PROJECT REPORT

ON

PHOTOCATALYTIC ACTIVITY OF ZnO AND Mn DOPED ZnO NANOPARTICLES

SUBMITTED BY

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REGISTER NO: AM22PHY012

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DEPARTMENT OF PHYSICS AND CENTRE FOR RESEARCH

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I , hereby declare that this project entitled "**PHOTOCATALYTIC ACTIVITY OF ZnO AND Mn DOPED ZnO NANOPARTICLES**" is an original work done by me under the guidance of Dr. Susan Mathew, Assistant Professor, Department of Physics and Centre for Research, St. Teresa's College ,Ernakulam in partial fulfilment for the award of the Degree of Masters in Physics. I further declare that the project entitled here is not partially or wholly submitted for any other purpose and the data included in this project is gathered from different sources and is true to the best of my knowledge.

Place : Ernakulam

Date : 19/04/24

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PHOTOCATALYTIC ACTIVITY OF ZnO AND Mn DOPED ZnO NANOPARTICLES

ABSTRACT

In this project, we successfully synthesized zinc oxide and manganese doped zinc oxide nanoparticles by co-precipitation method. The characterization of nanoparticles were studied by X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), Energy Dispersive X-ray (EDX) and UV - Visible spectroscopy. The crystal size of the nanoparticles were analyzed by X-Ray diffraction (XRD). The particles were found to be hexagonal structure. EDX confirms the presence of elements Zinc, Oxygen and manganese in doped sample. The photocatalysis activity of both ZnO and Mn- doped ZnO were studied using methyl orange dye in the presence of sunlight. The Mn- doped ZnO shows less photocatalytic degradation under sunlight while compared with pure ZnO. The decrease in the photocatalysis activity of dye is due to the recombination of photoinduced electron- hole pair which suppress the oxidative stress that result from high toxic reactive oxygen species (ROS).

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CHAPTER 1

INTRODUCTION

1.1 NANOTECHNOLOGY AND NANOSCIENCE

Nanotechnology is one of the promising technology in this era. It is the branch of science which deals with the synthesis, usage and control of structures and devices by manipulatingatoms and molecules at nanoscale in the range of 0.1 to 100nm. The term 'nano' derived from theGreek word 'nanos' meaning 'dwarf'. Richard Feynman, an American physicist and noble prize winner introduce the concept of nanotechnology in his lecture "There's plenty of room at the bottom" at Caltech in 1959. Later, Norio Taniguchi coined the term 'nanotechnology' in 1974 . Nanotechnology encompasses the understanding of fundamental physics, chemistry, biology and technology of nanometer scale objects. Nanotechnology emerged as a revolutionary area with numerous applications in all fields of science.

Nanoscience is the manipulation of molecules in the scale of nanometer and nanotechnology uses it in practical applications like devices. Nanoscience plays an important role in unveiling the potential of the nanoworld, where the quantum effects dominate. It involve in understanding the fundamental principles that govern the behavior of materials at nanoscale. Nanoscience is also an interdisciplinary science which means almost all fields of science are getting involved.

Due to quantum effects and ability to control surface area, nanomaterials shows rare properties that are not exhibited by bulky materials. By utilizing these properties of nanomaterials, innovative materials and devices can be developed with the help of nanotechnology

1.2 CLASSIFICATION OF NANOMATERIALS

When the size or dimension of a material is reduced into a nano range that is below 100 nm, dramatic changes in properties can occur . The classification of nanomaterials can be done according to the dimension they possess. The most properties of the nanomaterials which are helpful for the application of absorption and diffusion are dependent on this dimension parameter. Thus based on dimensions, nanomaterials are classified into four.

- Zero dimensional : Nanomaterials with all the three dimensions are in the nanoscale range. The resulting structure is referred as quantum dot. It includes structures such as nano spheres and nano clusters.
- One dimensional : If one dimension of material is reduced to the nano range while other two dimensions remain large then a structure known as quantum well is obtained. This leads to needle shaped nano materials. It includes structures such as nano tube and nano rod.
- Two dimensional : Here the two dimensions of the material is reduced to nano range and the one dimension remains large. The resulting structure is referred as quantum wire. It includes nano film, nano layer and nano coating within the nanometer thickness. This mostly exhibits plate-like shape.
- Three dimensional : Nanomaterials having three arbitrary dimensions beyond the nano range that is above 100 nm. They are not confined in the nanoscale range in any dimension. Bulk powders are example of 3-D nanomaterials.

1.3 PROPERTIES OF NANO MATERIALS

The properties of nanomaterials include mechanical, electrical, thermal and catalytic properties.

- Mechanical Properties : Mechanical properties are the mechanical characteristics of materials under different environments and various external loads. Different materials have different mechanical properties. These mechanical properties of nanomaterials are due to large number of surface atoms and interfaces which leads to an increase in the density of defects. Mechanical properties of nanomaterials include increased strength, ductility, toughness and hardness and decreased elasticity.
- Electrical Properties: The electrical properties of nanomaterials depends on dimensions like diameter and area of cross section. Nanomaterials have high density of grain boundaries which reduces their conductivity.
- Thermal Properties : Due to high density of defects, nanomaterials have high thermal expansion coefficient. The use of nanofluids will enhance the thermal transport.

- Optical Properties: Nanomaterials have distinctive optical characteristics such as increased scattering, absorption and luminescence. By changing the optical properties, size and shape of nanoparticles can be altered. Applications based on optical properties include optical detector, sensors, lasers, photocatalysis etc.
- Catalytic Properties: Surface area affects catalytic activity. Since nanomaterials have large number of surface atoms, which will increase the surface area, leading to an increase in catalytic activity.

1.4 SYNTHESIS METHODS

Nanomaterials are synthesized by two different approaches namely top-down and bottom-up. In top-down approach, metal nanoparticles are synthesized by the decomposition of bulk metal using mechanical force or vaporization. In bottom-up approach, the preparation starts from reduction of metal ion to metal atom followed by aggregation result in the production of nanoparticle.

Top down methods :

Top down method is known as a destructive method. Lithography, laser ablation, sputtering etc. are top down methods. The main problem of this method is the imperfection of surface structure.

- In ball milling or mechanical grinding, the size reduction is achieved through the impact caused by the ball drop from top of chamber where source is placed.
- Nanolithography have the ability to produce a cluster with desired shape and size.
- In sputtering the atoms are ejected from surface of material and it is collided with energetic particles.
- In laser ablation, the nanoparticles are synthesized by striking a powerful laser beam on the target.

Bottom-up methods :

Bottom up approach is also known as constructive method. CVD, solgel, pyrolysis etc. are bottom up approaches.

- In sol-gel method, condensation and hydrolysis are involved in the preparation of nanoparticles. The advantage of this method is the high purity of the nanoparticle and achieving a uniform nanostructure.
- In Chemical Vapor Deposition (CVD), a thin film of gaseous reactant is deposited on a substrate. By heating the substrate a chemical reaction occurs and this leads to deposition of thin film which can be recovered and reused.
- Hydrothermal and solvothermal methods are used in the production of nanowires, nanorods and nanosheets.
- Pyrolysis is used in the large scale production of nanomaterials. It is simple and cost-effective.

1.5 ADVANTAGES OF NANOTECHNOLOGY

Through nanotechnology the intrinsic properties of materials can be changed and it lead to obtain many applications. Some advantages of nanotechnology include:

- Nanotechnology enables new ways to obtain and store energy. It helps in replacing fossil fuels by renewable energy by making renewable energy sources like solar cells more effective and cheaper.
- By the use of nanochips, it is possible to built very precise circuits at an atomic level
- It helps in the reduction of pollution. Nano filters are used in removing wide range of pollutants.
- It helps in reducing the toxicity of drugs.
- In medical field nanotechnology is a boon. Nanoparticles are used in drug delivery due to their small size and large surface area.
- The materials which are created from nanotechnology more precise, lighter, stronger and cheaper.

1.6 DISADVANTAGES OF NANOTECHNOLOGY

Nanotechnology have many demerits too. Some of this include the following:

- Nanoparticles cause damage to human health as well as to the environment. For e.g., carbon nanoparticles cause infection to lungs and it have adverse effect on environment.

- Nanotechnology have the capability of producing dangerous weapons and drugs in large scale. Atomic weapons are very destructive.
- By increasing the development in field of nanotechnology, there is a high possibility of losing jobs in farming and manufacturing industries.
- Nanotechnology is very expensive and it is difficult to manufacture the nanoparticles since it is required to maintain certain conditions for its preparation.

1.7 APPLICATIONS

Nanotechnology is a promising field in this era. Nowadays, nanotechnology has achieved vast importance in almost all fields from medicine to robotics. Nanotechnology has opened up possibilities in many applications and it increased the use of materials in nanometer scale. Application of nanotechnology span diverse sectors from medicine to energy and material science. Nanotechnology, with its ability to manipulate matter at nanometer scale has revolutionized many industries and enabled the development of innovative application with profound impacts. This field holds the promise of shaping a future where materials are engineered at nanoscale, opening new frontiers in science and technology.

Many applications in this field replaces or create evolutionary development on existing technologies. We list some of the applications of nanotechnology below:

- Energy resources

  Nanotechnology is used in the conversion and storage of energy and it will enhance the renewable energy sources. By making production of fuels from low grade raw materials, which are cheaper, nanotechnology can address the shortage of fuel cell by increasing the mileage of engines and making the production of fuels from normal raw materials. Nanostructured materials like quantum dots and nanowires are used in designing solar cells thus helps in reducing the cost of such renewable energy sources. Nano technology helps in increasing the efficiency of solar cells.
- Batteries

  Nano engineered materials can improve the charging time of batteries and this will help in increasing the battery life. Nano materials have high surface to volume ratio so it will increase the battery capacity and power density. Nano technology plays a crucial role in miniaturizing batteries for use in small scale devices.

- Sensors

  Nano materials are used making miniaturized sensors. This will enable the development of portable sensors which can even be used in biomedical applications. The large surface to volume ratio enable an increased interaction between sensing element and target analyte.

- Water treatment

  Nanoparticles are used to purify industrial water pollutants in ground water through chemical reactions that are harmless and at lower cost.

- Food industry

  Applications of nanotechnology in food industry includes manufacturing, packaging and safety measures. Due to its high ability to resist absorption of moisture, light and oxygen nanomaterials are used in packaging.

- Catalysis

  Nanomaterials are a good class of catalysts. Nanoparticles which are used as catalyst have the ability to achieve perfect selectivity and desirable activity.

1.8 ZINC OXIDE NANOPARTICLES

Zinc and oxygen are the members of II and VI th group respectively so zinc oxide is a II-VI semiconductor in the field of material science. Zinc oxide is an inorganic metal oxide nanoparticle having the formula ZnO. The distinctive features of ZnO nanoparticles lead researchers to use many easy and cost-effective techniques to construct these nanoparticles for various applications. Zincate is the natural form of zinc oxide which is a slight yellowish color. Zinc oxide is a whitish powder which is insoluble in water. They are less than 100 nm in diameter.

Zinc oxide is a semiconductor with a wide band gap energy of 3.3eV and large binding excitation energy of 60 MeV. This large excitonic energy make ZnO an efficient excitonic emitter. The crystalline form of zinc oxide is wurtzite, which is the thermodynamically stable form, have hexagonal unit cell with two lattice parameter a and c. ZnO can absorb UV light with a wavelength less than or equal to 385nm. The unique and immense potential of zinc oxide nanoparticles make them available for the fabrication of nanodevices. The high electrochemical stability, biocompatibility, non-toxicity ,good optical transparency in visible region and radiation resistance are some of the advantages of zinc oxide nanoparticles

The properties of ZnO depends on the way by which it is synthesized. Both physical and chemical methods can be used in the synthesis of these nanoparticles. Chemical method includes sol-gel method, chemical vapor deposition techniques, hydrothermal methods etc. while physical methods include vapor condensation method, spray pyrolysis etc. Biological methods like green synthesis methods are also utilized in the production of zinc oxide nanoparticles.

Zinc oxide nanoparticles are an alternative to TiO_2 in photocatalytic reaction due to its thermal and chemical stability, opto- electronic properties and low cost. ZnO nanoparticles have large surface area. Because of their ability to absorb UV light, they can be used in the manufacture of sunscreen. ZnO nanoparticles are widely manufactured to use in many products like cement, ceramics, cosmetics, glass, oinment, lubricants etc. ZnO nanostructures have application in field effect transistors, solar cells, piezo-electronic devices and gas sensors.

1.9 MANGANESE DOPED ZINC OXIDE

Doping ZnO with certain dopants will help to achieve certain desired properties like ferromagnetism, wide or narrow bandgap etc. The doping element bring on a lattice defect and it will changes the carrier concentration in ZnO. On doping manganese to the zinc oxide matrix the band gap energy of the host material is changed from 3.3 to 3.7eV. Doping Mn with zinc can change the optical and chemical characteristics of the material as well. Since Mn doped ZnO showed ferromagnetism at room temperature, it is been used in spintronic applications. It behave as a dilute magnetic semiconductor it is been used in solar cells, gas sensors and piezo-electric transducers.

As compared to other transition metals which are used to dope with ZnO, manganese have the special advantage that the relative ionic radii between Mn^{2+} and Zn^{2+} is small and is having a large magnetic moment. The half-filled 3d orbitals of Mn will be incorporated into the matrix of ZnO. Mn doped ZnO can be synthesized using chemical vapor deposition technique, sol-gel method, atomic layer deposition as well as by pulsed laser deposition.

1.10 SHIELDING EFFECT

ZnO is having many advantages because of its high band gap energy, non-risky nature, high stability etc. making them transparent in the visible region. So they were used for blocking the UV but the problem of them using in sunscreen is that they generate ROS in presence of light due to

their photocatalytic activity. These ROS or Reactive Oxygen Species are formed from the radicals and they are harmful. So in order to reduce this effect ZnO is doped with metal ions.

The UV radiation from the sun have harmful effect to living beings and cause various damage to organic substances. Even the low energy UV rays cause adverse effects. Under UV irradiation electrons will move to higher energy states and will induce chain scission and cross linking in organic molecules. The free radicals also induce the same and lead to the formation of oxy and peroxy radicals on reacting with oxygen. These free radicals lead to the degradation of organic dyes.

Since ozone layer is depleting there is a large possibility of the harmful UVA and UVB to reach the earth which will in turn cause damage in paints, plastics, textiles etc. The UV induced degradation of organic materials including dyes and textiles have notable environmental problems. So it is necessary to develop UV shielding agents.

The characteristic photocatalytic properties of ZnO posses a major obstacle for using them in UV protection applications. On doping with Mn the photocatalytic activity of ZnO is reduced. And low levels of doping will help in the suppression of photocatalytic activity.

The deleterious effects of UV radiation are having a remarkable impact in our environment and life. In fact, along with the UV rays from the sun light, other devices such as LED s also have a contribution of UV emission. So it is necessary to develop UV shielding agents to protect humans as well asfabrics, plastic roofs etc. Among all the other nanoparticles ZnO as UV blocking had a major rolebut due to its detrimental photocatalytic effect UV shielding products based on ZnO is limited. SoZnO is expected to be used as a safe UV- screening agent by reducing photocatalysis in many applications.

1.11 CHARACTERIZATION METHODS

In this work, different characterization techniques are used to analyze the prepared samples. The analysis of components, the particle size etc. are carried out using UV-absorption spectrum, X-RD, EDAX and SEM.

1.11.1 UV-VISIBLE SPECTRUM

Spectroscopy look over the interaction of electromagnetic field with matter. UV-Visible is an important analysis technique which gives the value of maximum absorption and maximum wavelength absorbed. The principle of this spectroscopy is based on the absorption of uv or visible

light by the chemical compound which result in an interaction between matter and light leading to the production of spectrum. It is simple, accurate and a cost effective technique.

1.11.1.a) DIFFUSE REFLECTANCE SPECTROSCOPY(DRS)

It is a subset of absorption spectroscopy which is usually used in the uv region, visible region and NIR region. The advantage of this technique over UV-Visible spectroscopy is that it can be used effectively in the case of solid samples. In DRS, light from UV, visible or IR is allowed to fall on the sample and the intensity of the reflected light is measured for a particular range of wavelength. The spectrum is obtained by collecting and analyzing the surface reflected electromagnetic radiation as a function of wavelength. It is an excellent illustrating technique powdered crystalline materials in the middle of IR and NIR regions. In this technique usually the sample is mixed with a nonabsorbing matrix. By diluting, the incident beam will deeply penetrate into the sample and thus increases the contribution scattered part in the spectrum. This technique can also used in the case of liquid samples. The advantage of this technique is that it helps to analyze many solid samples easier, faster and with more accurate efficiency.

1.11.2 X-RAY DIFFRACTION

X-Ray Diffraction (XRD) is a method used to determine the molecular structure of crystal by diffracting a beam of X-Rays in every direction. This method will give the information like crystal structure, physical properties and chemical composition. 0.01-10nm is the wavelength range for X-Rays which is comparable with the lattice spacing. When an incident beam of X-Rays falls on a target atom, X-Ray photon will scatter in all directions. These scattered rays will constructively or destructively interfere to form a diffraction pattern. XRD is based on Bragg's law.

Bragg's Law :

This law explains the condition for the diffraction in Xray scattering. When an Xray is bombarded to a crystal surface at some certain angle and a fixed wavelength, then intense X rays are produced when the reflected rays constructively interfere. The path difference must be equal to an integer multiple of the wavelength used in order for the constructive interference of the waves.

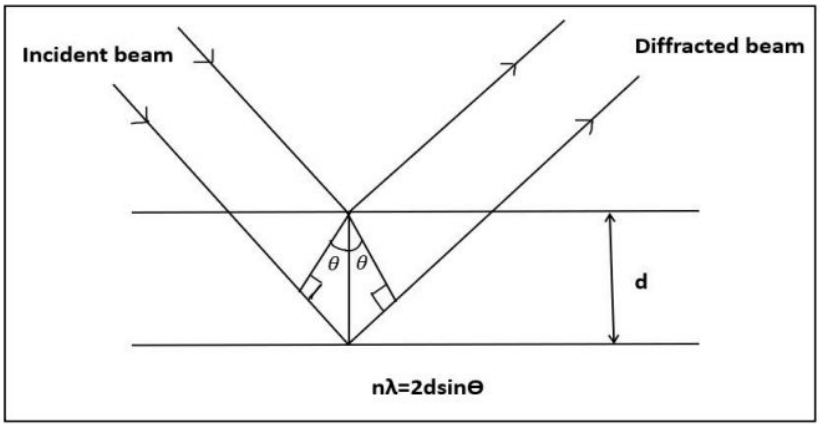

Figure 1.1 Bragg's law of diffraction

Bragg's equation (figure 1.1) is given by,

$$n\lambda = 2d\sin\Theta$$

where λ is the wavelength of light used, Θ is the incident angle, d is the distance between the lattice planes , n is a positive integer.

1.11.3 ENERGY DISPERSIVE X-RAY ANALYSIS (EDAX)

Energy Dispersive X-Ray Analysis (EDAX or EDX) is a technique in which the analysis is done by moving the electron beam across the sample to form the image of elements in the sample. It is similar to SEM technique. This technique helps to identify which all elements are there on a given sample. The chemical composition of the materials are analyzed using this technique. In this method, an electron beam is allowed to fall on the surface of the sample as a result the material will emit X ray, whose energy will depend on the material under consideration. The electron beam which strike on the sample is having an energy of 10-20keV.

1.11.4 SCANNING ELECTRON MICROSCOPY

Scanning Electron Microscopy or SEM is a technique used for the visualization and characterization of the surface of particles by using an electron beam. SEM is integrated with energy dispersive spectrometer. It is a rapid and nondestructive technique to scan the surface. An electron gun, located on the top of the column (figure 1.2), produces a beam of electron. These

electrons are having a large kinetic energy which is focused on the surface of the sample. Due to the interaction of these electrons on the surface signals will be produced. These combination of signals include secondary electrons, back scattered electrons and diffracted backscattered electrons. The secondary and backscattered electrons will produce the image of the sample. Using these techniques will help to get a variety of information like the chemical composition, orientation of sample crystal etc.

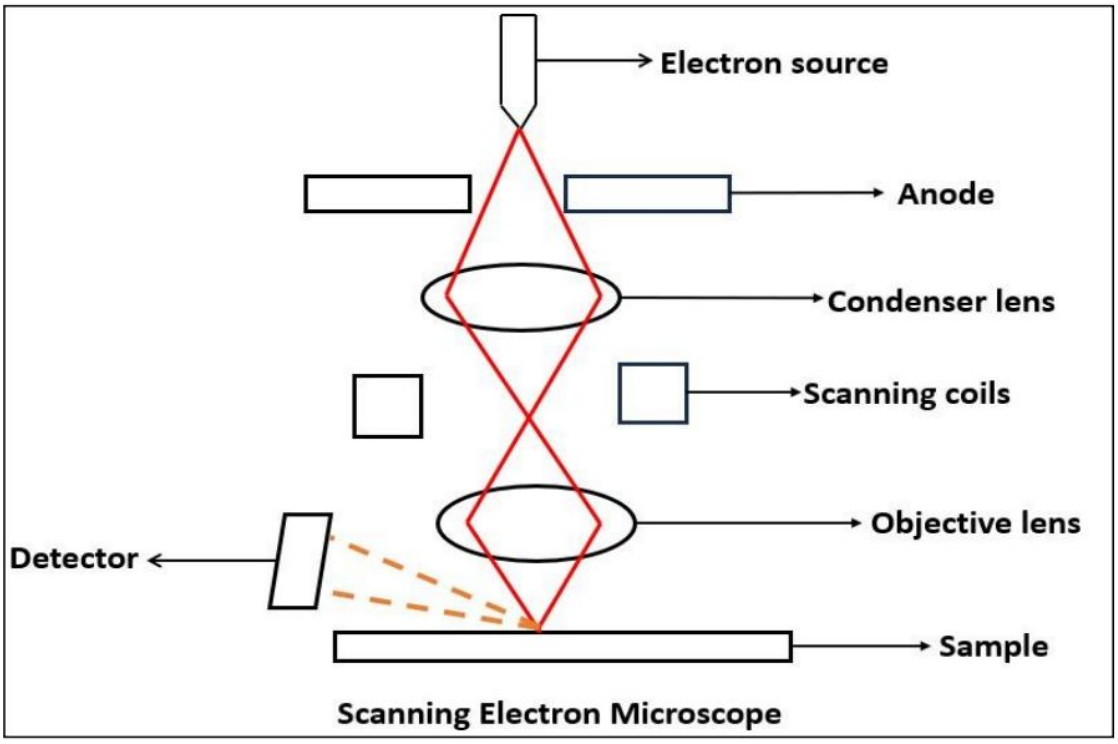

Figure 1.2: SEM

1.12 PHOTOCATALYSIS

Photocatalysis is a chemical reaction taking place in the presence of light. It comes from a Greek word which is having two parts- photo meaning light and catalysis meaning decompose. Accelerated photo-reaction in the presence of a catalyst is called photocatalysis. A photocatalyst is a semiconductor having valence band and conduction band separated by a band gap energy. When a photon of energy greater than or equal to this band gap energy incident on the semiconductor nanoparticle, the electrons in the valence band will move towards the conduction band and produces an electron hole pair(figure 1.3). At this stage there are two possibilities. First

possibility is that the charge carrier again recombine and produce energy in the form of heat. During this case, no reaction will takes place. The second possibility is that the charge carrier then react with electron acceptor or donor on the catalyst surface. At this time electron together with oxygen form superoxide radicals. A reaction between the electron-hole and water lead to the production of hydroxyl radicals, which are highly reactive and play major role in photo-oxidation reaction.

Photocatalytic reactions are of two types namely homogeneous and heterogeneous.

- Homogeneous photocatalysis : when both the reactant and the semiconductor are in same phase, then it is called homogeneous photocatalysis. It is applicable in chemical and pharmaceutical industries. The recovery of the catalyst from the medium is difficult for this method.
- Heterogeneous photocatalysis : when both the reactant and the semiconductor are in different phases, then it is called heterogeneous photocatalysis.

  It is an advanced oxidation process used in removal of pollutants from waste water and in the degradation of dye. In heterogeneous photocatalysis, simultaneous production of electron and hole lead to their recombination on the surface within nanoseconds. On the surface, they react with donor or acceptor species and initiating anodic and cathodic redox reactions. The energy level at the top of valence band and bottom of conduction band respectively determines the oxidizing ability of photoholes and reduction potential of photoelectrons.

  An ideal photocatalyst should have suitable bandgap, high efficiency, stable and available at low cost. The factors affecting photocatalysis include :

  - Effect of catalyst amount : In heterogeneous photocatalysis, as increasing the amount of catalyst will increase the photodegradation of dye and it is due to an increase in the number of active sites on the surface. The optimum value of catalyst concentration depend on the type and concentration of pollutant and also on the generation of free radicals.
  - Effect of pH : The surface charge of photocatalyst is determined by the pH. On varying the pH of solution, the potential of the catalytic reaction got shifted.
  - Effect of dye concentration : The percentage of degradation by photocatalysis will depend on the concentration of dye. If the dye concentration increases, more organic substrates will be

adsorbed by the surface and at the same time less number of photons are available to reach the surface thus resulting in a decrease in the percentage of degradation.

- Effect of dopants : On doping, the photocatalytic reaction can be increased or decreased based on the synthesis mechanism.
- Effect of surface area : As the surface area of the catalyst increases, photodegradation also increases due to an increase in the number of active sites.

  ZnO is a binary heterogeneous photocatalyst. ZnO have a large potential for photocatalysis. When Mn is doped with ZnO then recombination of electron hole pair takes place.

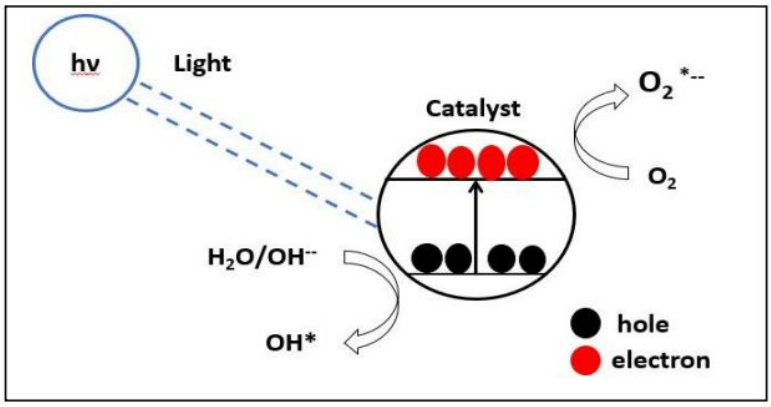

Figure 1.3: Photocatalysis

Photocatalysts are used in air purification, waste water treatment, dye sensitized solar cell, light filter, crude oil decomposition, conservation and energy storage. Photocatalysis is an alternative method for the degradation of dyes. Semiconductor photocatalysis have a huge potential for energy storage as well as for the degradation of organic compounds.

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CHAPTER-2

MATERIAL SYNTHESIS AND CHARACTERISATION

2.1 SYNTHESIS METHODS

Nanoparticles can be synthesized in two approaches via top-down and bottom-up. In top-down approach, nanoparticles are synthesized by the decomposition of bulk metal through any mechanical forces while in bottom-up approach, the preparation starts from reduction of metal ion to metal atom followed by aggregation result in the production of nanoparticle. Top-downapproach include mechanical milling, electrospinning, lithography, sputtering, arc dischargemethod and laser ablation.

Bottom-up method include chemical vapor deposition, solvothermal method, hydrothermal method, co-precipitation, sol-gel method, soft and hard templating method and reverse micelle method. The fabrication cost and the wastage through this method is less. Through this technique ultra fine nanoparticles and nanotubes can be synthesized.

2.2 COPRECIPITATION METHOD

Coprecipitation method is a bottom-up approach or for the synthesis of nanoparticle. It is used to prepare both inorganic and metal nanoparticles. This method involves simultaneous occurrence of nucleation, growth, coarsening and agglomeration process. In this method, a precipitate is formed at room temperature by adding a base usually in the form of oxalates, carbonates, chlorides and hydroxides, and that lead to the production of nanoparticles. The precipitate formed contain impurities along with it, which is washed and filtered to remove the impurities. As the particles are formed under high saturation, the products are insoluble. The time for mixing the precursors is long, as a result it took longer time for nucleation which leads to a wide distribution of crystalline size.

Through coprecipitation, heterogeneous catalyst with two or three components can be synthesized. The difference in solubility between the components in the precursor and the precipitation kinetics will determine the homogeneity of coprecipitation. If precipitate of one component is soluble than the other then there is a possibility of the occurrence of sequential precipitation and it again lead to the formation of concentration gradients in the final product.

The advantages of this method include the size distribution is narrow, solvent is environment friendly, having a high product yield, simple and low cost. This method do not require any hazardous solvents for its preparation.

2.3 COPRECIPITATION METHOD FOR THE SYNTHESIS OF ZnO NANOPARTICLES

The precursors required for the synthesis of ZnO nanoparticles are zinc acetate, sodium carbonate and distilled water. Zinc acetate provide both zinc and oxygen. Initially 13.5 g of zinc acetate ($Zn(CH_3COO)_2 2H_2O$) and 6.5g of sodium carbonate (Na_2CO_3) were separately dissolved in 50ml distilled water. Then Na_2CO_3 solution was added dropwise to the $Zn(CH_3COO)_2 2H_2O$ solution at a constant temperature in magnetic stirrer for 30 minute. As a result of this Zinc carbonate is formed which is given by the chemical reaction below:

$$Zn(CH_3COO)_2 2H_2O + Na_2CO_3 \rightarrow ZnCO_3 + 2Na(CH_3COO)$$

On adding the Na_2CO_3 solution a white precipitate is formed. This precipitate is needed to separate from the supernatant solution by centrifugation. Then washed this with deionized water in order to remove the by-products. The cleaned precipitate is then kept in oven for 30 minutes at a temperature of 90^0C followed by calcination in muffle furnace at 400^0C for 3 hours.

$$ZnCO_3 \xrightarrow{heat} ZnO + CO_2$$

At the end, a white powder is obtained which is then crushed using pestle and mortar. This white powder is ZnO(Figure 2.1).

Figure 2.1: ZnO

2.4 COPRECIPITATION METHOD FOR THE SYNTHESIS OF MANGANESE DOPED ZnO NANOPARTICLES

The starting materials used for the synthesis of manganese doped ZnO are zinc acetate ($Zn(CH_3COO)_22H_2O$), sodium carbonate (Na_2CO_3), manganese acetate ($Mn(CH_3COO)_24H_2O$) and deionized water. For this preparation 13.5g of zinc acetate and 3.653g of manganese acetate were together mixed in 50 ml of deionized water. Na_2CO_3 was added to 50 ml of deionized water separately. This solution of Na_2CO_3 was added dropwise to the solution of $Mn(CH_3COO)_24H_2O$ and $Zn(CH_3COO)_22H_2O$. Again a white precipitate is formed which is separated from the supernatant solution using a centrifuge. The reaction between these three is given by :

$$Zn(CH_3COO)_22H_2O + Mn(CH_3COO)_24H_2O + Na_2CO_3 \rightarrow ZnCO_3 + MnCO_3 + 2NaCH_3COO$$

$$ZnCO_3 + MnCO_3 \xrightarrow{heat} ZnMnO + CO_2$$

This separated precipitate is washed and then kept in oven for 30 minutes at a temperature of 90^0C. Then it is placed in a muffle furnace at 400^0C for 3 hours. As a result of that we obtain a yellow colored powder which is crushed in pestle and mortar to obtain manganese doped ZnO nanoparticles(figure 2.2).

Figure 2.2: Mn-doped ZnO

2.5 CHARACTERIZATION METHODS

2.5.1 ANALYSIS OF XRD SPECTRUM

2.5.1.a) XRD SPECTRUM OF ZnO

The XRD spectrum of the prepared pure ZnO is given in Figure 2.3.

The peaks of ZnO are at the 2Θ values of 31.759^0, 34.413^0, 36.243^0, 47.537^0, 56.588^0, 62.851^0, 66.356^0 corresponding to the crystal planes (100), (002), (101), (102), (110), (103), (200) respectively. The intense peak of ZnO shows a good crystallinity in the structure. The peaks of ZnO matches with the hexagonal wurtzite structure. All the peaks are in correspondence the provided JCPDS File No 00-036-1451.

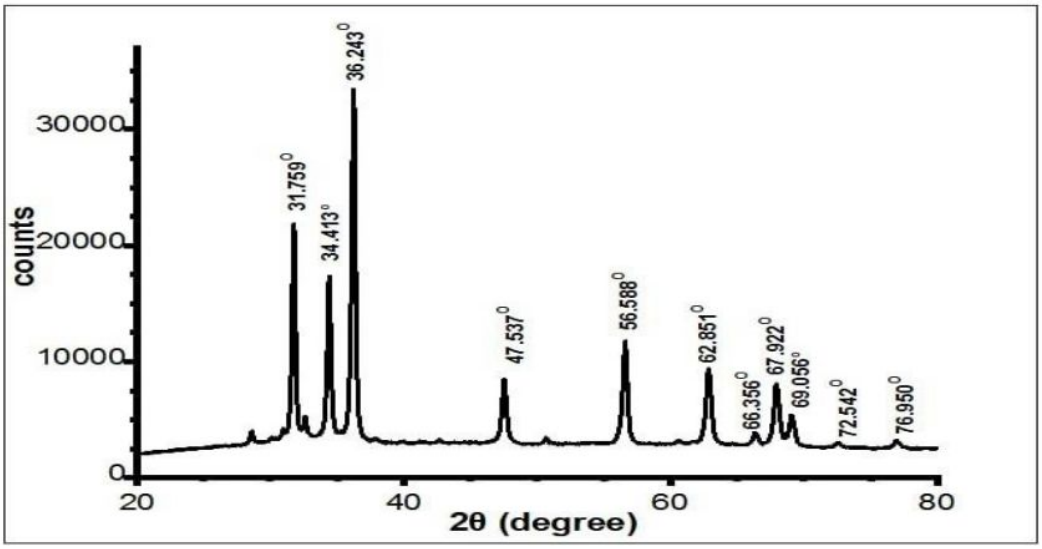

Figure 2.3: XRD of ZnO

The lattice constants a,b,c are calculated from the given XRD data using the formula

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

STANDARD VALUE		OBSERVED VALUE	
a(A^0)	**c(A^0)**	**a(A^0)**	**c(A^0)**
3.2498	**5.20661**	**3.2513**	**5.20508**
		3.2514	**5.2065**
		3.251005	**5.2029**

Table 2.1: Calculation of lattice parameters

The lattice constants of pure ZnO was found (Table 2.1) to be 3.25A^0 and 5.20A^0 which was equal to the standard value.

The particle size is calculated using the Debye-Scherrer formula,

$$\mathbf{D} = \frac{k\lambda}{Q cos\theta}$$

where k-constant = 0.9 ; λ-wavelength of the X-ray ; β – breadth of the diffraction profile or the FWHM ; Θ – Bragg's angle.

2Θ(Degree)	Θ(Degree)	FWHM,B(rad)	Size=0.9λ/B cosΘ(nm)
31.759	15.8795	0.00545	27.6420
34.413	17.2065	0.00581	26.0757
36.243	18.1215	0.00606	25.1289
47.537	23.7685	0.00662	23.9143
56.59	28.295	0.00707	23.2791
62.851	31.4255	0.00768	22.1028
67.922	33.961	0.00785	22.2489

Table 2.2: Determination of crystalline size

The calculated size for the pure ZnO at different planes is given in the Table 2.2. So the average particle size of pure ZnO is 24.342 nm.

2.5.1.b) XRD SPECTRUM OF Mn-ZnO

The XRD spectrum obtained for Mn-ZnO is shown in Figure 2.4. The observed peaks are at the 2Θ values of 31.9820, 34.6330,36.4650, 47.7470,56.8010, 63.0600 for the crystal planes (100), (002), (101), (102), (110), (103) respectively. On comparing the peaks with the provided JCPDS File No-01-078-3317, it is found that the prepared Mn-ZnO is in accordance with the data and is having a hexagonal structure.

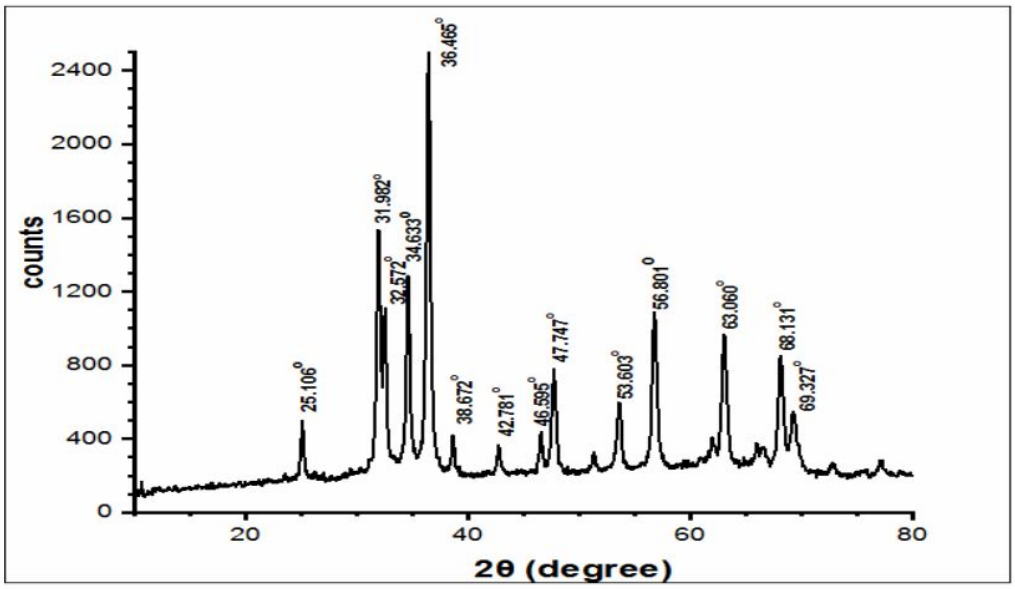

Figure 2.4: XRD of Mn-ZnO

The lattice constants are calculated using the same formula,

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

and it is given by the Table 2.3

STANDARD VALUE		OBSERVED VALUE	
a(A^0)	**c(A^0)**	**a(A^0)**	**c(A^0)**
3.253	**5.213**	**3.24004**	**5.19602**
		3.23878	**5.19026**

Table 2.3: lattice parameters

The lattice parameters of Mn-ZnO is found to be: a=b=3.239A^0 and c=5.193A^0.

The crystalline size calculated by using Debye-Scherrer formula and it is given in Table 2.4

2Θ(Degree)	Θ(Degree)	FWHM,B(rad)	Size=0.9λ/BcosΘ(nm)
31.13885	15.56943	0.00687	21.89528
34.6331	17.31655	0.00734	20.66236
36.459	18.2295	0.00793	19.21990
47.7528	23.8764	0.00818	19.35717
56.81139	28.4057	0.00896	18.3817
63.07739	31.5387	0.00975	17.41862
68.16723	34.08362	0.00973	17.97499

Table 2.4: Crystalline size determination

The crystalline size of Mn-ZnO was found to be 19.273 nm.

From the XRD analysis of pure ZnO and Mn-ZnO, it was found that they both shows almost similar peaks. And the XRD data confirms that the two prepared samples are having a hexagonal crystal structure. Since there is a slight decrease in lattice parameters of Mn-ZnO it shows that the manganese is doped in the crystal lattice of zinc and the Mn^{2+}ions replaced the Zn^{2+} ions because Mn ions are having smaller ionic radii than Zn ions .

2.5.2 EDX OF Mn-ZnO

The energy Dispersive X Ray analysis is done in order to check the presence of manganese in the prepared sample. The obtained graph is shown in Figure 2.5. It was found from the EDX that the prepared sample contain 3 at% of manganese. The EDX data provides the elemental composition of the prepared sample. The elemental distribution of the given sample is also provided in the table 2.5.

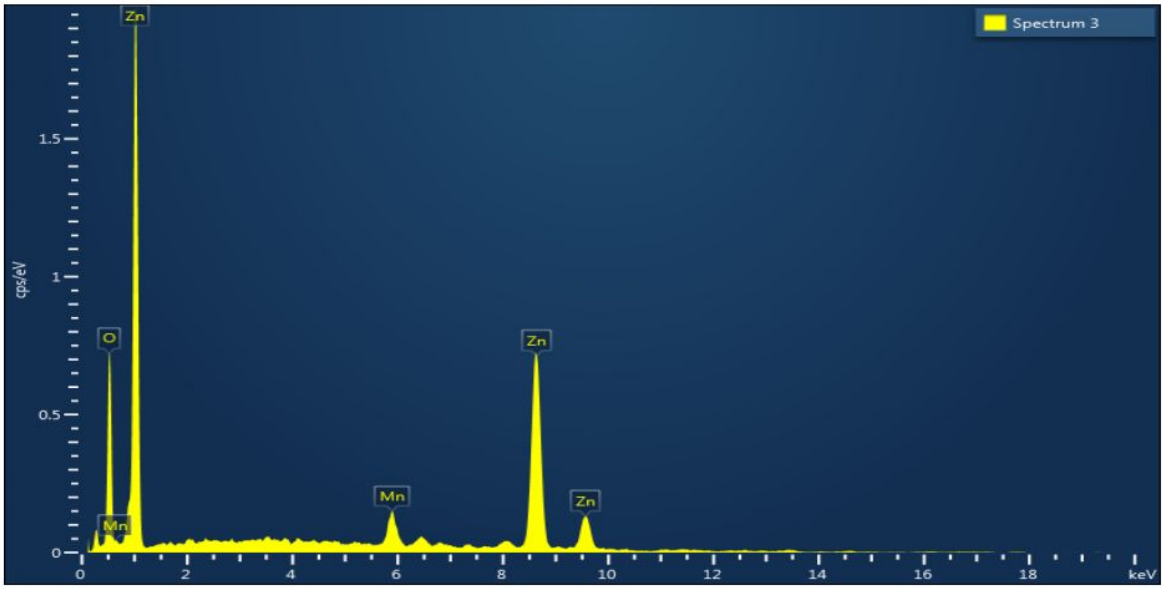

Figure 2.5: EDX

Element	Line Type	Wt%
O	K series	17.85
Mn	K series	3.72
Zn	K series	78.43
Total:		100

Table 2.5: Relative elemental composition of the sample

2.5.3 ANALYSIS OF UV VISIBLE ABSORPTION SPECTRUM

2.5.3.a) DIFFUSE REFLECTANCE SPECTRUM OF ZnO

Since ZnO is a powdered sample, Diffuse Reflectance Spectrum (DRS) is used to obtain the absorption graph. From the DRS data plotted the graph between absorbance and wavelength. We obtain a graph as given in Figure 2.6 and by using the graph calculated the value of bandgap energy using the formula

$$E_g = h\nu = \frac{hc}{\lambda}$$

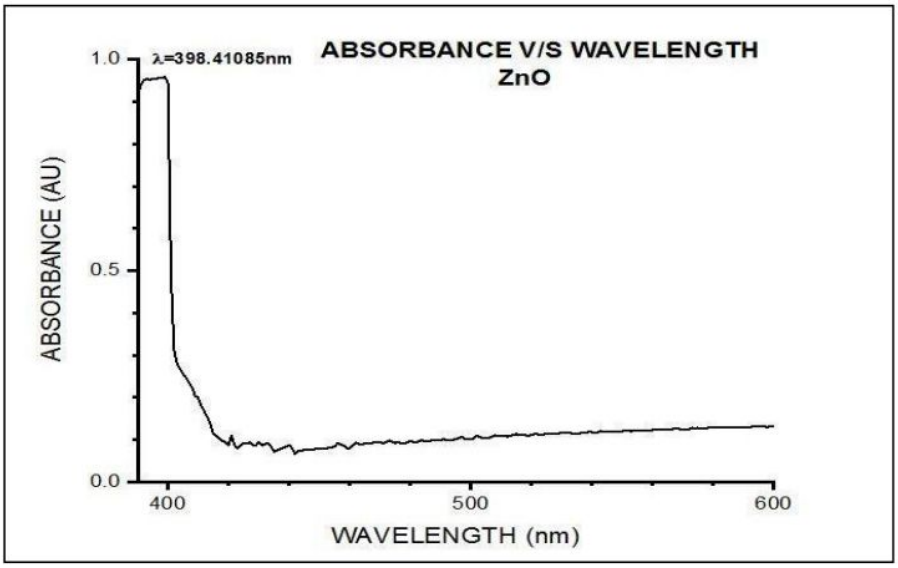

Figure 2.6: Absorption Spectra of ZnO

From the absorbance v/s wavelength graph the maximum peak was absorbed at a wavelength λ = 398.410nm and the bandgap energy was found to be 3.118eV.

A Tauc plot of ZnO was also constructed and band gap energy from that as well obtained. Since ZnO is having a direct allowed transition, $E_g=(\alpha h\nu)^{1/\gamma}=(\alpha h\nu)^2$. For the Tauc plot $(\alpha h\nu)^2$ was plotted along the y axis and energy along x axis and the band gap energy is found out by extrapolating the linear fit to the x-axis. The Tauc plot of ZnO is given in Figure 2.7.

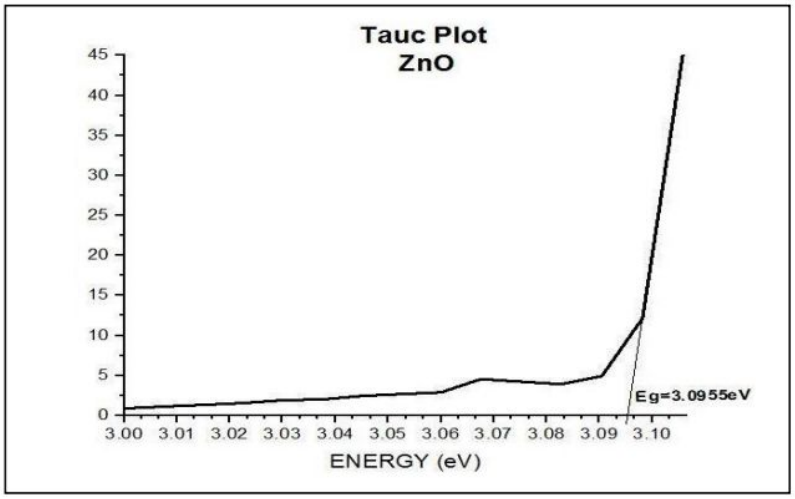

Figure 2.7: Tauc Plot of ZnO

The band gap energy was found out to be 3.095eV from the graph.

Similarly the band gap energy of Mn-ZnO was also calculated. From the DRS of the sample, the data is converted in terms of absorbances and a graph was plotted by taking absorbance and wavelength along y and x axis respectively. The obtained graph is given in Figure 2.8.

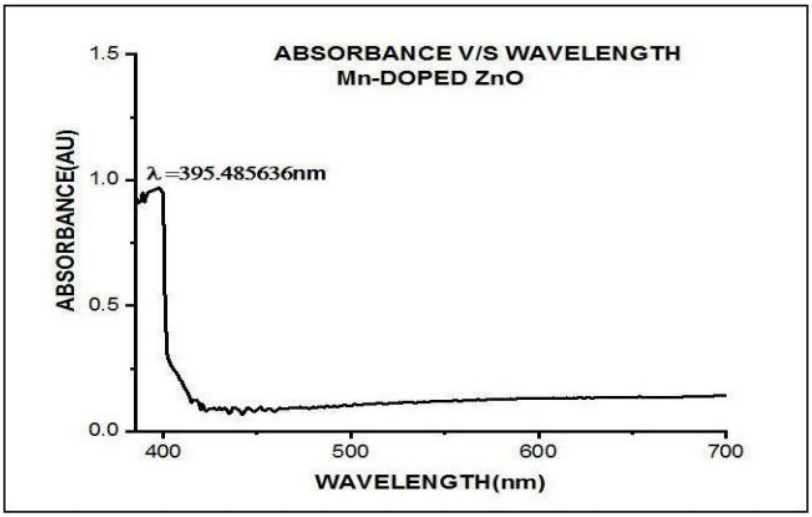

Figure 2.8: Absorption Spectrum of Mn-ZnO

From the absorption graph the maximum wavelength was found to be 395.485nm and the corresponding bandgap energy was calculated to be 3.1415eV.

The Tauc plot was also constructed and is given in Figure 2.9. From that calculated the bandgap energy as 3.317eV.

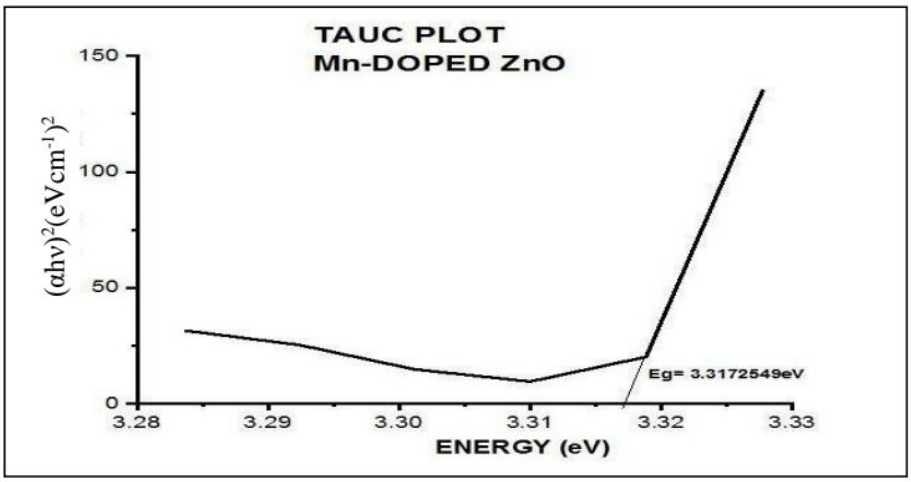

Figure 2.9: Tauc Plot of Mn-ZnO

The band gap energy of ZnO and Mn doped ZnO was calculated and it was found that there is a slight difference in the band gap energy of both. The bandgap energy of ZnO was close to its approximate value of 3.2eV. On doping with Mn, the bandgap energy of ZnO was slightly increased.

2.5.4 SCANNING ELECTRON MICROSCOPY(SEM)

The morphologies of the synthesized samples are examined using Scanning Electron Microscopy or SEM, which is operated at a voltage of 10kV.

The SEM images of ZnO and Mn-ZnO are represented in Figure 2.10 and Figure 2.11 respectively. The morphology shows their hexagonal structure.

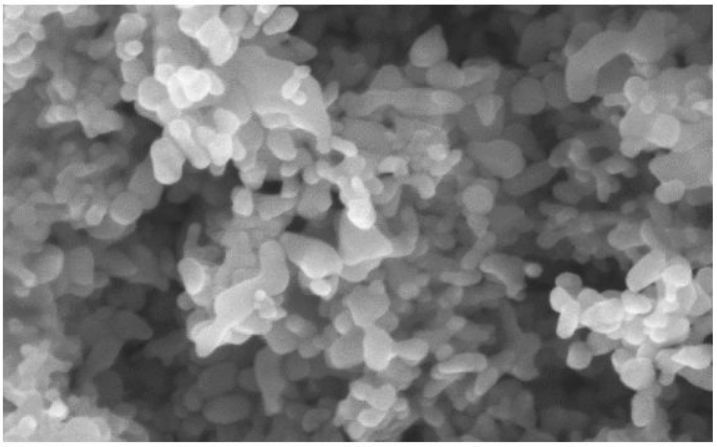

Figure 2.10: SEM image of ZnO

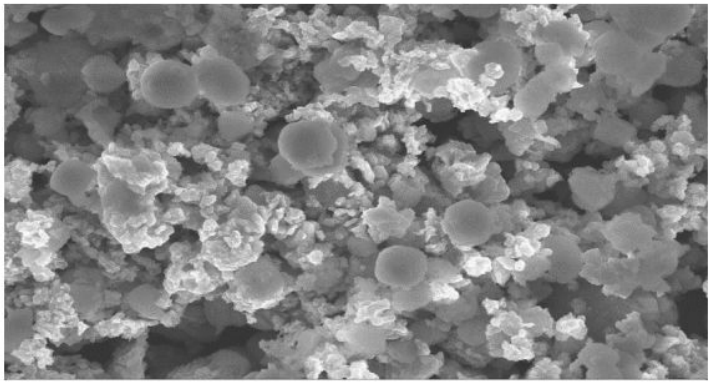

Figure 2.11: SEM image of Mn-ZnO

From the SEM result it is seen that the structure of undoped ZnO is slightly changed to spherical particles on doping.

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CHAPTER -3

RESULTS AND DISCUSSIONS

3.1 APPLICATION

3.1.1 PHOTOCATALYTIC STUDY

3.1.1a DEGRADATION OF METHYL ORANGE DYE BY ZnO

For the preparation of the sample, 0.0002g of Methyl Orange dye was dissolved in 60ml deionized water and stirred it well for 30 minute in dark. For 1mg/ml preparation of ZnO in solution, 0.06g of ZnO was added and stirred to 30 minute under dark.

In order to do the photocatalytic activity, the above prepared solution was kept under sunlight. A minimal amount say 4ml of the sample was taken from the solution before irradiating to the sunlight as well as from the pure MO solution. Then the sample was taken at regular interval of time, say 20 minute and the absorption spectrum of all the collected samples were taken. The graph obtained is plotted in the Figure 3.1.

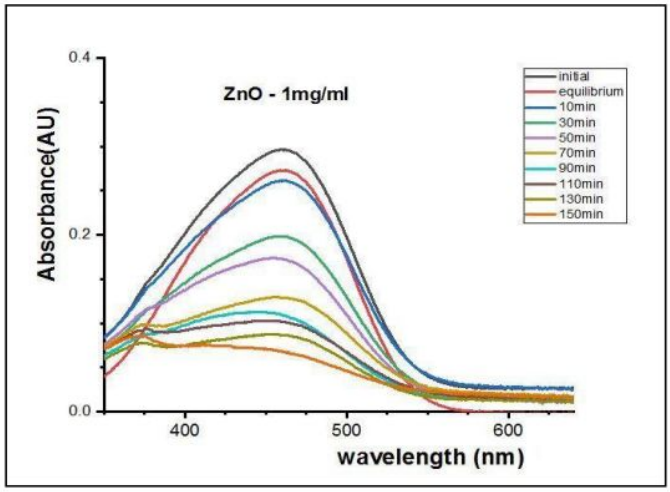

Figure 3.1: Absorption spectrum of MO dye with ZnO added

From the graph it is found that for 1mg/ml of ZnO, it took 150 min to degrade the dye.

The kinetics of degradation of the dye in presence of undoped ZnO was found using Langmuir-Hinshelwood model. According to this model in the first order degradation, the degradation rate (r) is proportional to photocatalytic surface factor covered by substrate(Θ)

$$r = \frac{-dC}{dt} = k\Theta$$

The half life time($t_{1/2}$) i.e the time needed to degrade the dye to a concentration half of its initial concentration, is given by

$$t_{1/2} = \frac{0.693}{k_{app}}$$

A graph is plotted by taking $\ln(C_0/C)$ along y axis and time along x axis, where C_0 and C are the initial concentration and the concentration at any instant. From that graph the rate constant is calculated, which is the slope of the graph and using this the half life can be found out. The $\ln(C_0/C)$ v/s time graph is given in Figure3.2.

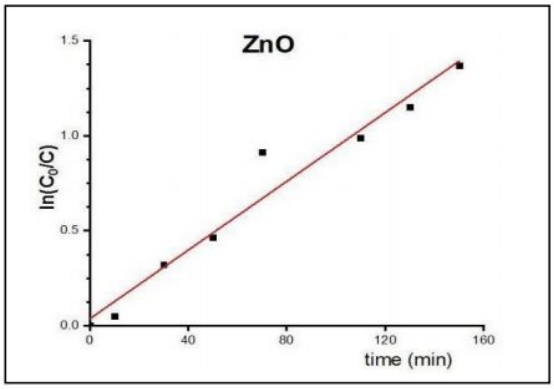

Figure 3.2: Graph to find rate constant

The rate constant was found to be k = 0.00911min^{-1} and so the half life time is 76.0318 min.

The percentage degradation was found out using the formula,

$$\% \text{ degradation} = \frac{A0 - A}{A_0} \times 100$$

And a graph was plotted ,which is shown in Figure 3.3, between the percentage degradation and time. The percentage degradation was found to be almost 80%.

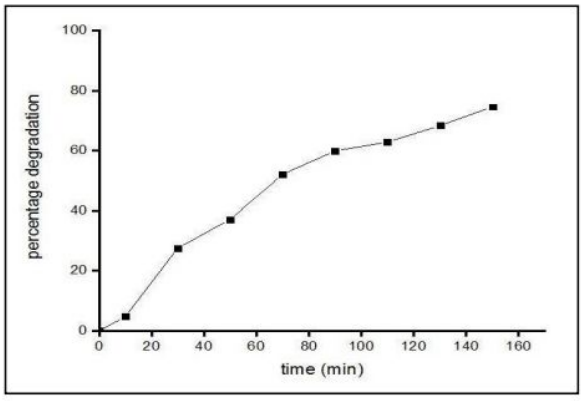

Figure 3.3: photodegradation curve

3.1.1.b DEGRADATION OF METHYL ORANGE DYE BY Mn-ZnO

The solution of methyl orange was prepared as mentioned above. To this solution 0.06g of Mn-ZnO (1mg/ml) was added and stirred for 30 minute under dark. Then 4ml of the pure MO solution as well as the one with Mn-ZnO doped before the sunlight irradiation was collected and then kept the solution under sunlight. 4 ml of sample was taken from this solution at regular interval of time and the absorption spectrum was taken for each. The obtained graph is plotted in Figure 3.4.

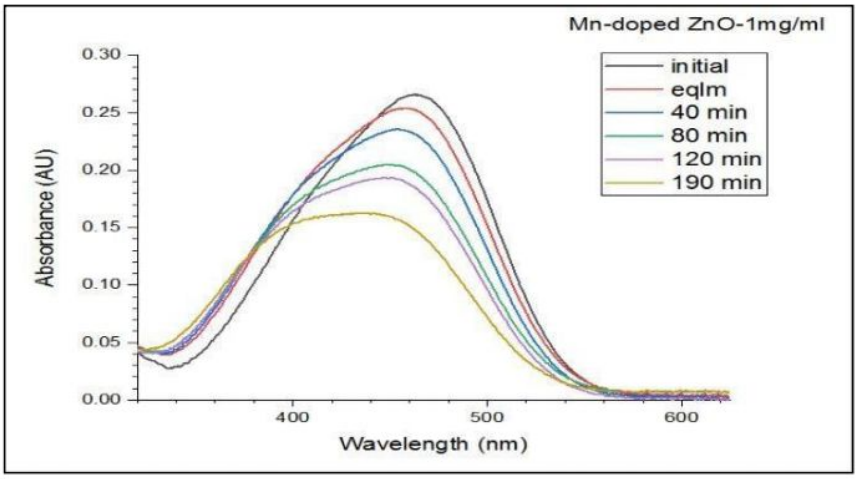

Figure 3.4: Absorption spectrum of MO dye with Mn-ZnO added

From the absorption graph it is found that for Mn-ZnO even after 190 minutes the dye was not completely degraded.

The rate constant is calculated from the time v/s $\ln(C_0/C)$ graph which is shown below (Figure 3.5):

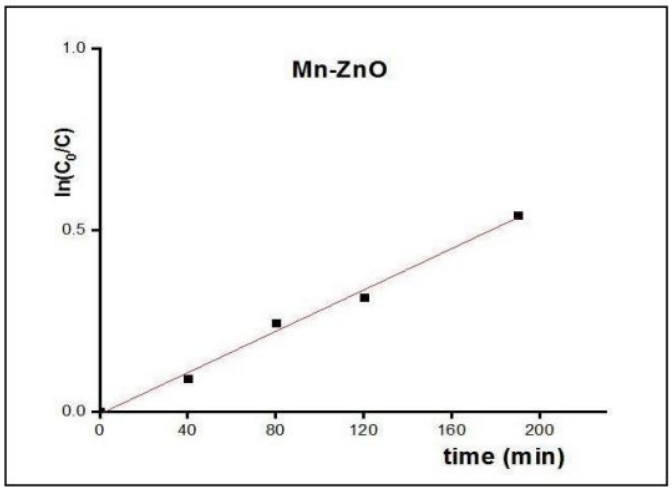

Figure 3.5 graph to find the rate constant

The rate constant k was found to be 0.002849 min^{-1}. The half life time was found to be 243.559 min.

The photodegradation graph was also plotted and is given by Figure 3.6.

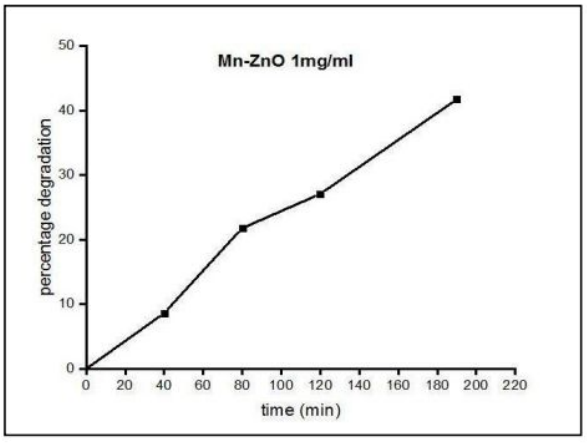

Figure 3.6

The percentage of degradation for Mn-ZnO was found to be almost 45%.

So from the analysis it was found that the photocatalytic activity of Mn doped ZnO is less than that for pure ZnO. The half life time of Mn-ZnO is almost three times that for the pure ZnO. The percentage degradation

is also reduced for Mn-ZnO. On doping Mn^{2+} ions replace the Zn^{2+} ions. As a result the electronic structure will get changed and that will in turn affect the photocatalytic activity.

Under sunlight irradiation this Mn-ZnO will have a shielding effect. The free radicals formed will be responsible for reactive oxygen species (ROS) formation. On doping there will be a possibility of recombination of photogenerated electrons and holes which will leads to a decrease in photocatalytic activity. Manganese is a transition metal so it have partially filled d orbital and under sunlight it will have d-d transition. The movement of the carriers to the surface becomes difficult since the d electrons are confined to the central transition metal ions and these carriers when moving on to the surface will only help in the photocatalysis.

Manganese can either increase or decrease the photocatalytic activity depending on the area where it gets doped i.e.., surface doping and crystal doping. In this case the preparation technique lead to a surface doping and which will lead to the decreased activity. As a result this manganese doped ZnO can be used as a shielding agent to protect skin from UV irradiated damages. Mn-ZnO can be used as a safe screening agent in so many applications. The ROS which are sometimes harmful and on doping with manganese its level can be reduced.

This result shown by Mn-ZnO have numerous scope in developing useful application in our day to day life such as preserving dye in fabric industry, make use of the UV shielding effect in sunscreens, paints etc.

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CHAPTER – 4

CONCLUSIONS AND FUTURE SCOPE

4.1 CONCLUSION

Zinc oxide and manganese doped zinc oxide nanoparticles were synthesized using co-precipitation method. The structural characterization of both nanoparticles confirmed the formation of hexagonal wurtzite structure. The particle size and lattice constants of nanoparticles were calculated from XRD data. The value of crystalline size obtained for ZnO is 24.342 nm and for Mn-doped ZnO it is about 19.273 nm. The lattice parameter c calculated for Mn-doped ZnO is $5.193A^0$ and that for undoped one is $5.20A^0$. The decrease of lattice parameter indicates that Mn is introduced into the ZnO crystal lattice and thereby it substitute Zn^{2+} sites. The Diffuse Reflectance Spectrum of both the samples were taken and studied the absorption v/s wavelength graph. From that the band gap energy of ZnO and Mn-doped ZnO was calculated as well as it was calculated using Tauc plot . The band gap energy of ZnO is obtained as 3.0955 eV and for Mn-doped ZnO it is 3.31725 eV. The bandgap energy of ZnO was slightly increased on doping. This can be due to Moss-Burstein effect which results in electrons generation by oxygen vacancies. The electronegativity and ionic radius difference between Zn and Mg results in an increase in oxygen vacancies and electron concentration when Zn^{2+} is substituted by Mg^{2+}.Thus band gap widening in Mn-doped ZnO is due to the increase in carrier density which results in shifting the Fermi-level into the conduction band.

The morphology of both the ZnO as well as Mn-ZnO were obtained using Scanning Electron Microscopy (SEM). It was found that ZnO is having rode like shape and as on doping the structure becomes slightly spherical, that may be due to shielding effect of manganese.

The photocatalysis study of undoped ZnO and Mn-doped ZnO nanoparticles was done using the methyl orange dye under sunlight. The photocatalytic degradation of methyl orange decreases in the presence of Mn-doped ZnO when compared to un doped ZnO. It is due to the increase in possibility of recombination of the excited electron and hole on surface doping. Through the preparation by coprecipitation method, the manganese is surface doped. This surface doping will increase the recombination rate. So both the preparation method and the location of dopant will affect the photocatalytic activity.

ROS or Reactive Oxygen Species are highly reactive ions or small molecules that contain oxygen ions, free radicles as well as peroxides. The high photon absorption and usage of electron/hole pairs during semiconductor metal oxide irradiance predict the generation of high rate of reactive oxygen species which can be further used to degrade the fabrics but it will cause various health problems to human. Doping with some transition metals will reduce the photocatalytic activity due to the recombination of the charge carriers and this in fact will help in reducing the presence of these oxygen species. Therefore the reduction in the photocatalytic activity of Mn-ZnO will help in the suppression of oxidative stress due to this ROS. So this will help in using these materials in UV shielding applications in order to protect the skin from the harmful UV radiations.

4.2 FUTURE SCOPE

Doping will either increase or decrease the photocatalytic activity depending on the location of dopant. More studies can be planned for the determination of manganese ions. The photocatalysis study of manganese doped ZnO can be done by varying doping level below 1at% or above 12 at%.

The effect of Mn-ZnO for a simulated UV environment is studied and to find how it will differ from that under visible light. How the photocatalytic activity will change on doping is further studied.

The thermal and magnetic studies of Mn-ZnO is needed to study. On changing the concentration of doping as well as changing other parameters like temperature, pH etc. is used to investigate the photocatalytic activity.

We wish to investigate the influence of CNTs on this doped ZnO as well as try some methods to enhancethe efficiency of Mn-ZnO.

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