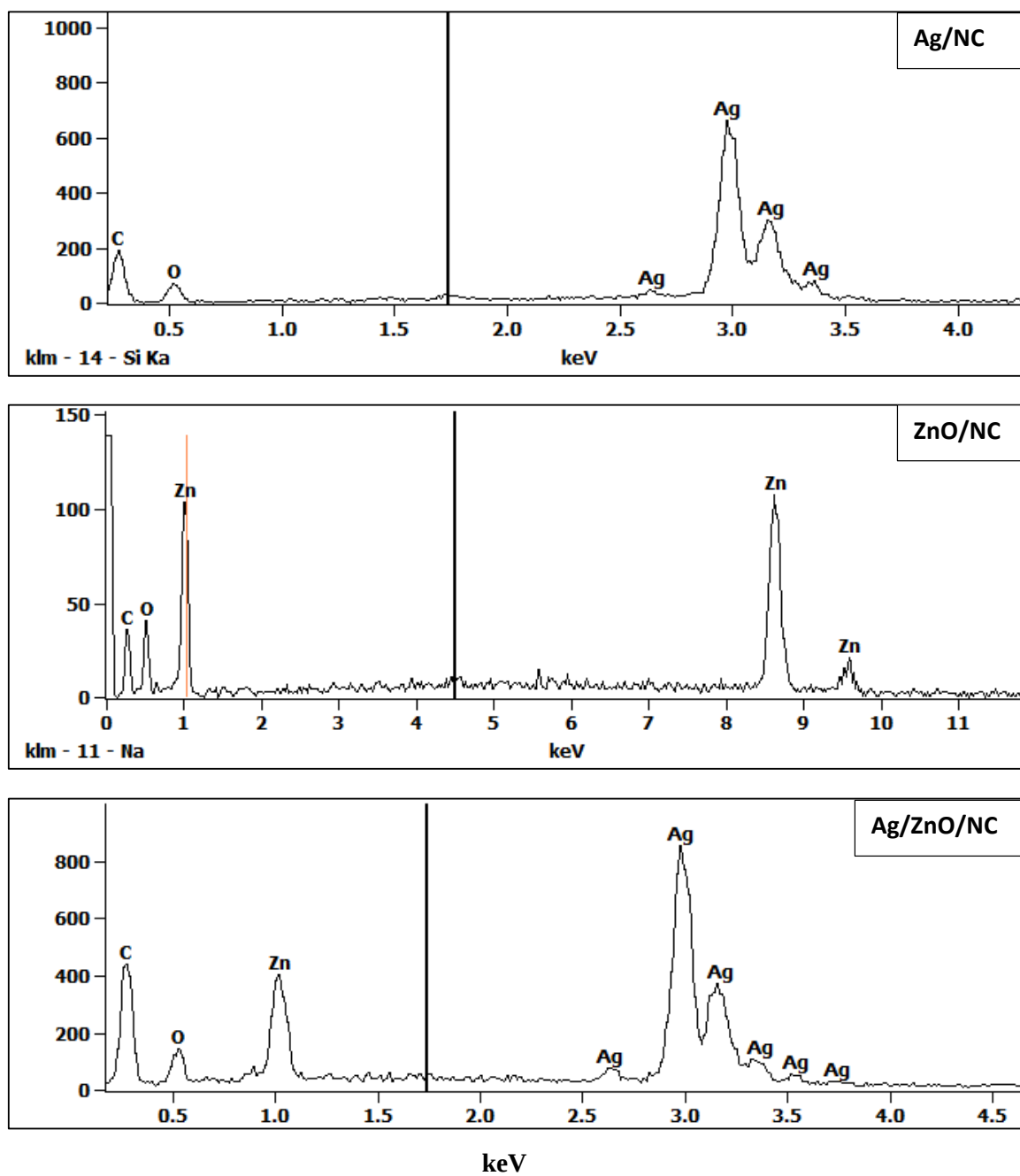


Figure 4.4: Energy dispersive spectra of Ag/NC, ZnO/NC and Ag/ZnO/NC

4.2. Optical Characterization Results

4.2.1 Absorbance and optical band gap energy

The optical properties of semiconductor metals and their compounds are systematically influenced by their energy band structures. It is pivotal to know the band gap of a material in order to determine its potential applications. Different theoretical approaches have been employed to determine the band gap of nanomaterials. The optical properties of the synthesised materials were investigated by measuring the absorbance. From these measurements useful parameters such as the optical band gap energy (E_{gap}) can be calculated.

4.2.1.1: Absorbance measurements

For measurement of absorbance, a very fine amount of the synthesised samples was dispersed in de-ionized water and ultrasonicated for several hours. The mixture was then transferred into a cuvette which was then loaded in a UV-Vis-NIR spectrophotometer for absorbance measurements. The absorbance spectrum of ZnO, ZnO/NC, Ag, Ag/NC and Ag/ZnO/NC nanocomposite at room temperature are shown in Figure 4.5. The absorption spectrum of ZnO reveals a well-defined exciton band at wavelength ~ 370 nm. A blue shift is observed in the absorption edges of the composites as compared to that of pristine ZnO. This is due to the quantum confinement effect as there is a reduced particle size of ZnO in the composites.

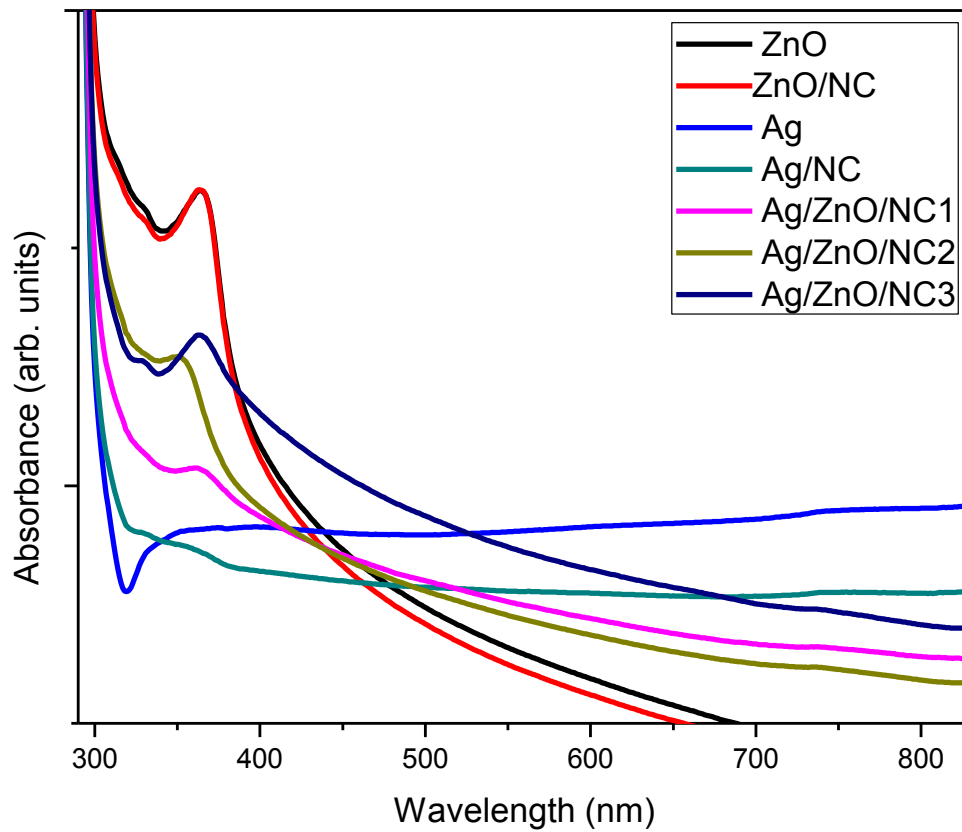


Figure 4.5: Absorbance curves of ZnO, ZnO/NC, Ag, Ag/NC, Ag/ZnO/NC1, Ag/ZnO/NC2 and Ag/ZnO/NC3

4.2.1.2: Determination of the band gaps

The optical band gap of the samples was determined using the absorption spectrum fitting (ASF) method [180-181]. The optical band gap (E_{gap}) of a semiconductor material is related to the optical absorption coefficient (α) and the incident photon energy as given by the equation 11, [161];

$$\alpha(h\nu) = B(h\nu - E_{\text{gap}})^n \quad (11)$$

where α is the optical adsorption coefficient defined by Beer-Lambert 's law $h\nu$ is the incident photon energy [h , Plank's constant ($4.135667662 \times 10^{-15}$ eV.s) and ν -the frequency of the light], B is an energy dependent proportionality constant, E_{gap} is the band gap energy and n is an index which is dependent on the optical transition. Since the absorbance of the samples is normally measured as a function of wavelength, introducing the ASF concept, equation 11 can be written as;

$$\alpha(\lambda) = B(hc)^{n-1} \lambda \left(\frac{1}{\lambda} - \frac{1}{\lambda_g} \right) \quad (12)$$

Still applying Beer Lambert's law [182] equation 12 can be rewritten as;

$$A(\lambda) = B_1 \lambda \left(\frac{1}{\lambda} - \frac{1}{\lambda_g} \right)^n + B_2 \quad (13)$$

Where $B_1 = B(hc)^{n-1} * d/2.303$, B_2 is a reflection constant

From all this equations a conclusion can be made that optical band gap from ASF plot (E_{gap}^{ASF}) is calculated as;

$$E_{gap}^{ASF} = \frac{1239.83}{\lambda_g} \quad (14)$$

The value of n varies according to the type of the material. It can take values of $\frac{1}{2}$, $3/2$, 2 , or 3 for direct-allowed, direct-forbidden, indirect allowed and indirect forbidden respectively. ZnO is a direct allowed semiconductor material [180], and in this case $n = \frac{1}{2}$. A plot of Figure 4.6 for variation of $(A/\lambda)^n$ against $(1/\lambda)$ was extrapolated at $(A/\lambda)^n = 0$ to determine λ_g .

From the extrapolated graphs, λ_g was determined and E_{gap} calculated for each sample using equation 14. The values of band gap calculated from ASF method for the samples are given in Table 4.4. The band gap of bare ZnO and ZnO dispersed on cellulose was found to be 3.22 eV, which is in agreement to what has been reported in literature [48-49, 51, 82]. Dispersing ZnO on cellulose did not affect its band gap structure; however upon introducing Ag there is a slight increase in the band gap. Small defects in the crystal structure of ZnO can affect its band gap as transition metals will lead to ferromagnetic properties thus creating some unoccupied states that will consequently alter the band gap.

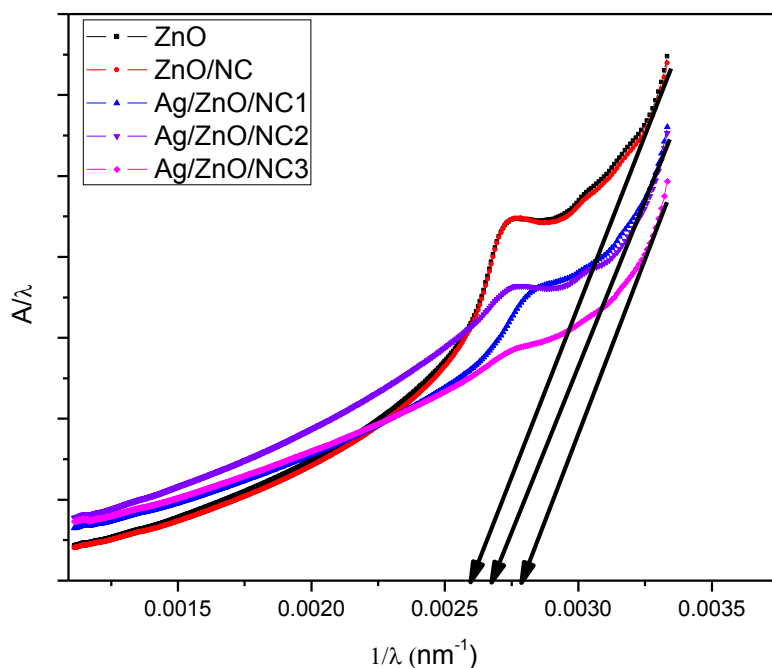


Figure 4.6: A plot of (A/λ) against $(1/\lambda)$ for determining the optical band gap of ZnO, ZnO/NC, Ag/ZnO/NC1, Ag/ZnO/NC2 and Ag/ZnO/NC3

Table 4.4: Optical band gaps of synthesised samples

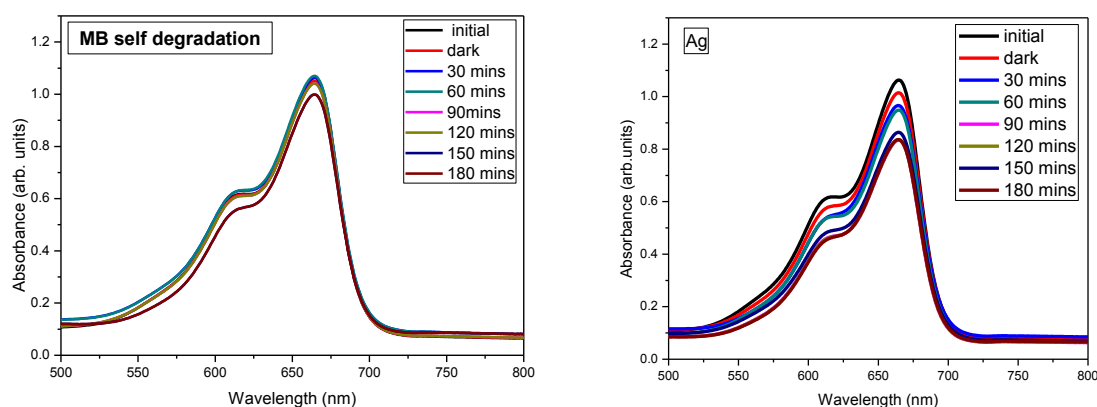
Sample	λ_g (nm)	E_{gap}^{ASF} (eV)
ZnO	385.1	3.22
ZnO/NC	385.1	3.22
Ag/ZnO/NC1	371.9	3.33
Ag/ZnO/NC2	371.9	3.33
Ag/ZnO/NC3	358.9	3.45

4.3. Photocatalytic Activity Assessments

The photocatalytic activity of the samples was evaluated by monitoring the degradation of methylene blue (MB) dye under visible light irradiation direct from the sun. MB shows a maximum characteristic absorption band (λ_{max}) at wavelength 664 nm, which was monitored in order to examine the degradation. The activity of Ag/ZnO/cellulose (Ag/ZnO/NC) nanocomposites of different Ag and ZnO content ratios were investigated.

Different ratios of Ag to ZnO (ZnO/Ag) were used to investigate the effect of Ag loading on the photocatalytic activity of ZnO. The activities of Ag, ZnO, Ag/cellulose (Ag/NC) and ZnO/cellulose (ZnO/NC) are also presented for comparison. A blank experiment was carried out for the degradation of MB without a catalyst in order to assess the extent that visible light can assist in self-decomposition of MB. The experimental conditions are outlined in more details in the experimental procedure/ methodology (section 3.3.1).

Figure 4.7 shows the spectral profiles as MB was degraded using different nanostructured materials as labeled in each graph. There was no substantial change observed on the absorption peak upon irradiation of MB without a catalyst. A relatively small change in the absorption peak of MB was observed in the absence of a catalyst for 180 minutes under visible light illumination, thus it can be said that self-degradation of organic dyes and other pollutants is not a remedy for environmental mitigation as the effect is negligible. All samples exhibited some significant activity against MB. A varying noticeable change on the intensity of the absorption band immediately after irradiation for only 30 minutes in the presence of either of the samples was observed. This indicates that in the presence of these samples and upon irradiation with visible light, a chemical reaction is induced or initiated.



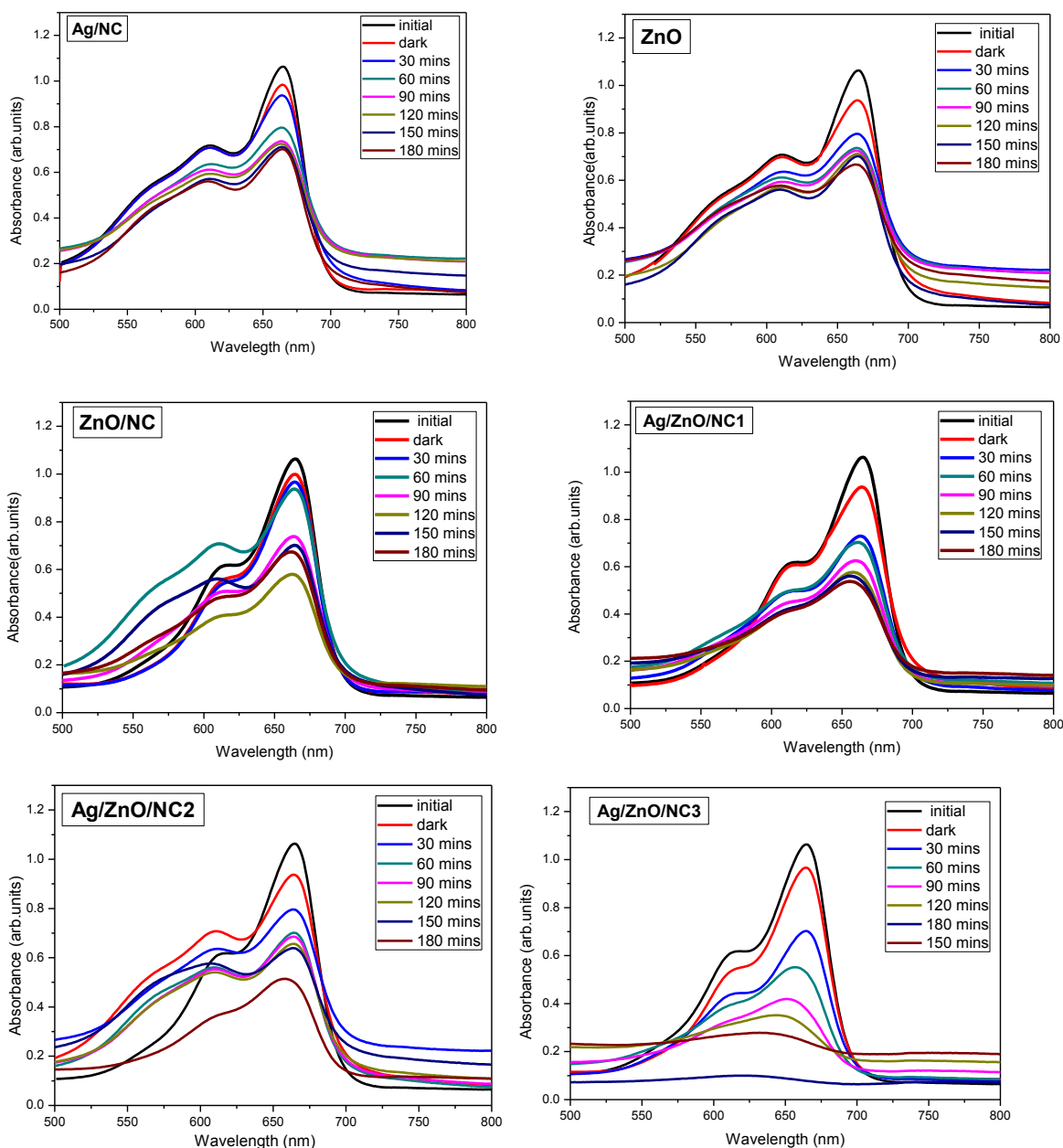


Figure 4.7: Time-dependent UV-Vis absorption spectra for degradation of MB using different photocatalysts as indicated on the graphs.

The extent of MB degradation increases as time of irradiation increases. This is evidenced by a further apparent decrease of the absorption band intensity, indicating that the dye was being degraded. Also a change in the color of the solution was observed during the experiment. The solution changed from a dark blue color to some sort of faint to colorless clear solution depending on the sample used. The change in color indicates that the chromophore structure of MB was being degraded. The total percentage of

methylene blue degraded after exposure to visible light irradiation in the presence of different samples at different time intervals was calculated using equation 15;

$$\% \text{ degradation} = \left(\frac{C_0 - C}{C_0} \right) * 100 = \frac{A_0 - A}{A_0} * 100 \quad (15)$$

Where C_0 is the initial concentration of the dye, C is the final concentration of the dye, A_0 is the initial absorption of the dye and A is the final absorption of the dye after certain time of irradiation. The correlation of percentage of methylene blue absorbed under sunlight irradiation against time of irradiation using different photocatalysts is shown in Figure 4.8.

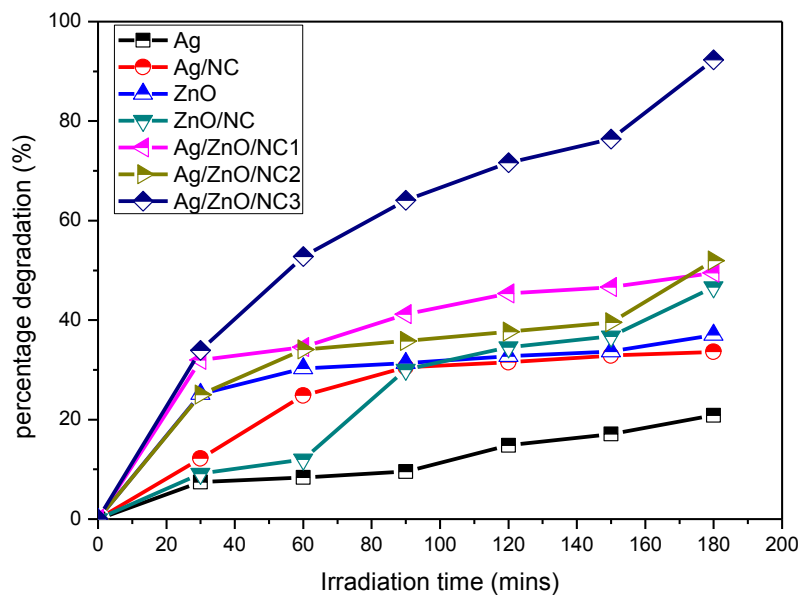


Figure 4.8: Plot of percentage degradation of MB as a function of time under sunlight irradiation photocatalysed by different samples.

The calculated percentages of degradation for all samples after 30 and 180 minutes of irradiation are presented in Table 4.7. After 180 minutes the overall percentage of MB degraded by the photocatalysts has the order of: Ag < Ag/NC < ZnO < ZnO/NC < Ag/ZnO/NC1 < Ag/ZnO/NC2 < Ag/ZnO/NC3 with corresponding values of 20.9, 33.6, 37.0, 46.6, 49.5, 51.9 and 92.3 %, respectively.

Table 4.5: Percentages of MB degraded by different samples at 30 and 180 minutes

CATALYST	PERCENTAGE DEGRADED (%)	
	30 mins	180 mins
Ag	7.5	20.9
ZnO	25.1	37.0
Ag/NC	12.2	33.6
ZnO/NC	9.14	46.6
Ag/ZnO/NC1	32.0	49.5
Ag/ZnO/NC2	25.0	51.9
Ag/ZnO/NC3	33.9	92.3

Figure 4.9 shows the relative absorbance (A/A_0) which reduces as time of irradiation is increased for all samples.

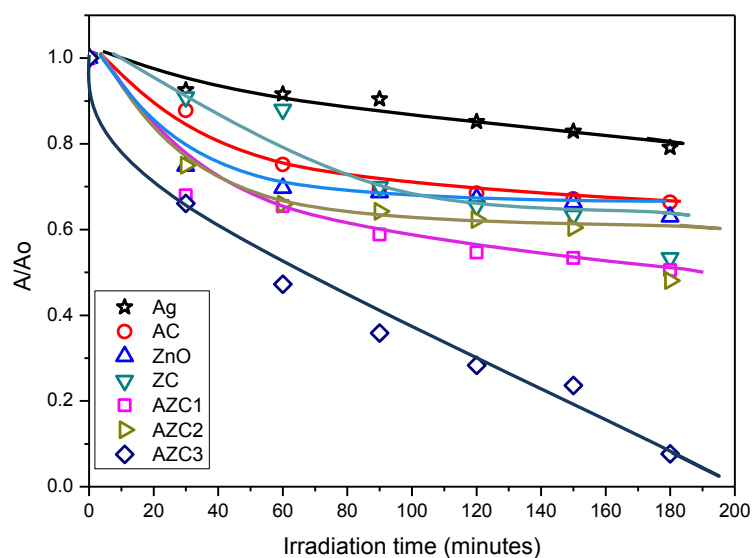


Figure 4.9: Relative absorbance of MB against irradiation time for Ag, Ag/NC (AC), ZnO, ZnO/NC (ZC), Ag/ZnO/NC1 (AZC1), Ag/ZnO/NC2 (AZC2) and Ag/ZnO/NC3 (AZC3)

The process of heterogeneous photocatalysis occurs predominantly on the surface of a photocatalyst and it involves a series of reported steps [183]. At foremost, reactants diffuse to the surface of the catalyst where they get adsorbed. This induces a reaction on the surface of the semiconductor leading to desorption of products and consequently resulting in diffusion of the formed products from the surface of the semiconductor into the medium. The photocatalytic activity of metal oxides is also dependent upon a number of several factors such as their particle size, composition, crystallinity, phase structures, surface defects, functional groups, surface metal/non-metal deposits, and adsorbates.

The intrinsic crystalline structure, morphology and composition of SMOs influence their photocatalytic activity. As stated before, heterogeneous photocatalysis takes place on the surface of a semiconductor, thus making surface area an important aspect in photocatalysis. Due to their dimensions, nanostructured materials have a larger surface area that gives them great unique properties. All samples used for the photocatalytic assessment experiment are in nano-dimensions. The size of nanomaterials is inversely proportional to their surface area. Smaller nanomaterials tend to have a larger surface area.

Comparing the activity of the two main components Ag and ZnO on Figure 4.7-4.9, it can be clearly observed that the nanosized Ag exhibited a lower activity as compared to the nanosized ZnO. Ag showed the least percentage of MB degraded compared to all the samples. The catalytic ability of Ag is ascribed to the surface plasmon resonance (SPR) effect, which enables noble metals to intensively absorb under visible light [88]. Ag did not display any activity against MB under dark conditions. Due to the position of the valence band of ZnO resulting into a wide band gap, its photogenerated holes have a strong enough oxidizing power to decompose most organic compounds through generation of ROS. The primary mechanism that contributes to the photocatalytic degradation of MB is the generation of ROS. Therefore, any process that enhances the generation of ROS will lead to enhanced activity.

An increase in the surface area of nanostructured materials generally increases their reactive sites available for irradiation thus consequentially elevated properties including

photocatalytic activity [184-185]. In this project, this increase was successfully achieved by dispersing Ag and ZnO on cellulose polymer matrix. The results indicate a significant improvement of the photocatalytic performance of ZnO nanodiscs and Ag nanospheres dispersed on cellulose matrix as compared to bare Ag and ZnO. About 33.6 % and 46.6 % of the dye was decomposed after 180 minutes of irradiation in the presence of Ag/NC and ZnO/NC respectively (shown in Table 4.6).

A strong electronic interaction between the between the polymer and metal nanoparticles can help in controlling the size and growth of metal nanostructures thus improving their properties. Cellulose promotes well dispersion of metallic nanoparticles thus circumventing the issue of agglomeration. As shown in SEM images (Figure 4.3), ZnO nanodiscs agglomerated on their own whereas when dispersed on cellulose they did not coagulate. Agglomeration of nanostructures reduces the amount of active sites available for photocatalysis and this leads to lower photon absorption and as a consequence results in lower activity. Another point from XRD analysis, the particle size was calculated to be 30 and 20 nm (Table 4.4) for pristine ZnO and ZnO dispersed on cellulose respectively. The synergistically larger specific surface area of ZnO/NC resulted in higher activities compared to bare ZnO. It can be said that in-situ casting ZnO in cellulose increased the surface area of ZnO as it reduced its size, thus as expected ZnO/NC showed better photocatalytic activity compared to individual ZnO.

Nevertheless these improved activities could not match the efficiency of the Ag/ZnO/NC composites. The photocatalytic activity of all the Ag/ZnO/NC composites surpassed that of ZnO/NC. This clearly indicates that the presence of Ag on the surface of the photocatalyst ZnO drastically enhances its photocatalytic performance. The presence of a small amount of Ag on the interface of ZnO nanodiscs greatly enhanced its activity. All the three Ag/ZnO/NC nanocomposites of different ZnO: Ag ratio exhibited significant photocatalytic activity against MB degradation under solar light irradiation. However, the activity of these composites was dependent on ZnO: Ag ratio. The percentage of methylene blue absorbed by the composites gradually increased with an increase in the ZnO: Ag content ratio. Modifying photocatalytic properties by introducing transitional metals on the surface of SMO gives effective results when the content of the transitional metal is lower than that of the SMO under study [62, 90, 186-187]. Ag/ZnO/NC₃ which

contained the least Ag content (0.25 Ag) and a greater ZnO content (0.75) gave the highest percentage of MB degraded, followed by Ag/ZnO/NC2 and finally the least being Ag/ZnO/NC1. This agrees to what has been reported in literature [187]. The percentage absorption of Ag/ZnO/NC3 is 2.49 and 4.42 times more than the activity of ZnO and Ag respectively. The synergistic effects of Ag and ZnO are emphasised.

The enhanced activity of the composites can be explained in terms of the symbiotic contributions made by both the noble metal (Ag) and the polymer support material (cellulose) on the surface of the SMO photocatalyst (ZnO). The role of cellulose is to control the size and morphology as already mentioned. Moreover, the visible absorption from the plasmonic effect of Ag attributes to the elevated activity for Ag/ZnO/NC. Deposition of noble metals on the surface of metal oxides induces both charge separation and the interfacial charge transfer kinetics. In the absence of electron scavengers photogenerated electrons are stored in the conduction band (CB) of the SMO and could partake in non-radiation recombination processes with the available oxygen vacancies, however in the presence of Ag interfacial charge transfer is facilitated to use these CB electrons for photooxidation [6].

Interaction of metallic Ag with aqueous medium produces Ag ions. When Ag comes into contact with ZnO, its Fermi level ($F_{Ag} = 4.26$ eV) [188] shifts towards that of ZnO ($F_{ZnO} = 5.2$ eV) [188], resulting in a new Fermi level equilibrium ($F_{Ag/ZnO}$). This shifting creates a gateway for transfer of photogenerated negatively charged electrons from the CB of ZnO leaving behind the positively charged consequential holes. During this transfer process, a Schottky barrier is created. This interband barrier acts as an electron sink by trapping electrons thus suppressing e^-/h^+ recombination [189]. When there is protracted separation between the e^-/h^+ pair each can then undergo oxidation with the absorbed molecules leading to pollutants degradation. The photo generated holes oxidize water molecules to form a strong ROS $OH^\bullet$.

Even though depositing transition metals on the surface of metal oxides has been reported to enhance the photocatalytic through inducing charge separation, there is considerable controversy on their effect [190]. Excessive amount of transition metals deposited can retard their positive effect [191]. As noted from the results, Ag/ZnO/NC1

with high silver content shows the lowest activity compared to other two Ag/ZnO/NC composites. Ag produces electrons on interaction with an aqueous medium, and a higher content of Ag leads to creation of more electrons thus increasing their probability to recombine with the holes on the surface of the metal oxides. Thus being said, increasing the Ag content doesn't necessarily induce charge separation as expected. A high content of silver in the composite also means a higher surface coverage thus reducing the accessibility of ZnO active sites available for visible light irradiation thus resulting in lower activity. From our pristine Ag and ZnO photocatalytic assessment results it was observed that Ag is not as effective as a photocatalyst compared to ZnO, thus an increase of the photodecomposition activity of the composite results from an increase of ZnO content and unfortunately due to reasons stated an increase in Ag content decreases the activity.

The reaction kinetics of MB degradation by the nanostructured materials was studied. There were described using the Langmuir-Hinshelwood model [190] which is expressed as;

$$-\frac{dC}{dt} = K_r \frac{K_a C}{1 + K_a C} \quad (16)$$

Where; $-dC/dt$ is the change in the concentration (C) of methylene blue dye as irradiation time (t) changes which is simply the rate of MB degradation, K_r is the reaction rate constant and K_a is the adsorption coefficient of the reactants.

The concentration of MB used was 0.0004g/ml which is relatively low. If the concentration of the dye is low, K_a is small and negligible.

Equation 16 then becomes;

$$-\frac{dC}{dt} = K_r \quad (17)$$

The apparent constant K_{app} was calculated using this linear relation;

$$\ln\left(\frac{C_0}{C}\right) = K_{app} t \quad (18)$$

Where: C_0 is taken as A_0 (initial absorbance of MB), C as A_t (absorbance of MB at time t) and K_{app} is the apparent rate constant which was calculated from the slope of $\ln(C_0/C)$

versus irradiation time t . A graph of $\ln(C_0/C)$ against time of irradiation was plotted and shown in Figure 4.10.

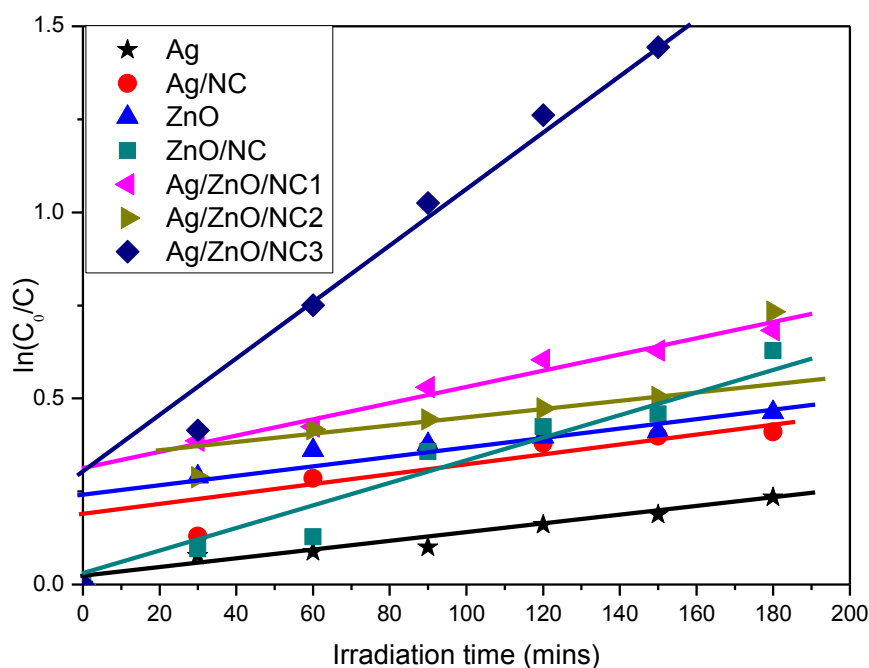


Figure 4.10: Kinetic plots for the decomposition of MB

Table 4.8 shows the calculated rate constants for methylene blue dye photodecomposition by means of linear least- square fit. From the calculation it was found that the degradation of MB exhibited pseudo-first order kinetics. The apparent constants for the degradation of MB in decreasing order are: Ag/ZnO/NC3 > ZnO/NC > Ag/ZnO/NC1 > Ag/ZnO/NC2 > ZnO > Ag/NC > Ag. The apparent rate constant of ZnO/NC is greater than that of Ag/ZnO/NC2 and Ag/ZnO/NC1. As pointed earlier, deposition of transition metals on the surfaces of SMO can decrease the apparent constant rate of degradation [191-192].

Table 4.8: Apparent constants rate for the photodecomposition of MB

Photocatalysts	MB photodecomposition rate (K_{app})
	[%/min]
Ag	0.001193
Ag/NC	0.001277
ZnO	0.001294
ZnO/NC	0.003402
Ag/ZnO/NC1	0.002157
Ag/ZnO/NC2	0.001938
Ag/ZnO/NC3	0.007530

4.4 Antibacterial Assessment Results

The antibacterial activity of different Ag/ZnO/NC nanocomposites was tested using the agar well diffusion method also known as the zone of inhibition (ZOI). Ag, ZnO, Ag/NC and ZnO/NC were also tested for comparison reasons. Three representative microorganisms; Gram negative *E.coli* and Gram positive *S.aureus* as well as a more resistant spore-forming *B.subtilis* were used as the probable microbes for the antibacterial tests. Wells of 7 mm diameter were aseptically made on the cultured bacterial lawns. Samples of 5mg/ml concentration were loaded onto the wells and the zone of inhibition measured across the wells after 24 hours at 37°C incubation, as described fully in section 3.3.2. Tetracycline was used as a standard antibacterial agent against all the three strains because it is known to inhibit a broad range of both Gram negative and Gram positive microorganisms.

Figure 4.11 shows the antibacterial activity for ZnO, cellulose, ZnO/NC and Tetracycline against Gram positive *S.aureus* and Gram negative *E.coli*. It can be noted that cellulose on its own did not display any antibacterial activity. Similar results for antibacterial activity of cellulose against tested strains are reported, [109, 193-195]. This implies that the activity exhibited by the composites will be primarily from either the metal or metal oxides only, and not from individual cellulose.

The antibacterial activity of Ag, Ag/NC, ZnO, ZnO/NC, Ag/ZnO/NC1, Ag/ZnO/NC2, Ag/ZnO/NC3 and Tetracycline are shown in Figure 4.12. From visual inspection, all samples exhibited excellent significant antibacterial effect against *S.aureus*, *E.coli* and *B.subtilis*. A quantifiable clear zone was observed around the wells and the measured zones are presented in Table 4.9.

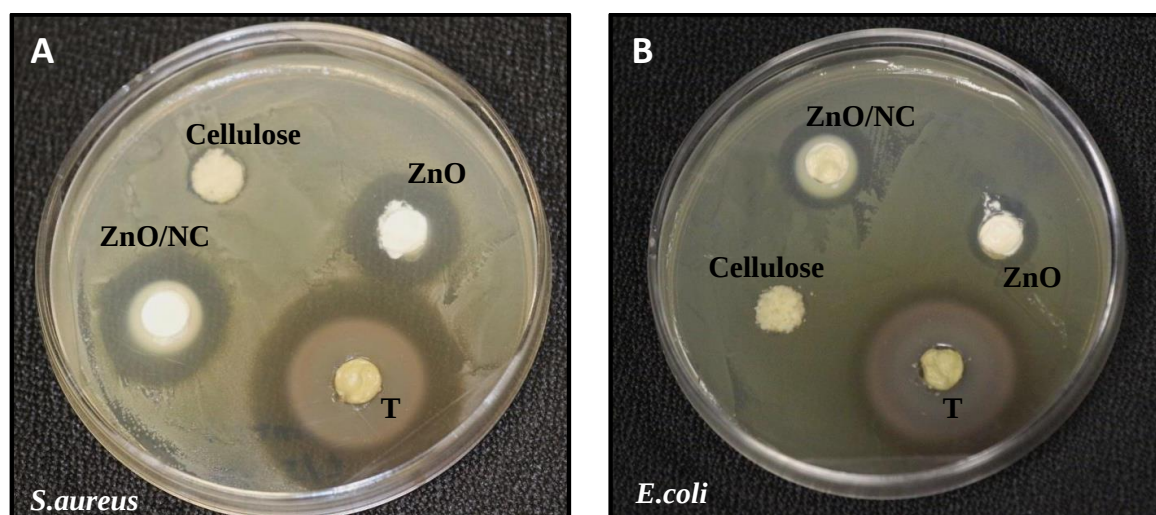


Figure 4.11: Antibacterial zone of inhibition of cellulose, ZnO, ZnO/NC and Tetracycline (T) against *S.aureus* (A) and *E.coli* (B)

Ag is known to possess a much stronger antimicrobial activity even against the well-known antibacterial resistant microorganisms. Its high surface area and high fraction of surface atoms ultimately leads to higher release of Ag ions for antimicrobial action. As expected, Ag displayed highest activity against all the bacterial strains, with the highest against the growth of the more sensitive *B.subtilis*. Higher activities of Ag against *B.subtilis* as compared to other strains were previously reported [196]. The measured zone of inhibition as displayed by different samples against *E.coli*, *S.aureus* and *B.subtilis* are given in Table 4.6.

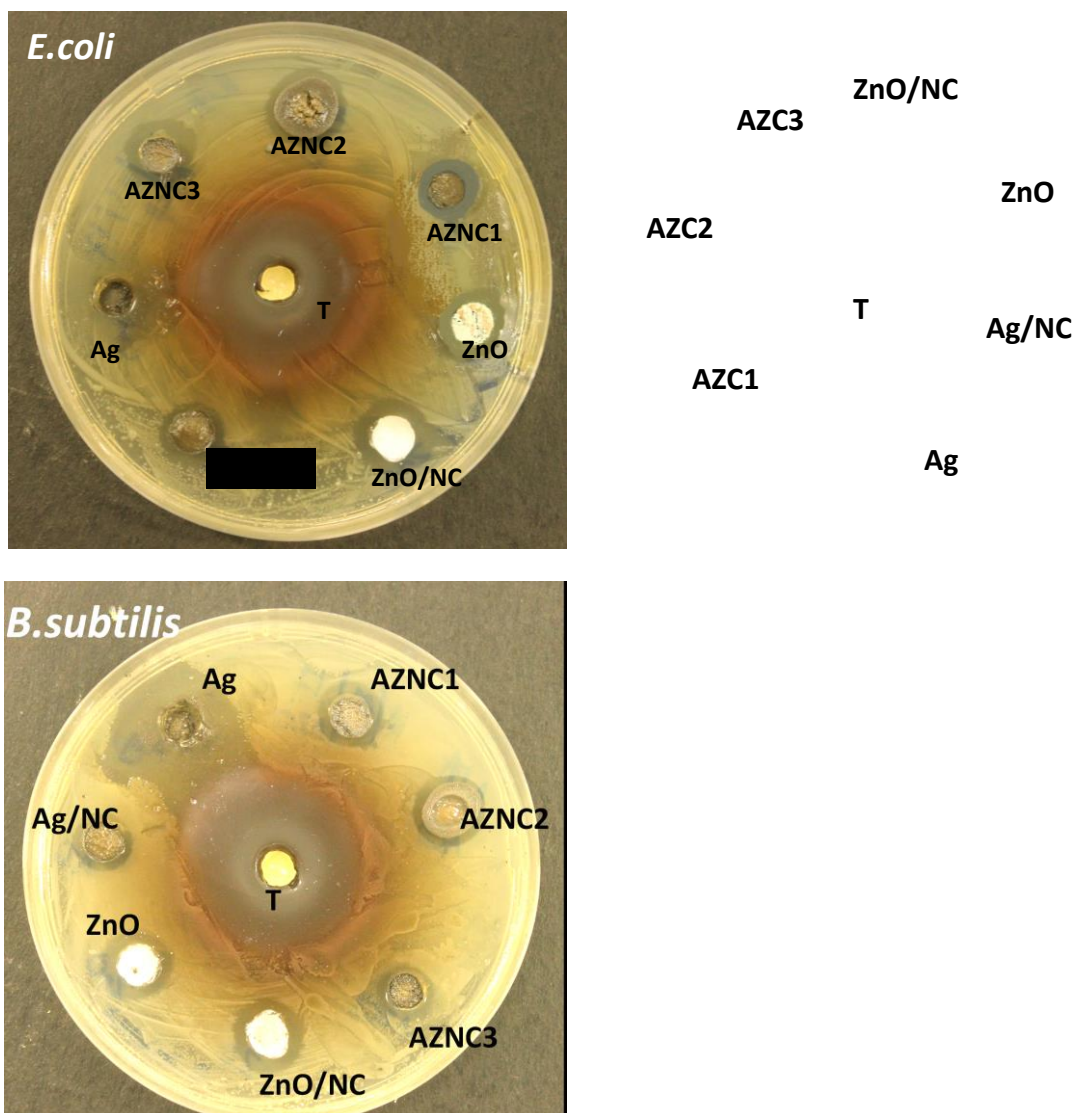


Figure 4.12 Antibacterial Activities of ZnO, ZnO/NC, Ag, Ag/NC, Ag/ZnO/NC1 (AZNC1), Ag/ZnO/NC2 (AZNC2) and Ag/ZnO/NC3 (AZNC3) and Tetracycline (T) against *E. coli*, *S. aureus* and *B. subtilis*.

Table 4.6: Average zone of inhibition of different antibacterial agents against Gram positive (*S.aureus* and *B.subtilis*) and Gram negative (*E.coli*)

Samples	Average diameter/measured zone of inhibition (mm)		
	Gram negative	Gram positive	
	<i>E.coli</i>	<i>S.aureus</i>	<i>B.subtilis</i>
Ag	15	20	22
Ag/NC	9	10	11
ZnO	11	12	11
ZnO/NC	14	15	12
Ag/ZnO/NC1	10	18	11
Ag/ZnO/NC2	12	15	13
Ag/ZnO/NC3	12	14	11
Tetracycline (Control)	25	35	28

Different antibacterial mechanisms of Ag nanoparticles have been proposed through inactivation and growth inhibition of bacteria. In aqueous medium, metallic silver (Ag^0) is oxidized to positive Ag ions (Ag^+). The accumulation of cationic Ag ions have a great influence on the antimicrobial mechanism as it has been reported that zero valent metallic silver is non-reactive and does not exhibit any antimicrobial activity [197]. The microbial surface is the primary target of the antibacterial agents. A bacterial surface is known to be negatively charged and because of the opposite charges there is an interaction between the bacterial surface and Ag^+ ions. When in contact with the bacterial cell, Ag nanostructures target its protective outer membrane and destroy its permeability. This creates a gateway movement of Ag ions into the cell. A greater affinity of Ag^+ results in electrostatic interactions with cellular biomacromolecules including proteins and nucleic acids causing disruption of some cellular activities including DNA replication, ATP production and respiration and eventually result in cell death [198-200]. In addition, Ag^+ has the ability to catalyze the production of oxygen radicals that oxidize the molecular structure of the bacterial cell. The produced oxygen interacts with the absorbed species in most cases water due to moist environments and produces a very

critical reactive oxygen species known as hydrogen peroxide (H_2O_2) which then destroys the constituents of the cell including chromosomes and ribosomes [198, 201]

ZnO on its own also showed significant antibacterial activity against all the three bacterial strains. The antibacterial performance of SMOs is attributed to their photocatalytic ability. Similar to other metals, ZnO carry a positive charge [202], thus results in electromagnetic attraction between the microorganism and treated surface. ZnO produces reactive oxygen species (ROS) such as superoxides (O^{2-}), hydroxyl radicals ($\text{OH}^\bullet$) and hydrogen peroxide (H_2O_2) [174, 203] which may partake in antibacterial activity by promoting peroxidation of the polyunsaturated phospholipids component of the lipid in the microorganism [204]. In addition, other studies suggest that H_2O_2 formation is the primary effect contributing to the antibacterial activity, taking place via penetration of H_2O_2 through the cell walls [205-206].

A plot of the measured inhibition in Figure 4.12 illustrates that all samples showed higher activity against Gram positive strains as compared to Gram negative strain. The average antibacterial activity of all samples was stronger against *S.aureus* and *B.subtilis* than *E.coli* which is in agreement with the findings reported in previous studies [174, 207-209]. The difference in the susceptibility of the bacterial species could be attributed to the structure, and composition of the membrane cell wall between *S. aureus*, *B.subtilis* and *E. coli*. The outer membrane serves as a protective layer preventing or slowing entry of antibacterial agents that might kill or cause injury to bacteria. In *E. coli*, the cell wall consists of the peptidoglycan layer that is about 2 nm thick and makes up only 10% of cell wall. However, the outer membrane consists of 50% lipopolysaccharides, 35% phospholipids and 15% lipoproteins that accounts for the rest of the cell wall [210]. The outer membrane and the peptidoglycan not only provide protection but determine sensitivity to antibacterial agents. The peptidoglycan layer forms 80% of cell wall of *S. aureus* and the rest are 10–20% of teichoic acids and others such as proteins and lipopolysaccharides [211-212]. The cell wall of *E. coli* is thus much more complex than of *S. aureus* and *B.subtilis* making it to be less prone to antibacterial action of the ZnO nanocomposite. The cell wall of *S. aureus* and *B.subtilis* though thick, has plenty of pores, which could contribute to its susceptibility to antibacterial agents [209].

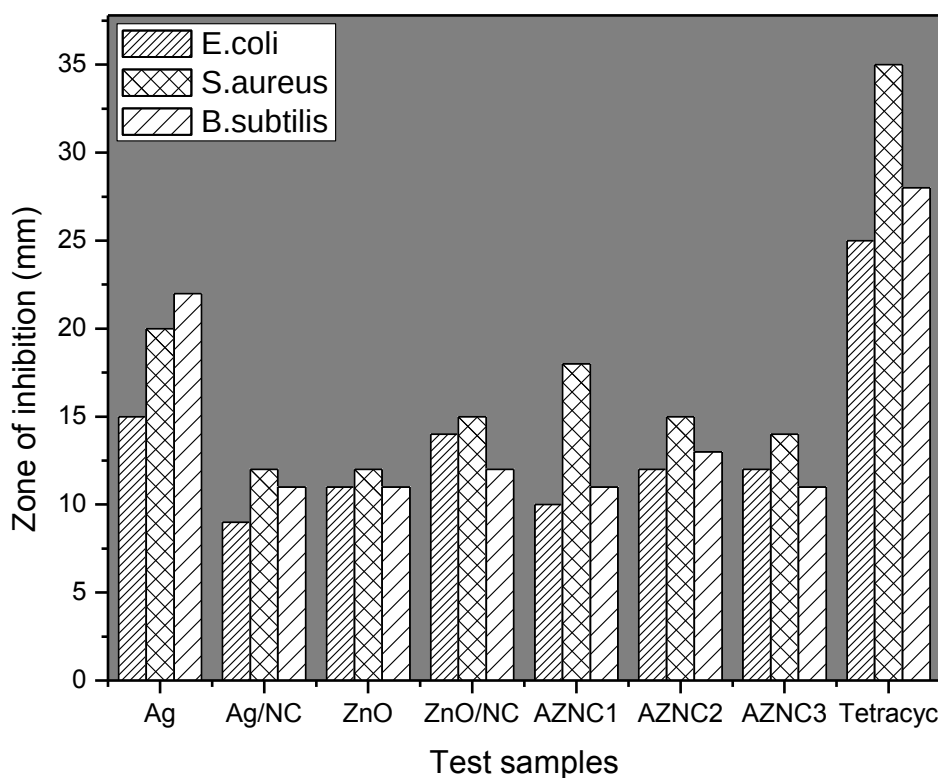


Figure 4.13 Growth inhibition plots of *E. coli*, *S. aureus* and *B. subtilis* as subjected to various nanostructures; Ag, Ag/NC, ZnO, ZnO/NC, Ag/ZnO/NC1 (AZNC1), Ag/ZnO/NC2 (AZNC2), Ag/ZnO/NC3 (AZNC3) and Tetracycline.

The generation of ROS depends strongly on the specific surface area of SMO_5 [213-214]. The larger the surface area, the more ROS generated hence higher antibacterial activity. As explained in section 4.3, cellulose polymer promotes a well dispersion of ZnO nanostructures [215], thus leading to a larger surface area. It is also believed that microorganisms carry a negative charge while metal oxides carry a positive charge, thus this interaction creates an “electromagnetic” attraction between the microorganism and treated surface [210]. This means when contact is made; the microorganism is oxidized resulting in inactivation of bacterial proteins, decreasing cell permeability and eventually microbial cell death.

It was expected that Ag/NC and ZnO/NC would indicate enhanced activities compared to pristine Ag and ZnO due to the strong interaction of metal ions with the negatively charged surface of cellulose. Elevated activity was observed in the presence of ZnO dispersed onto cellulose matrix. The enhanced antibacterial action displayed by ZnO/NC

is attributed to the smaller crystal size of ZnO in the composite and a larger exposed surface area influenced by the cellulose polymer.

Contrary, Ag/NC showed less activity when dispersed on cellulose or in the composite. Ag/NC shows lower activities compared to Ag for all the three tested bacteria strains. This implies that an additional factor is taking place. Many authors have reported that this decrease may be due to the nature and distribution of Ag nanostructures within the polymer matrix. The reduced antibacterial activity can be ascribed to the electrostatic interference of the surface negative charge of cellulose from the OH^- with absorption of negatively charged microbes on the surface of Ag^+ . The ability of cellulose to absorb water also facilitates the oxidation of metal nanoparticles, which also contributes to higher antibacterial activity.

An elevated bacteriostatic activity does not make silver nanostructures ideal to be applied as bare structures because of high rate of leaching when in contact with an aqueous medium. Embedding Ag nanostructures in a polymer matrix prevents their irreversible aggregation and in turn enhancing its overall suitability as an antibacterial agent. From SEM analysis a uniform distribution of Ag nanospheres over the surface of the cellulose sheets was observed. Due to its hydroxyl groups, cellulose strongly binds with Ag ions leading to slow release of Ag into the aquatic environment [216]. Furthermore, cellulose is a sorbent and thus can help in the recovery of silver nanoparticles. Even though a slow release of Ag ions result in lower activity, an outstanding advantage is the reduction on the leaching rate of Ag nanostructures, thus making them to be useful in a wide range of antibacterial applications including water purification systems, biomedicine and food industry [201].

All Ag/ZnO/NC nanocomposites displayed excellent antibacterial activity against both Gram negative and Gram positive bacteria despite the Ag/ZnO content ratios as depicted in Figure 4.12. Not much difference was observed for the three composites. This could be ascribed to the antibacterial release of Ag^+ ions and the diffusion of photogenerated ROS from excitation of ZnO. Introducing Ag onto ZnO induces charge accumulation carriers on the surface of metal oxides [22]. In normal cases this is expected to increase

the overall efficiency as the activity of the composite is a synergic contribution from both ZnO and Ag.

The diffusion rate of Ag ions in a composite is influenced by a number of variables including the Ag concentration gradient, moisture soaking time, the nature of the morphology of all components of the composite, environmental osmolarity, the nature of the composite material that entraps the Ag nanostructures and also the nature of dispersion [217]. The lower activity of Ag/ZnO/NC may be attributed to the agglomeration of silver nanoparticles in the composites. Silver alone shows higher activities, and on Figure 4.3 (section 4.1.3), the particles on their own are widely dispersed thus a greater surface area to volume ratio. Agglomeration reduces the number of effective surface nanoparticles, thus the number of surface active sites and leading to diminished activities.

Incorporation of Ag into biomaterials is reported to lead to reduced cytotoxicity [218]. Permanence of antibacterial activity over time is an important property for effective antibacterial applications [195]. A slow and continual release of silver nanoparticles allows a significant interaction of these ions with the bacterial cells thus leading to prolonged antimicrobial effect. Even though lower Activities were observed for Ag/ZnO/NC composites as compared to Ag, composites are advantageous over use of bare Ag. Their benefit lies in their ability to offer reduced cytotoxicity towards humans when ingested as they are more stable compared to bare Ag nanoparticles [219-220]. In addition, encapsulating Ag in polymer matrix can lead to extended steady time-release properties which results in prolonged antibacterial effectiveness.

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

A three component Ag/ZnO/NC nanocomposite was successfully synthesized through a low cost in-situ solution casting method. In-situ synthesis allows for uniform dispersion of materials over each other. The presence of all Ag, ZnO and cellulose in the composite was confirmed by XRD, SEM, FTIR, and EDS. Wurtzite, face centered cubic and monoclinic structures were identified from XRD analysis for ZnO, Ag and cellulose, respectively as bare materials or in the composites. FESEM showed same shape for each individual component and in the composite. Nano disc-like, hierarchical strips and nanospheres were observed from FESEM morphology assessment of ZnO, cellulose and Ag powders, respectively. From FESEM analysis it was observed that both Ag and ZnO were uniformly dispersed on the cellulose polymer matrix. This was also confirmed through elemental mapping using the EDX. The FTIR showed respective characteristic functional groups and absorption bands for Ag, ZnO and cellulose as reported in literature.

The photocatalytic degradation of methylene blue was investigated in the presence and absence of photocatalysts. Results demonstrated that self-degradation of methylene blue whether under dark condition or under visible light irradiation is insignificant and also Ag/ZnO/cellulose composite exhibited elevated photocatalytic activity against aqueous MB dye under visible light irradiation as compared to pristine Ag, ZnO, Ag/NC and ZnO/NC. A greater percentage of MB was degraded in the presence of Ag/ZnO/NC as compared to other test samples. This was attributed to the synergic contribution of both the semiconductor and noble metal as well as the favorable contributions from cellulose. An extended light absorption and delayed e^-/h^+ pair recombination leads to an increased activity. Because of its wide band gap ZnO absorbs much energy in the solar spectrum and undergoes excitation to emit an e^-/h^+ pair. In the presence of Ag metal, the probability of this generated pair recombining is lessened because Ag ions act as electron sink, they trap electrons. Ag on its own showed some photoactivity even though in minimal measures. Dispersing ZnO and Ag on cellulose support material enhanced their

photoactivity as cellulose controlled agglomeration and also decreased the particle size of both Ag and ZnO, thus it can be elucidated that anchoring ZnO and Ag nanostructures onto cellulose increased their active surface area thus enhancing their properties. Ag/ZnO/NC also showed excellent antibacterial activities against all the three bacterial strains; *S.aureus*, *B.subtilis* and *E.coli* for the employed disc diffusion method also known as the zone of inhibition method. However, it can be drawn that Gram positive bacteria showed more susceptibility to all the samples as compared to Gram negative bacteria. Based on the results, hybridization of Ag and ZnO on cellulose matrix could be adopted as a novel, cheaper, simple, efficient and environmentally friendly approach for environmental remediation.

5.2 Recommendations for Future Work

The aim of this study was successfully attained; however there are few recommendations that need to be implemented in future to broaden the scope of antibacterial and photocatalytic application of Ag/ZnO/NC nanocomposites.

It is hence recommended that:

- ✚ The specific surface area of the samples should be determined through Brunauer Emmett-Teller (BET) studies.
- ✚ It should be considered to electrospin the nanocomposite to make mats. Electrospinning is reported to effectively increase the surface area of material so it's believed that electrospun Ag/ZnO/NC will have more enhanced photocatalytic and antibacterial activities.
- ✚ Investigation of the leaching rate, reusability and recyclability of Ag/ZnO/NC nanocomposite should be done. This is a key requirement for a possible industrial application.
- ✚ Further variations such as temperature effects, catalyst loading, and pH of the environment should be investigated.
- ✚ The photocatalytic and antibacterial activities of Ag/ZnO/cellulose should be tested in wastewater.

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