SYNTHESIS AND CHARACTERIZATIONS OF ZINC OXIDE NANOPARTICLES FOR THE APPLICATION OF UV ABSORBERS IN TEXTILES

BY ALEMAYEHU NIGUSA

A THESIS SUBMITTED TO THE APPLIED PHYSICS PROGRAM

SCHOOL OF APPLIED NATURAL SCIENCE

FOR THE PARTIAL FULFILLMENT OF THE REQUAREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN PHYSICS

OFFICE OF GRADUATE STUDIES

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ADVISOR, ABEBE BELAY (PhD)

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APPROVAL SHEET

ADAMA SCIENCE AND TECHNOLOGY UNIVERSITY

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APPLIED PHYSICS PROGRAM

This is to certify that the thesis prepared by **Alemayehu Nigusa Urgessa** entitled " **synthesis and characterization of zinc oxide nanoparticle for the application of uv absorbers in textile** " submitted for partial fulfillment of the requirements for the master of degree of science in physics complies with the regulation of the university and meets the accepted standards with respect to originality.

Signed by the examination committee

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External examiner		
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Internal examiner		

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DEDICATION

THIS WORK IS DEDICATED TO MY FAMILY

DECLARATION.

The work incorporated in this thesis has beencarried out in the reaserch laboratories of depaaetment of physics school of applied natural science,Adama Science and Technology Unversity. The extentof the information derived from the existing letrature has been indicated in the body of the thesis at appropriate places giving the referance. The work embodied in this thesis is original and I declare that it has not been submitted in part or in full for any degree or diploma of any other university.

Adama,Ehiopia _____

Date 15/1/2011 Alemayehu Nigusa

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LIST OF ABREVATION.

DMSO	Dimethyl Sulfoxide.
FDA	Food and Drug Administration.
FWHM	Full width at half- maximum
NPs	Nanoparticles
SEM	Scanning Electron Microscopy
UPF	Ultra violet Protection Factor
UV-vis	Ultra Violet -Visible
X-RD	X-Ray Difractometer.
ZnO	Zinc Oxide.

Abstract

ZnO NPs were synthesized by precipitation method from zinc sulphate heptahydrate and zinc nitrate hexahydrate as a precursors with sodiumhydroxide at different annealing temperatures.

The synthesised ZnO NPS were characterized using X-Ray Diffraction (X-RD), UV-vis Spectroscopy, Scanning Electron Microscopy (SEM) and Fluorescence spectroscopy.The X-ray diffraction (XRD) study revealed that the synthesized ZnO product has wurtzite hexagonal structure with the average crystallite size 19.41 - 25.69 nm from zinc sulphate heptahydrate precursor at calcinating temperature of 200 and 400^{o}C respectively. Similarly the average crystallite size of ZnO NPS from zinc nitrate hexhydrate precursors found to be 26.33 - 28.74 nm at calcinating temperature of 400 and 500^{o}C respectively. The SEM images of synthesized zinc oxide nanoparticles (ZnO NPs) using zinc nitrate hexhydrate precursor at 400 and 500 ^{o}C were spherical in shape and agreed with XRD results obtained. The UV absorption peaks were observed at 368 and 377 nm for zinc sulphate heptahydrate and 370 and 378 nm for zinc nitrate hexhydrate respectively. The opticl absorption of ZnO NPS at different annealing temperature indicates red shift as the annealing temperature increses. The fluorescence emission peaks were observed at (392, 399, 396 and 396) nm in UV region and at (449, 464, 474, 519, 521 and 524) nm in vissible region. The synthesized ZnO NPs were then applied on cotton and wool samples to impart sunscreen activity to the treated textile. The effectiveness of treatment was assessed using UV–Vis spectroscopy. The ultraviolet protection factor (UPF) and Percent of tranismission (%T) found to be ZnO NPs good UV radiation blockers

1. INTRODUCTION

1.1. Background of the study

Nanoscience is the study of phenomenon and manipulation of materials at atomic, molecular and micro molecular scale where the properties are significantly different from bulk matter. It is a science in which materials with small dimension shows new physical phenomenon.

Nanoparticles are particles that exist on a nanometer scale below 100 nm in at least one dimension. They can possess physical properties such as uniformity, conductance or special optical properties that make them desirable in materials science and biology. People are interested in the nanoscale, because at this scale the properties of materials can be different from those at a larger scale [1]. Materials can be produced at nanoscale in one dimension (nanowires and nanotubes), in two dimensions (very thin surface coatings) or in all three dimensions (nanoflowers). As a particle decreases in size, a greater proportion of atoms are found at the surface compared to those inside. Thus nanoparticles have a much greater surface area per unit mass compared with larger particles. As growth and catalytic chemical reactions occur at surfaces, this means that a given mass of material in nanoparticulated form was much more reactive than the same mass of material made up of larger particles.

Synthesis of metal particles with specific properties is newly established research area that attracts a great deal of attention. The properties of metal nanoparticles depends largely on their synthesis procedure. This indeed allow as to think in both bottom up or top down approaches (i.e either to assemble atoms together or disassemble) bulky solid in to finer pieces until they are constituted of a few atoms [2]. This domain is a pure example of interdisciplinay work in composing physics, chemistry and engineering up to medicine. Several synthesis routes

are reported in different literatures to obtain NPs. Among these, Synthesis of NPs by ultrasonic radiation method [3], precipitation method [4], sol-gel method [5] and Wet Chemical Method [6] are some of the synthesized routes of synthesizing nanoparticles. Although various techniques have been summarized there are some features to consider that are common to all the methods. Control of particle size, size distribution, shape, crystal structure and composition distribution, improvement of the purity of nanoparticles (lower impurities),control of aggregation, stabilization of physical properties, structures and reactants, higher reproducibility and higher mass production, scale-up and lower costs.

Precipitation methods is the creation of a solid from a solution.When the reaction occurs in a liquid solution, the solid formed was called the precipitate.The chemical that causes the solid to form is called precipitant.Without sufficient forceof gravity to bring the solid particles together,the pricipitate remains in suspention. After sedimentation the pricipitate may be reffered to as a pellet. The pricipitate free liquid remaining above the solid is called the supernatant.The main advantage of this methods is providimg small enough crystal size.

Metallic oxide nanoparticle play a very important role in many areas of chemistry, physics and material science [7]. The metal element are able to form a large diversity of oxide compounds [8]. This can adopt a vast number of structural geometries with an electronic structure that can exhibit metallic, semiconductor or insulator character. Metallic nano particles have a large surface area to volume ratio that results in a significant increasing of the effectiveness in blocking UV radiation when compared to bulky material [9] and can provide high durability for treated fabrics, because they posses large surface area and high surface energy that ensure better affinity for fabric and lead to an increase in durability of the textile function.[10]. The use of nanotechnology in the textile industry has increased rapidly. This is

mainly due to the fact that conventional methods used to impart different properties to fabrics often do not lead to permanent effects and will lose their functions after laundering or wearing. Hence the interest of scientist and researcher for the use of nanotechnology in the textile industry has increased rapidly.

The application of nanoparticles to textile materials has been aimed at producing finished fabrics with different performance. All the leading textile industries are focusing on value added applications such as microbe resistance, electromagnetic protection and thermoregulatory fabrics. Materials and system for human protection will enhance the performance and well being of the human society. To protect defense personnel from microbe ,cross infection and UV radiation a special finish like antimicrobial and UV absorber finish has become a necessity on clothing, socks, blankets and bed linens used by them. For examples, nano silver has been used to imparting anti bacterial properties [11], nano titanium oxide for UV blocking and self cleaning properties [12]. and zinc oxide nanoparticle for antibacterial and UV blocking properties [13]. In fact zinc oxide and titanium oxide are non toxic and chemically stable under exposure to both high temperature and UV radiation

Among different types of metal oxide nanoparticles, zinc oxide (ZnO) is nontoxic and chemically stable under exposure to high temperature and is capable of photo-catalytic oxidation. Zinc oxide is one of the semiconductor with a formula of ZnO. It has a unique physical and chemical properties, such as high chemical stability, broad range of absorption and high photo stability with multifunctional material[14]. It has a wide band gap energy (3.37 eV) and large excitation binding energy (60 eV). It widely used in numerous materials and products including plastics, ceramics, glass, cement, rubber manufacturing, cosmetics and etc, because of its unique photo catalytic, electrical, optical,dermatological and antibacterial properties[15].

It is one of the best bio- friendly absorbers of UV radiation that mainly come on earth from the sun through the atmospheric ozone layer [16]. Since ZnO nanoparticle is nontoxic; it is used to coat textiles [17].

As reported in different letirature, the protection provided by fabrics depends on several parameters: fiber type, color, the presence of UV absorbers and additives, the porosity, thickness, mass per unit surface, other finishing processes and laundering, and the wearing conditions [18]

In this research the synthesis and characterization of zinc oxide (ZnO) nanoparticle that was prepared through homogeneous phase reaction between Zinc Sulphate heptaydrate($ZnSO_4$. $7H_2O$) and Zinc Nitrate hex hydrate ($Zn(NO3)_2.6H_2O$) as a precursor and sodium hydroxide (NaOH)) as a precipitating agent at different temperature using Precipitation methods. The synthesized ZnO nanoparticle at different annealing temperature was characterized using varies physical techniques such as X-rays diffraction (XRD), UV.vis spectroscopy, Fluorescence spectroscopy, Scanning Electron Microscopy (SEM) and applied on cotton and wool as UV absorber.

1.3. Objectives of the study

1.3.1.General objective

The general objective of this study is synthesis ,characterization and apply zinc oxide nanoparticles to cotton and wool in order to increase UV absorption.

1.3.2. Specific objectives of the study

The specific objectives of this research are

- Synthesis of ZnO nanoparticle by precipitation method using, zinc sulphate heptahydrate ($ZnSO_4$).$7H_2O$), Zinc Nitrate hex hydrate ($Zn(NO3)_2.6H_2O$) as a precursor with sodium hydroxide(NaOH).

- Characterize the synthesized zinc oxide nanoparticle using different spectroscopic techniques, such as UV-vis spectroscopy, Fluorescence spectroscopy, XRD, SEM,
- Apply the synthesized ZnO nanoparticles in cotton and wool for UV absorber.

1.4. Scope and limitation of the study

The study was indeed to assess the application of ZnO NPS in textile as UV absorber and antimicrobial activity. However,due to the financial and time conistraint the study was limitted to the application of ZnO NPS as UV absorber in textile. As a result the study could not allowed for the application of zinc oxide nanoparticle as antimicrobial. Due to the time conistraint to apply ZnO NPS on many fabrics,the scope of the study was narrowed to cotton and wool fabrics

1.5. Significance of the study

zinc oxide nanoparticle has many application in industrial (i.e as textile as UV absorber, transparent conducting film, acoustic wave devices and gas sensors) and medical(therapeutic imaging, cancer treatment etc.). Therefore, using zinc oxide nanoparticle is necessary for all types of application by controlling morphology, composition and structure. The final result of this investigation is to provide the most appropriate ingredient for textile industries.

The thesis is organized as follows.In Chapter 1 introduction to nanoparticles related to zinc oxide nanoparticles and objectives of the study were presented.

In Chapter 2,Nanothecnology, Nanoparticle, properties of nano particle,the crystal structure of ZnO nanoparticles and synthesis methods of ZnO NPs, physical characterization teqniques and application tecniques of ZnO NPS in textile are presented.

In Chapter 3, the materials and methods used in this work were presented. This chapter has four sections; the first section of this chapter describes chemicals and solvents used to carry out this research. The second section of this chapter deals with the apparatus and instruments used to carry out this research. The third section describes methods of synthesizing zinc oxide nanoparticles from different zinc salt precursors and fourth section describes characterization mechanisms of zinc oxide nanoparticles are presented.

In Chapter 4, the results and discussion of the thesis were presented. The calculated values of crystal size of ZnO NPs, the absorption peaks and emission peaks, morphologies are presented. Finally, conclusion is given in Chapter 5.

2. REVIEW OF RELATED LITERATURE

2.1.Nanotechnology

Nanotechnology is the ability to create structure that have excellent properties by controlling atoms and molecules functional materials, devices and systems on the nanometer scale by involving prices placement of individual atoms of size around 1-100nm. Hence the interest of scientist and researcher for the use of nanotechnology in the textile industry has increased rapidly. This is mainly due to the fact that textile is one of the best areas for deploying nanotechnology and also conventional methods used to impart different properties of fabric often do not lead to the permanent effect and will lose their functions after laundering or wearing [10]. The synergy (interaction) between nanotechnology and textile industry uses this property of large interfacial area and drastic change in energetic is experienced by macromolecular or super molecular cluster in the vicinity of fabric when changing from wet state to dry state [19].

2.2. Nanoparticle

Nanoparticles are the class of materials and remarkable scientific tools that has been used for various biotechnological, pharmacological and technological uses. They are cornerstones of nanoscience and nanotechnology. Nanoparticles are different from bulk materials due to their small size, higher surface area to volume ratio, crystallographic surface structure, specific magnetic properties and new quantum effects. They also exhibit unique physical and chemical properties which exist due to the presence of a high concentration of defects like electrical, catalytic, magnetic, mechanical, thermal, or imaging features. Nanomaterials may be metals, ceramics, polymers as well as composites. Metal elements have better performance to form a

large diversity of oxide compounds used in the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells,

2.3. Properties of nanoparticle

Nanoparticle have the structural feature in between of those of atoms and the bulk matter, while most microstructure materials have similar properties to the corresponding bulk material. The properties of material with nanometer dimension are significantly different from those of atom and bulk matter [20]. This is mainly due to the nanometer size of material which render them: I, large fraction of surface atom. II, High surface energy. III, Spatial confinement. IV,Reduced imperfection which do not exist in the corresponding bulk material.

The optical properties of nanomaterial depends on the parameters such as feature size, shape, surface characteristics and other variable. Shape can have a dramatic influence on optical properties of metal nano structure and a simple change in size alters the optical properties of nano particles [21]. In single molecules the optical properties are determined by the energetic gap between molecular orbital, especially the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) [22].

Electrical properties of nanoparticle discuss about fundamentals of electrical conductivity in nano tube and nanorod, carbon nano tubes, photoconductivity of nanorods, electrical conductivity of nano composites. One interesting method which can be used to determine the steps in conductance is the mechanical thinning of nano wire and measurement of electrical current at constant applied voltage. The important point is that with decreasing the diameter of the wire the number of electron wave modes contributing to the electrical conductivity is becoming increasingly smaller by well defined quantized step [23].

2.4 . Zinc oxide nanoparticle (ZnO NPS)

Among several nanoparticle zinc oxide (ZnO) nanoparticle have received moreattention, due to its various application like gas sensors [24], Chemical sensors [25], Biosensors [26], super conductors [27], photo catalyst [28], optoelectronic devises[29], cosmetics [30]. Zinc oxide is a wide band gap (3.37ev) semiconductor having excitation binding energy of 60 ev at room temperature which is significantly larger than other material and it has high transmittance and good electrical conductivity [31]. The large band gap gives ZnO the advantages of higher voltage breakdown; reduce electronic noise, ability to sustain (establish or strengthen as with new evidence) large electric fields and higher power operation than smaller band gap materials [32]. The wide band gap and large excitation binding energy of ZnO also make it a potential candidate to be applied in chemical sensors, luminescence devices and solar cells.

ZnO generally occurs as a white powder known as mineral zincite or zinc white. This mineral usually contains some manganese particles or other elements thus making it red or yellow in color [33]. When heated crystalline zinc oxide changes its color from white to yellow due to the loss of oxygen. Upon cooling it turns back into its original color by regaining oxygen.

Zinc oxide (ZnO) has attracted much interest as one of the multifunctional inorganic nanoparticle due its unique combination of superior physicl,chemical,biological,elctrical,optical,biocompata bility,antibacterial and composites [34]. Zinc (Zn) is a necessary to our health and ZnO nano particle also have good biocompatibility to human cell. Recently ZnO is listed as generally documented as safe material by FDA (Food and Drug Administration) [35].

2.5. Crystal structure of ZnO

Zinc oxide (ZnO) is an inexpensive material and is relatively abundant. It has high chemical and thermal stability, and non-toxic, easy to prepare and therefore, it is one of the most studied materials. It has many useful properties such as high carrier mobility and transparency as well as a wide band gap of 3.37 eV. ZnO occurs in nature as the mineral zincite and has the ionic and polar crystal structure of wurtzite. This structure is related to a hexagonal close packed (HCP) structure with zinc atoms and oxygen atoms tetrahedral four-coordinated as shown in figure 2.1 below. Wurtzite zinc oxide has a hexagonal structure (space group C6mc) with lattice parameters a = 0.3296 and c = 0.52065 nm, in the ratio of 1.57964. The structure of ZnO can be simply described as a number of alternating planes composed of tetrahedrally coordinated O2- and Zn2+ ions, stacked alternately along the c-axis (figure 2.1). The tetrahedral coordination in ZnO results in non central symmetric structure which consequently gives piezoelectricity and pyroelectricity. Another important characteristic of ZnO is polar surfaces. The most common polar surface is the basal plane. The oppositely charged ions produce positively charged Zn-(0001) and negatively charged O-$(000\bar{1})$ surfaces, resulting in a normal dipole moment and spontaneous polarization along the c-axis as well as a divergence in surface energy. To maintain a stable structure, the polar surfaces generally have facets or exhibit massive surface reconstructions, but ZnO-±(0001) are exceptions: they are atomically flat, stable and without reconstruction . The other two most commonly observed facets for ZnO are $\{2\bar{1}0\bar{1}\}$ and $\{01\bar{1}0\}$, which are non-polar surfaces and have lower energy than the {0001} facets .

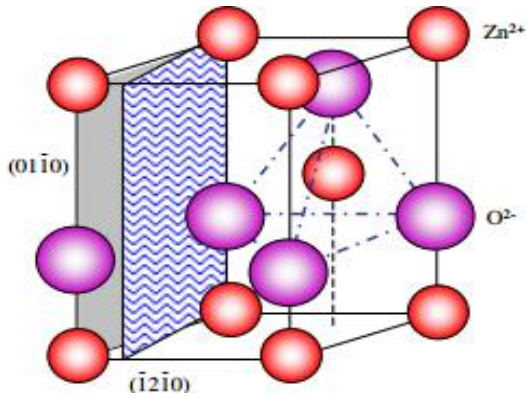


Figure 2.1: The wurtzite structure model of ZnO NPS

2.6. Synthesis of ZnO Nanoparticle

Several synthetic approaches have been developed for synthesizing zinc oxide nanoparticles over the past several decades. Regardless of the technique, the goal of particle synthesis generally focuses on: minimizing and controlling particle size, maintaining a narrow size distribution, control of particle morphology, and control of crystalline. The ability to control size enables the variation of particle properties, while the narrow size distribution allows greater precision and is required for studies of size-dependent effects. Particle shape and crystal structure can also influence material properties. The physical and chemical properties of nonmaterial depend not only on their composition but also on the particle size and shape. Accordingly, a high quality synthesis protocol must first of all provide control over particle size [36] and shape [37].Two approaches have been known in the preparation ultrafine particles from an ancient time [2]. The first is the break down (top down) method by which an external force is applied to the solid that lead to its break up in to smaller particles. The second is the build -up (bottom up) method that produce nanoparticle starting from atoms or liquids based on atomic transformation or molecular condensation. The top down method is the method of breaking up a solid substance. It sup divided in to dry and wet grinding. A characteristic of particle in grain refining processes is that their surface energy increases which causes the aggregation of particles to increase. The bottom

up approach is roughly divided in to gaseous phase method and liquid phase method. For the former the chemical vapor deposition method (CVD) involves chemical reaction, where as the physical vapor deposition method (PVD) uses cooling of evaporated materials. For many years liquid phase method have been the major preparation methods of nanoparticle. sedimentation method is one of the method of liquid method.

The general techniques in the sedimentation method is a precipitation process which has been used extensively for the fabrication of metal oxide nanoparticle. This procedures transforms a solution of a metal oxide in to hydrolysis,followed by polycondensation to gel [4]. The mechanism involved in the synthesis of zinc oxide nanoparticles from zinc salt precursors is:

$$2NaOH_{(s)} \longrightarrow 2Na+_{(aq)} + 2OH-_{(aq)}$$

$$Zn(NO_3)_2 .6H_2O \longrightarrow Zn2+_{(aq)} + 2NO_3-_{(aq)} + 6H_2O$$

$$ZnSO_4.7H_2O \longrightarrow Zn2+_{(aq)} + SO_4-_{(aq)} + 7H_2O$$

$$Zn2+_{(aq)} + 2OH-_{(aq)}\, XH_2O \longrightarrow Zn(OH)_2.XH_2O_{(s)} \downarrow 60\ ^0C$$

$$Zn(OH)_2.XH_2O_{(s)} \longrightarrow Zn(OH)_{2(s)} + XH_2O_{(g)} \text{ at high temprature}$$

$$Zn(OH)_{2(s)} \longrightarrow ZnO_{(s)} + H_2O_{(g)} \uparrow$$

2.8. Characterization of ZnO NPs

The ZnO nanoparticle synthesized by different condition of temperature was characterized by different spectroscopic techniques such as X-ray powder diffractometery (X-RD), UV-vis spectroscopy,Fluorescence spectroscopy and Scanning Electron Microscopy (SEM) and these inistrument were used to characterize the nanoparticle size,Absorption spectra, Emission spectra , crystallite shape and morphology.

2.8.1. X- ray Diffraction characterization

The X-RD spectra of zinc oxide nanoparticle determines the crystallite of the synthesized solid. This method uses a monochromatic source of X-rays and measures the pattern of diffracted radiation, which is a result of the constructive interference due to the crystalline structure of powder [38] .Traditionally the broadening of the peaks in the X-RD pattern of solids is attributed to the particle size effect. The mean crystalline size of the powder sample is estimated from the full width at half maximum of the diffraction peak (Δw),according to the Scherrer's equation [39]

$$D = \frac{0.89\lambda}{\Delta w \cos\theta} \qquad 2.1$$

where λ is the wave length of the incident X-ray beam ($\lambda = 1.54A$ for Cu kα), θ is the bragg's diffraction angle and Δw is the width of the X-ray pattern line at half peak height in radiance. It is important to realize that the Scherer formula provides a lower bound on the particle size. The reason for this is that a variety of factors can contribute to the width of a diffraction peak besides instrumental effects and crystallite size; the most important of these are usually inhomogeneous strain and crystal lattice imperfections. The sources of peak broadening are: dislocations, stacking faults, twinning, micro stresses, grain boundaries, sub-boundaries, coherency strain, chemical heterogeneities, and crystallite smallness. (Some of those and other imperfections may also result in peak shift, peak asymmetry, anisotropic peak broadening, or affect peak shape).

The lattice parameters "a" and "c" and spacing distance "d_{hkl}" for the wurtzite structure of ZnO can be calculated according to the following equations.

$$a = \sqrt{\frac{1}{3}} \frac{\lambda}{\sin\theta} \tag{2.2}$$

$$c = \frac{\lambda}{\sin\theta} \tag{2.3}$$

$$dhkl = \frac{ac}{2} \sqrt{\frac{3}{c2\left(h2 + hk + k2\right) + 3\frac{(al)2}{4}}} \tag{2.4}$$

2.8.2. Scanning Electron Microscpy

Scanning Electron Microscopy (SEM) uses a mignified electron microscopy to generate high resolution image and presisely measure very small features and objects. It used to obtain three dimension-like topographical images of a wide variety of samples. It is a very good technique for investigating the surface morphology of nanoparticles [40]. This versatile method allows sample images to be quickly collected in the magnification range of 10 to 250,000X.

2.8.3. UV-vis Spectroscopy

Spectroscopy is a simple technique used to measure absorbance of solutions. Ultraviolet-visible spectroscopy (UV-Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible region. The UV and UV-visible range is only a small part of the total electromagnetic spectrum, and is generally defined from wavelengths of 190 nm at the high energy UV end to about 750 nm at the low energy red end of the spectrum. Absorption of visible and ultraviolet (UV) radiation is associated with excitation of electrons in nanoparticles from lower to higher energy levels. Since the energy levels of matter are quantized, only light with the precise amount of energy can cause transitions from one level to another will be absorbed. An electron is excited from a ground state into an excited state. Each wavelength of light has a particular energy associated with it. If that particular amount of energy is just right for making

one of these electronic transitions, then that wavelength will be absorbed. The larger the gap between the energy levels, the greater the energy required to promote the electron to the higher energy level, resulting in light of higher frequency and therefore shorter wavelength being absorbed. Nanoparticles undergo electronic excitation following absorption of light.

Zinc oxide nanoparticle have wide band energy and a high excitation binding energy compared to its bulk. This can be evaluated according to the Brus equation [41].

$$E_g^n = E_g^b + \left(\frac{h^2}{8R^2}\right)\left(\frac{1}{m_e} + \frac{1}{m_h}\right) - \left(\frac{1.8e^2}{4\pi\varepsilon_\circ\varepsilon R}\right) \quad (2.5)$$

where E_g^n and E_g^b are the band gap energies of nanoparticle and bulk solid respectively, R is the radius of the quantum dots, m_e is the effective mass of electron in solid (m_e =9.11 x 10^{-31}kg), e is elementary charge of electron (e = 1.6 x 10^{-19}c), h is plank's constant(h = 6.626 x 10^{-34} J.s), m_h is the effective mass of hole (1.62x10^{-27}kg) in the solid, $\mathcal{E}$ is the dielectric constant of the solid.

2.8.4. Fluorescence spectroscopy

Fluorescence spectroscopy can yeald low detection limits, high sensitivity and high specificity. The high specificity is largly due to the fact that fluorophores exhibit specific excitation (absorption) and emission (fluorescence) wavelengeth. The emission spectrum provides informaion for both qualitative and quantative analysis. Generally ZnO exhibits two kind of emission; one is at UV emission at approximately 380 nm and the other is the visible deep level emission with a peak range from 400 - 700 nm. [42]. When the crystal are heated,they tend to lose oxygen [43]. For this reason the ZnO shows n-type semiconducting properties with many defects such as lack of oxygen and the excess of zinc. It is known that visible emission is due to defects that are related to deep level emission such as zinc interstitials and oxygen vacances [44]. The emission in UV region is caused from recombination between the electron in the conduction

band and holes in the valance band. Hot body that emits radiation solely because of its high temperature is said to exhibit incandescence. All other forms of light emission are called luminescence. Photoluminescence is divided into two categories, Fluorescence and phosphorescence. Other forms of luminescence include chemo luminescence, derived from the energy of a chemical reaction, and bioluminescence when the reactions take place within living organisms, for example, glow-worms and fireflies. When the external energy supply is by means of the absorption of infrared, visible or ultraviolet light, the emitted light is called photoluminescence and this is the process that takes place in any fluorimetric analysis [45]

2.9. Application of nanoparticles in textiles

The textile industry is one of the most important industries for consumer goods worldwide generating textiles for clothing, household goods, furnishing and technical purposes. Like other chemical processes and technologies, nanomaterials are used to add or improve different functionalities for the textiles. These materials could have an adverse effect on humans and environment. Proper selection of nanomaterials and their careful integration in the fabric will help to reduce these possible impacts. Nanomaterials are expected to either improve the existing properties or bring new functionalities to textiles such as dirty and water repellence, breathability, UV protection, conductive and antistatic properties, wear and wrinkle resistance or resistance to stains, bacteria or fungi [46].

Nano titanium dioxide is currently used in textiles for UV protection and researchers are looking into its applicability for antibacterial purposes by combining nano titanium dioxide with nano silver. Such equipped textiles should be able to attack microorganisms, degrade organic pollutants and neutralize bad odors. Once a reliable and stable integration of the nanomaterials in the fabric is achieved, they are known as "self-cleaning" fabrics [47].

In textiles, silver can be applied in form of silver salts (e.g. silver chloride), nanoparticles or nanoscale coating on the surface of the fibres. It reduces bacterial growth on the textile (clothing, household, and furnishing) by releasing silver ions, which are active on the fibre surface. Nano-enhanced silver textiles usually contain substantially less amounts of silver compared to conventional textiles for the same biocidal effects [48].

Nanoparticle coating may affect other fabric properties like dyeing capacity, tensile strength, bursting strength, bending rigidity, air permeability (comfort) and fabric friction that play a crucial role in textile industries. Cotton fabrics treated with bulk-ZnO or nano-ZnO show different physical and mechanical properties. This reflects the improved properties of nano-sized particles with respect to conventional materials. Air permeability of the fabric is reduced when the coating process is carried out with bulk-ZnO, while it is improved when nano-ZnO is used. This basic difference has great consequences on the garment's breathability, and eventually on the comfort of the treated fabrics

Currently, zinc oxide nanoparticles and nano-rods are being investigated due to their antibacterial activity and UV protection. Coating cotton fabric with zinc oxide nano-rods creates textiles with "super hydrophobic properties" (i.e. water-repellence) and using zinc oxide nanowires helps to produce electricity, which is generated when the nanowires are rubbing against each other through the movement of the textile. Carbon nanotubes (CNTs) can equip textiles and fibers with flame-retardant properties, generate electrical conductivity and improve heat conduction in the textiles.

The performance of zinc oxide nanoparticle as UV absorbers can be efficiently transferred to the fabric materials through the application of ZnO nanoparticle on the surface of

the cotton and wool blended fabrics. The effectiveness in shielding UV radiation was evaluated by measuring the UV Absorption, Transmission and reflection. The Transmission data was used to calculate the UPF and percent of transmission, according to the following equation [49]

$$UPF = \int_{\lambda 1}^{\lambda 2} \frac{E(\lambda).S(\lambda)d\lambda}{E(\lambda).S(\lambda).T(\lambda)d\lambda} \tag{2.8}$$

$$\%Transmission = \sum_{\lambda 1}^{\lambda 2} \frac{T(\lambda)}{(\lambda 2 - \lambda 1)} \tag{2.9}$$

where E(λ) is the relative erythermal spectral effectiveness, S(λ) is the solar spectral irradiance in $Wm^{-2}nm^{-1}$ and T(λ) is the spectral transmission specimen obtained from UV spectrometric experiments. E(λ) and S(λ) will obtain from the national oceanic and atmospheric administration data base (NOAA).

3. MATERIALS AND METHODS

3.1. Chemicals and solvents

The following chemicals and solvent were used in this work. Zinc nitrate hexhydrate (Zn(NO3)2.6H_2O Assay 98.5-103%) (Himedia,India),Zinc sulphate heptahydrate (ZnSO4).7H_2O Assay 98.5-103%) (Himedia, India), sodium hydroxide (NaOH, Assay 98-103 %) (Himedia, India) distilled water, dimethylsulfoxide (DMSO, Assay 99.9 %).

3.2. Apparatus

The laboratory apparatus used for this work were Analytical balance (FA2104,Zhejiang,China), Magnetic stirrer with hot plate (MH-2lt,India), Heating Oven (model: DHG-9055,China),FurnaCe (model: BK5 12GJ, China) Beakers, puddle, Aluminum paper, spatula, cuvette, different textile samples, examination glove, crucible, .Mortar,

3.3. Synthesis of zinc oxide nanoparticle

S1 ZnO nanoparticle was prepared by precipitation method according to the procedure developed by [4]. 12g of Zinc nitrate hexahydrate (Zn $(NO_3)_2$.6H_2O) was dissolved in 200 ml deionized water in beaker and vigorously stirred by magnetic stirrer for 15 min held at 60 ^{0}C. Again 4 g of Sodium hydroxide (NaOH) was dissolved in 100 mL deionized water in separate vessel and vigorously stirred by magnetic stirrer for 5 min at 60 ^{o}C. The solution of sodium hydroxide was slowly dropped to Zinc nitrate hexahydrate and the aqueous solution turned into a milky white. The mixed solution was stirred for 1 hr after complete addition of sodium hydroxide at 60^{o}C. After the complete reaction, the solution was allowed to settle and the supernatant solution was removed and the remaining suspension washed with distilled water 3 times. The prepared solution was maintained in oven for 4 hrs at 160 ^{0}C. Again this sample was put in crucible which has high temperature resistance and calcinated in muffle furnace for 2 hrs

at 400^{O}C. Similarly S2 ZnO NPS was synthesised with same procdures mentioned above and calcintaed at 500 ^{o}C.

S3 ZnO nanoparticle was be prepared by precipitation method [4]. 12g of Zinc sulphate heptahydrate (Zn (SO4).7H_2O) was dissolved in 200 ml deionized water in beaker and vigorously stirred by magnetic stirrer for 15 min at 60 ^{0}C. Again 4 g of Sodium hydroxide (NaOH) was dissolved in 100 mL deionized water in separate vessel and vigorously stirred by magnetic stirrer for 5 min at 60 ^{o}C. The solution of sodium hydroxide was slowly added drop-wise to Zinc sulphate heptahydrate and the aqueous solution turned into a milky white colloid. The mixed solution was stirred for 1 hr after complete addition of sodium hydroxide at 60^{o}C. After the complete reaction, the solution was allowed to settle and the supernatant solution was removed and the remaining suspension was washed with distilled water 3 times. After complete washing the prepared solution was maintained at oven for 4 hrs at 160 ^{0}C. Again this sample was put in crucible which has high temperature resistance and calcinated in muffle furnace for 2 hrs. at 400^{O}C. Similarly S4 ZnO NPS was synthesised with same procdures mentioned above and calcintaed at 200 ^{o}C

3.4. Characterization methods for zinc oxide nanoparticle

Various techniques can be used for characterization of synthesized zinc oxide nanoparticle. The most common used in this work was X-ray diffractometry (X-RD), UV-vis spectroscopy, Fluores cence spectroscopy and Scanning Electron Microscopy (SEM).

The X-ray diffraction pattern for zinc oxide nanoparticle was analyzed using (XRD-7000) X-ray diffractometer by generating cu-kα radiation($\lambda = 1.5418 A\circ$). It was used to determined the crystalline phase of the synthesized zinc oxide nano particle.In this work small

amount of sample in powder form was used for characterization. Difractometer was connected to the computer for data collection and characterization displays. An X-ray generator operates at a voltage of 40kV and applied current of 30mA at room temperature. Intensities were measured at room temperature for angle range of $2\theta = 10^0 \leq 2\theta \leq 100$. The crystallite domain diameter (D) was obtained from X-RD peaks according to the Debye Scherer's equation Eq (2.1).

The lattice parameters "a" and "c" and spacing distance "d_{hkl}" for the wurtzite structure of ZnO can be calculated according to Eq (2.2, 2.3 and 2.4).

The morphological property of synthesized ZnO NPs were determined by using Scanning Electron Microscopy (SEM) (Hitachi, H-7600), using electron beam energy of 10 KV and15 KV. The synthesized ZnO NPs powder is mounted on a sample holder followed by coating with a conductive metal. The sample is then scanned with focused fine beam of electrons. The surface characteristics of the sample are obtained from the secondary electrons emitted from the sample surface. The mean size obtained by SEM is comparable with results obtained by X-RD diffractometry .

The optical characterization of ZnO NPs was carried out using UV-vis Spectroscopy *(*Perkin–Elmer lambda, 19UV-vis Spectrophotometry with double monocramater using 1cm fused quartz cuvette) in the wavelength region of 200 - 600 nm. First the powder of ZnO nanoparticle was dissolved in a dimethyl sulfoxide (DMSO) solvent in a beaker and stirred by magnetic stirrer for a few minute. DMSO solvent was added to 1 cm cuvette placed in a UV- vis spectroscopy as a base line. Next the zinc oxide nanoparticle solution added to another 1 cm cuvette and placed in UV-vis spectroscopy. Almost all the visible spectrum radiations are transmitted by the ZnO nanoparticles. The ASC files of the measured spectra were collected by

computer which interfaced with the instrument. Zinc oxide nanoparticle have wide band energy and a high excitation binding energy compared to its bulk. This can be evaluated according to the Brus equation Eq (2.5)

The photoluminescence properties of ZnO nanoparticle were measured using (FLS 1000 Photoluminiscence spectrometer) at room temperature with Xe lamp as the excitation light source at resolution 1 nm. The samples were dissolved in DMSO and stirred until it dissolved and put in 1 cm quartz cuvette. The excitation and emission spectra were set at 325 nm and 360-600 nm respectively .

3.5. Application of ZnO nanoparticle to textile

To study the effect of ZnO nanoparticle as UV absorber the fabric treatment was done according to the following procedures. The fabric was purchesed from Local market Adama, Ethiopia. The samples(10 cm x 10 cm) with mass per unit surface of 52 g/ m^2 for cotton and 227 g/ m^2 for wool was prepared. Inorder to remove unnecessary particles from the fabric sample it was washed several times using distilled water and ethanol alcohol. The fiber was soaked in a solution of ZnO NPS, for 10 min under gentle magnetic stirring. The cloth was then squeezed to remove the excess dispersion and was dry in oven at 130 c^o for 15 min.

The effectiveness in shielding UV radiation was evaluated by measuring the UV Absorption, Transmission and reflection [49]. The UPF and percent of transmission were calculated using Eq (2.8) and Eq (2.9).

4. RESULT AND DISCUSSION

4.1. X-ray diffraction (X-RD) analysis

ZnO NPs with different grain sizes can be obtained from different precursors. Figure 4.1 shows the X-RD pattern of S1 and S2 powder synthesized by precipitation method revealing that hexagonal wurtzite pattern. Eleven characteristics peaks were appeared at 2Theta = 31.7545^{o}, 34.4055^{o}, 36.25^{o}, 47.5268^{o}, 56.5774^{o}, 62.843^{o}, 66.3516^{o}, 67.9391^{o}, 69.0819^{o} ,72.5599^{o} and 76.9528^{o} corresponding to (100), (002), (101), (102), (110), (103), (200), (112) , (201) (004) and (202) of crystal planes.The samples (101) peak is the most intense peak. The diffraction peak intencity increases with annealing temperature as shown in fig 4.1 below. This may indicate high annealing temperature provides sufficient energy and couses an increase in intencity. The average particle size of synthesized ZnO nanoparticle using S1 and S2 were calculated by Scherrer equation and the calculated average particle size were 26.334 and 28.74 nm respectively. This result indicates that as the annealing temperature increases the crystillite size increases as agglmeration of ZnO NPS increases with annealing temperature. The calculated average crystallite size were listed in Table 4.1 bellow.

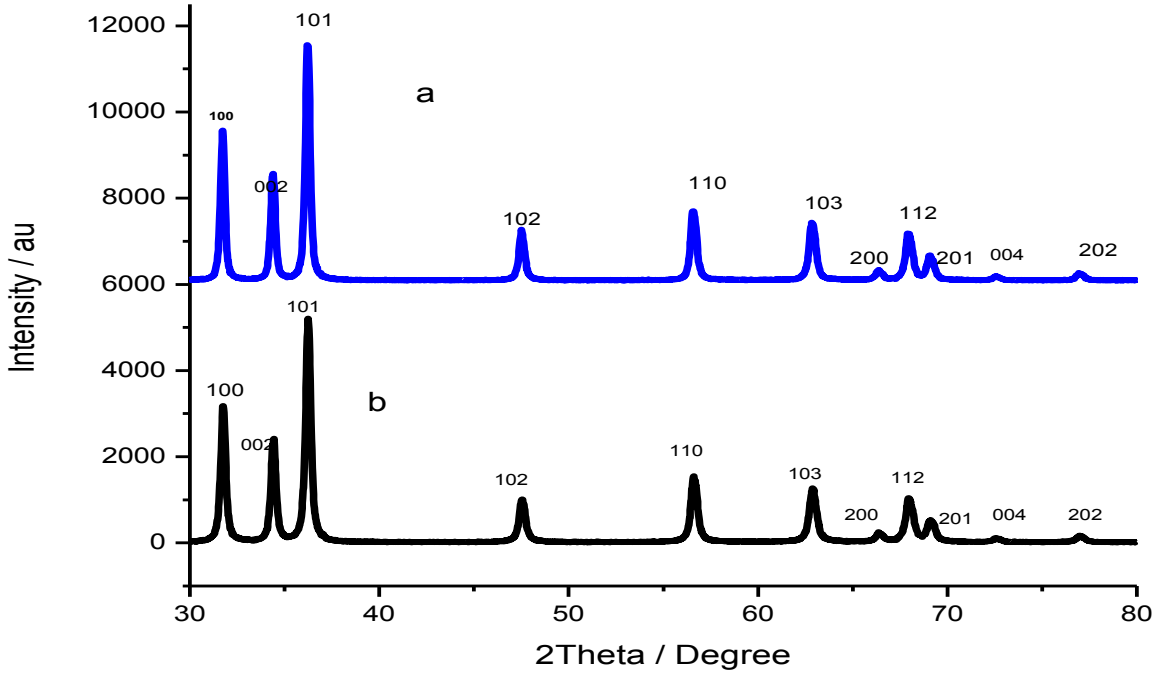


Figure 4.1: X-RD patterns of ZnO NPs synthesized from a) precursor S1 and b) S2

Table 4.1: Average crystal size of S1 and S2 ZnO NPS at different annealing temperature

Sample	Annealing Temperature (^{o}C)	Average particle size (nm)
S1	400^{o}C	26.334
S2	500^{o}C	28.74

Figure 4.2 shows the X-RD pattern of 'S3' and 'S4' powder synthesized by precipitation method revealing that hexagonal wurtzite pattern. Eleven characteristics peaks were appeared at 2Theta = 31.7545^{o},34.4055^{o},36.25^{o},47.5268^{o}, 56.5774^{o}, 62.843^{o}, 66.3516^{o}, 67.9391^{o}, 69.0819^{o}, 72.5599^{o} and 76.9528^{o} correspondig to (100), (002), (101), (102), (110), (103), (200), (112) , (201),(004) and (202) of crystal planes. The samples (101) peak is the most intense peak. The diffraction peak intencity increases with annealing temperature as shown in fig 4.2 below.

This may indicate high annealing temperature provides sufficient energy and couses an increase in intencity. The average particle size of synthesized ZnO nanoparticle using S3 and S4 were calculated by Scherrer equation and the calculated average particle size were 25.69 and 19.41 nm respectively. This result indicates that as the annealing temperature increases the crystillite size increases as agglmeration of ZnO NPS increases with annealing temperature. The calculated average crystallite size were listed in Table 4.2 bellow

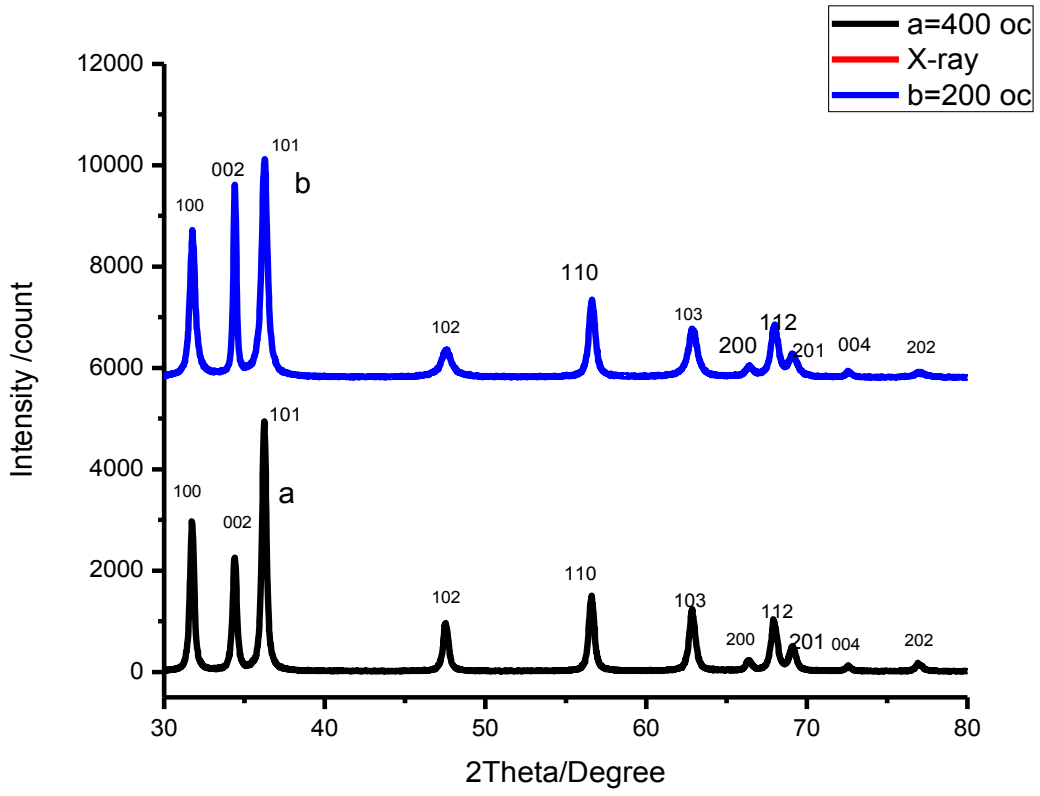


Figure 4.2: X-RD patterns of ZnO NPs synthesized from a) S3 and b) S4

Table 4.2: Average crystal size of S3 and S4 ZnO NPS at different annealing temperature.

Sample	Annealing Temperature (^{o}C)	Average particle size (nm)
S3	400	25.69
S4	200	19.41

The above two results of synthesized ZnO NPs from S1, S2, S3 and S4 shows that, the average particle size of ZnO NPs increased as the calcinating temperature increases. On the other hand, the Full-width at Half Maxima (FWHM) of ZnO NPs decreases as the annealing temperature increases.

All X-RD differaction peaks of synthesized ZnO NPS using S1, S2, S3, and S4 were shown slight agreement with wurtzite stucture of ZnO with lattice parameter of a = b =0.3249 nm and c = 0.5206 nm as reported in JCPDS card (no.36 - 1451). The lattice parameter 'a' and 'c' of ZnO NPS for S1, S2, S3 and S4 were calculated using Eq (2.2, 2.3 and 2.4) and slight change in littice parameter values were observed. The deviation may be coused due to slight change in the position of the peaks. The lattice parameter are temperature dependant, i.e. an increase in temperature leads to expansion of lattice parameter.

The littice parameter of wurtzite structure of ZnO NPS synthesized using S1, S2, S3 and S4 were calculated and listed in Table 4.3 bellow.

Table 4.3: Lattice parameter of ZnO NPs synthesized using S1,S2, S3, and S4 at diffrent annealing temperature.

Sample	Hkl	Lattice parameter			d_{hkl} (nm)
		a (nm)	c(nm)	c/a	
S1	101	0.2857	0.49493	1.732	0.2213
S2	101	0.2859	0.495	1.731	0.2214
S3	101	0.2859	0.497	1.738	0.2216
S4	101	0.286	0.49496	1.73	0.2214

4.2. SEM analysis

Figure 4.5 and Figure 4.4 shows the SEM images of the synthesized ZnO NPs using S1 and S2 at calcinating temperature of 400^{o}C and 500^{o}C. As it shown the morphology of the particles are uniform and well dispersed Spherical shape in both S1 and S2. The SEM image results also agreed with XRD results obtained, i.e. the crystal sizes in XRD with big size have also big shapes in SEM images. This indicates that ZnO NPs have successfully prepared using different zinc salt precursors within a nano range.

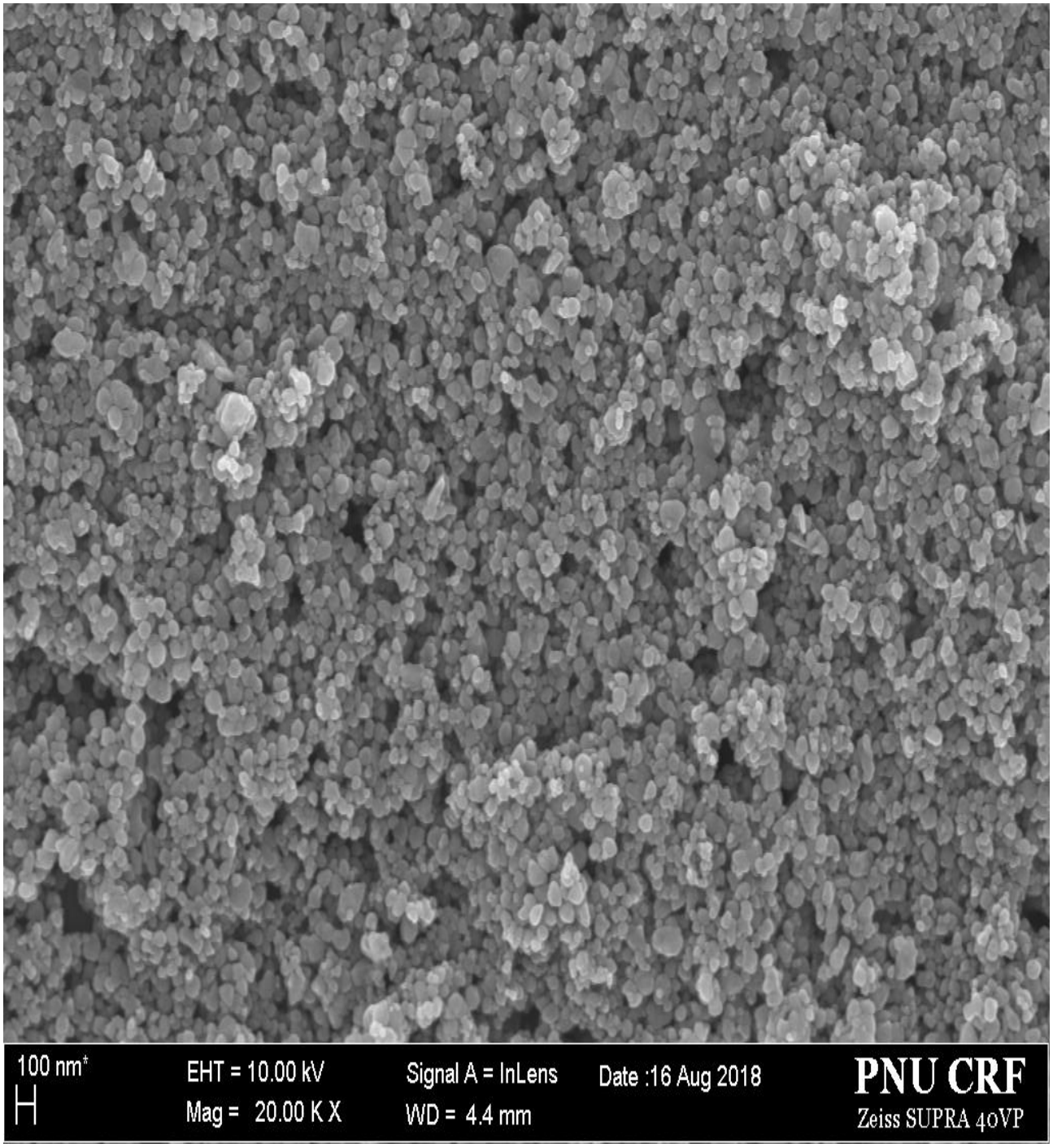


Figure 4.3: SEM images of ZnO NPs syntheszed using S1 at annealing temperature of 400^{o}C

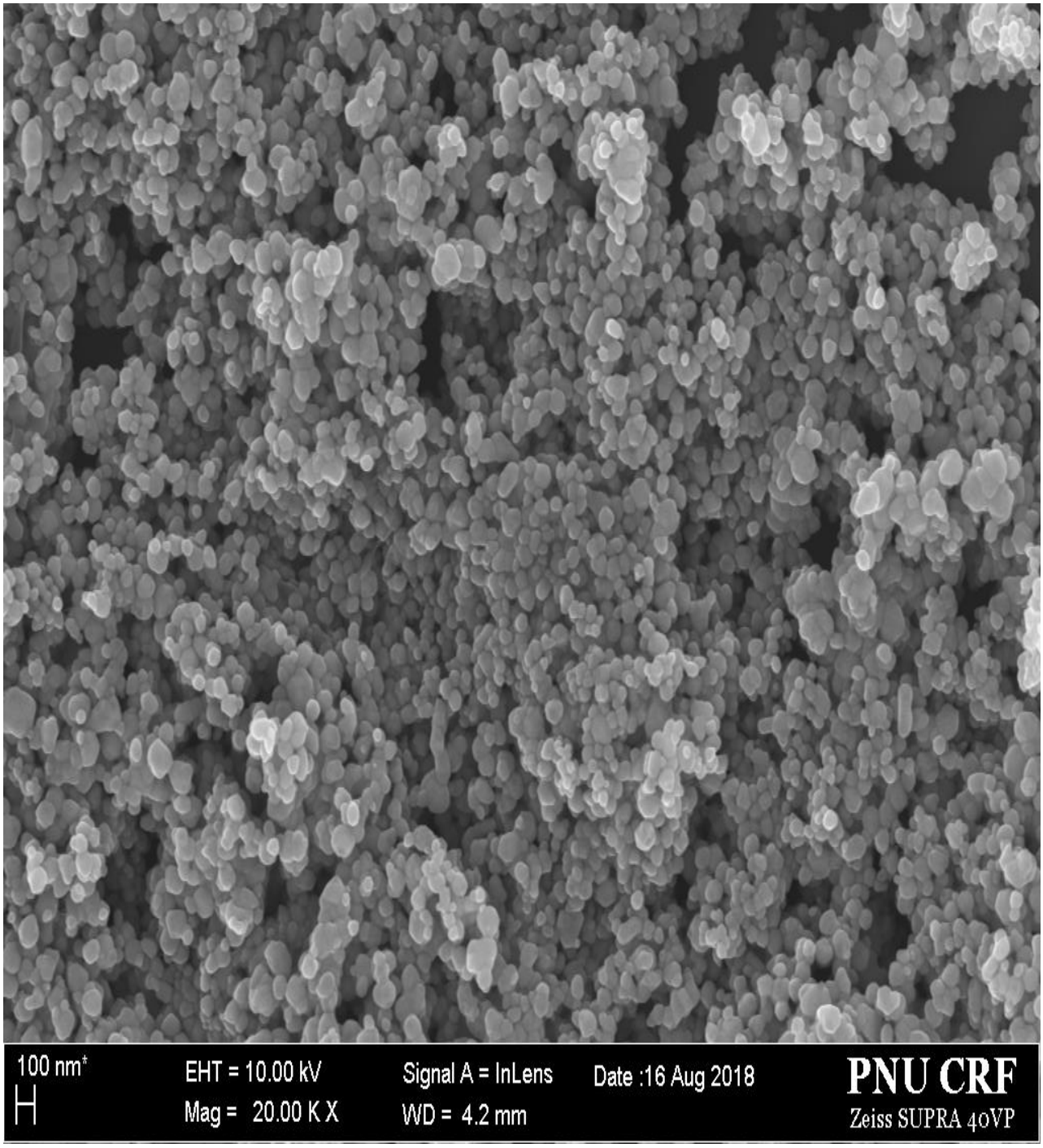
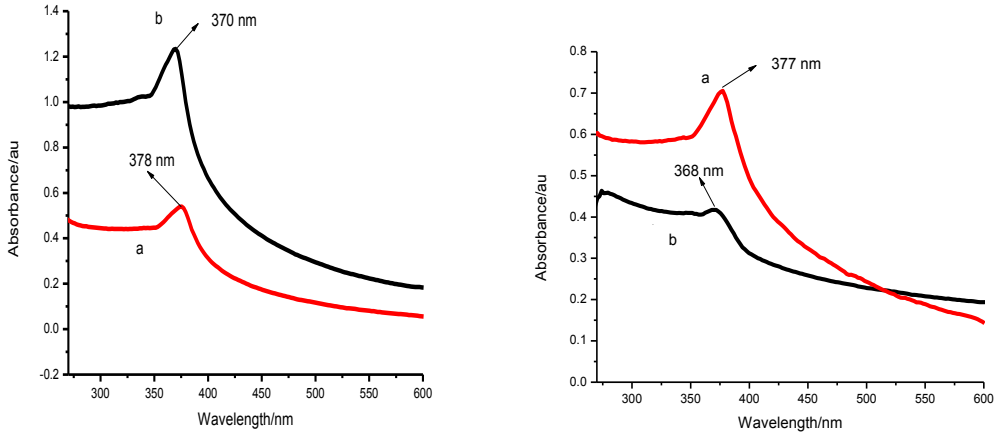


Figure 4.4: SEM images of ZnO NPs synthesized using S2 at annealing temperature of 500^{o}C.

4.2. Absorption spectrum analysis

Figure 4.5 (1,2) shows UV-vis absorption spectra of ZnO NPs synthesized using S2, S1, S3 and S4 at different annealing temperature. The absorption peak was observed at 378 , 370, 377 and 368 nm respectively. As the temperature of calcination increases, peak absorbance wavelength increases and shifted to red due to decreasing in quantum confinement of the particle.



1 2

Figure 4.5: Absorption spectrum of ZnO NPS Synthesised using 1) S2, S1 2) S3 ,S4 .

The band-gap energy of the bulk ZnO material was 3.2 eV (388 nm) at room temperature [41]. The band gap energy of ZnO NPs synthesised from S2, S1, S3 and S4 were calculated based on effective mass approximation using Brus Equation (Eq 2.5) and exhibits 3.437, 3.449, 3.454 and 3.517 eV respectively,because the band-gap of the ZnO nanoparticle was blue-shifted by the quantum confinement effect when compared with bulk ZnO. The peaks were due to electronic transition from valancy band to conducrtion band. The relationship between the band gap of nanoparticle *E* and particle radius *R* is given according to Brus equation given in Eq (2.5) above

and listed in Table 4.4. The band gap energy of ZnO NPs decreases with increasing temperature, due to particle size increases with Temperature.

Table 4.4: Relation between band gap Energy and crystal size at diffrent annealing temperature.

Sample	Calcinating temperature	Average particle size	Energy band gap
S2	500^{o}C	28.74 nm	3.437 eV
S1	400^{o}C	26.334 nm	3.449 eV
S3	400^{o}C	25.69 nm	3.454 eV
S4	200^{o}C	19.41 nm	3.517 eV

4.3. Fluorescence spectroscopy analysis

Figure 4.6: (3-4) shows the emission spectra of ZnO NPs synthesized from S1, S2, S3 and S4 precursor at different annealing temperature. Emission spectra of ZnO NPs consist two emission band: one in UV region (370 - 400 nm) and the other in visible regions (400 -700 nm). Thus in this case the samples S1, S2, S3 and S4 exhibit UV emission peak at 396, 396,399 and 392 nm respectively.The emission in UV region is caused from recombination between the electron in the conduction band and holes in the valance band. The other is the visible deep level emission with a peak range from 400 - 700 nm [42]. The emission in visible region is caused deu to transition from deep donor level to valance band due to oxygen vacancies and by transition from conduction band to deep accepter level due to impurities and defect states [43]. Then visible emission peaks at 449, 464 and 474 nm (blue region),is coused dou to singly ionized V_{zn}- .The green emission peaks at 519, 521 and 524 nm atributed to the radiativ transition from conduction band to the edge of the accepter level of O_{zn} caused by oxygen antisites [44].

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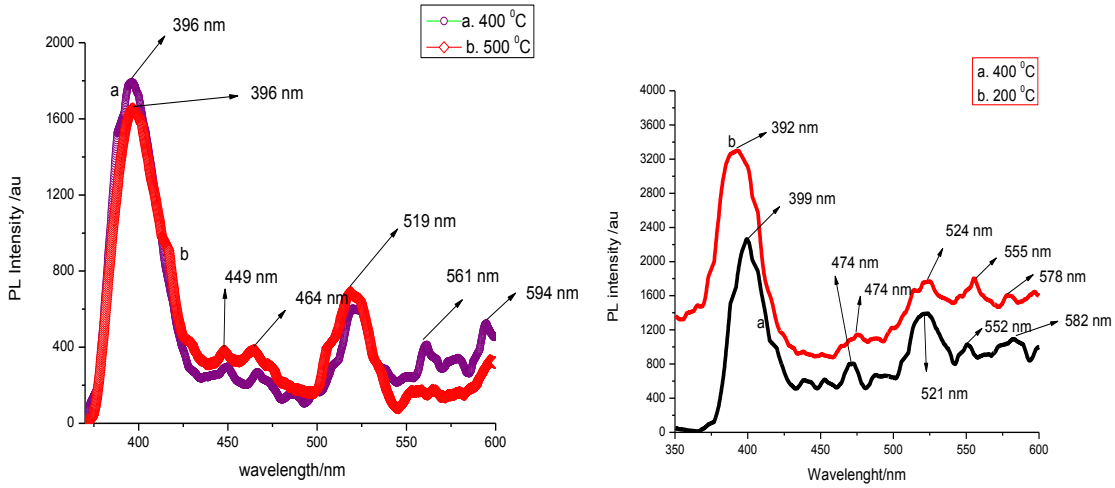

3 4

Figure 4.6: Emission spectra of ZnO NPs synthesized using 3a) S1, 3b) S2 and 4a) S3, 4b) S4 .

The peak emission is independent of the temperature ,because Fluorescence spectroscopy works at fixed (λex)and fixed (λemi). But emission intensity is temperature dependant. i.e. it increases as the temperature of calcination increases.This may indicate high temperature provide sufficient energy to crystallites and couse an increse in intensity.

4.4. Application of ZnO NPS on cotton and wool

The application of nano sized ZnO NPS on the cotton and wool fabric increases the absorption of UV light.The performance of zinc oxide nanoparticle as UV absorbers was efficiently transferred to the fabric materials through the application of ZnO nanoparticle on the surface of the cotton and wool blended fabrics, (see fig 4.7) the application of ZnO NPS on cotton and wool fabrics.

a) b) c)

d) e) f)

Figure 4.7: shows treated and untreated fabric sample.a) treated cotton with zinc sulphate b) Treated cotton with zinc nitrate c) un treated cotton d) Treated wool with zinc sulphate e) Treated wool with zinc nitrate f) untreated wool

Higher values of UV absorbance were obtained when ZnO NPS synthesized from zinc sulphate hepthydrate were appllied on a cotton. See fig 4.8 (5,6). Similar result were obtained for the treated wool sample as shown in fig 4.7 (7,8). The application of nano sized ZnO NPS on a wool fabrics increases UV light absorbance. The result implys that the effectiveness in shelding UV

radiation is due to the UV absorbance capacity of ZnO NPS in the fabrics surface. The percent of tranismitance confirm these conclusion as the ZnO NPS treated cotton and wool sample has low percent of tranismitance while un treated fabrics has high percent of tranismitance. The value of ultravioletprotection fuctor (UPF) and percent of tranismitance (%T) were calculated accordingto Eq (2.8) and Eq (2.9) respectively and listed in table 4.5.

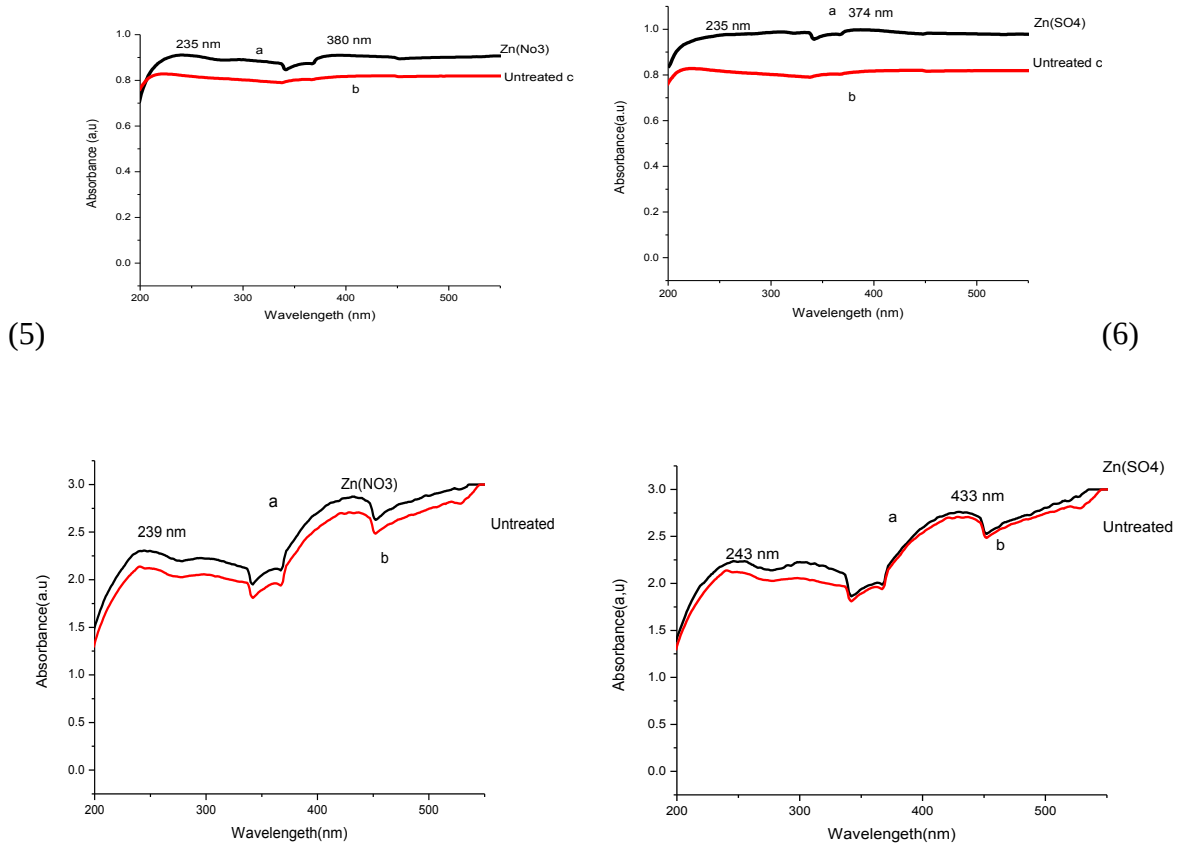

Figure 4.8: Absorption spectra of treated and un treated fabric samples: (5a) treated cotton by ZnO NPs synthesized using S1 and (b) untreated cotton, (6a) treated cotton by ZnO NPs synthesized using S3 and untreated cotton (b), (7a) treated wool by ZnO NPs synthesized using S1 and (b) untreated wool, (8a) treated wool by ZnO NPs synthesized using S3 and (b) untreated wool.

Table 4.5: UPF and Percent of Transmission for S1 and S3 samples for UV A (315-400 nm) and UV B (280- 315 nm).

Sample	UPF		UV transmission (%)	
	UV 'A'	UV 'B'	UV'A'	UV'B'
Cotton				
Untreated	0.064	0.0629	16.29	16.19
S3 treated	0.0935	0.097	10.5	10.66
S1 treated	0.077	0.085	13.25	13.3
WOOL				
Untreated	1.378	1.09	0.967	0.928
S3 treated	1.4	1.66	0.772	0.66
S1 treated	1.81	1.667	0.63	0.617

The data reflects the protection against UV radiation provided by the ZnO nanoparticle treated fabrics. Although the calculated UPF are significantly lower than the standard value required the result confirm the protection againest UV radiation produced by the treatment with nano sized ZnO on the fabrics. Such result can be exploited for the protection of the body against solar radiation .

5. CONCLUSION

ZnO NPs were synthesized via precipitation method by using zinc sulphate heptahydrate and zinc nitrate hexhydrate as a precursor with sodium hydroxide. The synthesized ZnO nano particles were characterized by using different spectroscopic techniques such as X-RD, UV-vis spectroscopy, Fluorescence spectroscopy and Scanning Electron Microscopy (SEM) .The X-RD analysis revealed that the synthesized nanoparticle were in nanometer range with average particle size about 19.41-28.74 nm using Scherrer's formula. The absorbance peak and emission peak of ZnO nanoparticle synthesised from S1, S2, S3 and S4 were investigated from UV-vis spectrosco py and Fluorescene spectroscopy and observed at 370 nm, 378 nm, 377 nm, 368 nm and at 396 nm, 396 nm, 399 nm and 392 nm respectively. The effect of optical properties of ZnO nanoparticles was investigated using UV-vis spectroscopy .The morphology of ZnO NPs characterized by SEM shows spherical shape and the SEM image results also agreed with XRD results obtained, i.e. the crystal sizes in XRD with big size have also big shapes in SEM images..

The strange performance of ZnO nanoparticles as UV-absorbers can be efficiently transferred to fabric materials through the application of ZnO nanoparticles on the surface of wool and cotton fabrics. The UV tests indicate an increment of UV absorbing activity of ZnO NPs treated fabrics. The results imply that the effectiveness in shielding UV radiation is due to the UV absorption capacity of ZnO nanoparticles on the fabrics surface. The calculated value of ultravioletprotection fuctor (UPF) and percent of tranismitance (%T) were reflects the protection against UV radiation provided by the ZnO nanoparticle treated fabrics. Such result can be exploited for the protection of the body against solar radiation and for other technological applications.

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