SYNTHESIS OF ZnO AND ITS PHOTOCATALYTIC ACTIVITY

A Major Project dissertation submitted

in partial fulfilment of the requirement for the degree of

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In

BioMedical Engineering

Submitted by

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DECLARATION

I hereby declare that the work presented in this thesis entitled "**Synthesis of ZnO And its Photocatalytic activity"** has been carried out under the guidance and supervision of Dr.Jai Gopal Associate Professor, Department of Biotechnology, Delhi Technological University, Delhi. The work presented in this thesis is original and has not been submitted in part or in full to any university or Institution for award of any degree, diploma, membership or similar title(s).

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CERTIFICATE

This is to certify that the M. Tech. dissertation entitled **“SYNTHESIS OF ZnO AND ITS PHOTOCATALYTIC ACTIVITY”**, submitted by **PREETI KUSHWAHA (2K13/BME/16)** in partial fulfilment of the requirement for the award of the degree of Master of Technology, Delhi Technological University, is an authentic record of the candidate’s own work carried out by her under my guidance. The information and data enclosed in this dissertation is original and has not been submitted elsewhere for honouring of any other degree.

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Abstract

In the present work, mesoporous ZnO are successfully prepared with the help of hydrothermal method and sol gel method. Zinc nitrate hexahydrate, ctab, urea are used as precursor materials. The ZnO powder obtained is calcined at 800 ^{0}C and analyzed different properties and behavior of nanoparticles. The method which is used ,has been implicated with some modification with the aim to reduce the size of nanoparticles followed by the paper, and changes are studied with the help of different experimental characterization as XRD conferred ZnO, SEM and TEM revealed different morphology, shape and structure of particles. BET gives pores size and diameter, advantage of lesser size of particles with pores of having large surface area due to which it will take less time to degrade dye which is required and present research need for efficient applications and then determining the photocatalytic degradation of rhodamine-b dye on mesoporous ZnO nanoparticles. Photocatalysis is a well defined approach in which UV light energy is focussed to excite the semiconductor material producing electron/hole pair which eventually involves in the detoxification of pollutants (in water or air) and water splitting. Existing photocatalysts suffer from poor activity or no activity in visible light irradiation which restricts them from solar light utilization. Photocatalytic oxidation processes with ultra violet (UV) radiation and semiconductor photocatalyst like zinc oxide (ZnO) have gained an interest as an effective wastewater purification method because of its efficacy in decomposing and mineralising the hazardous organic pollutants and also utilizing the solar UV and visible spectrum. Rhodamine B is a significant dye. Color is one of the vital characteristics of these effluent streams and seems to be the most undesired, as it affects the nature of water by inhibiting sunlight penetration hence reducing photosynthetic action. Thus, to remove color from industrial effluents is a major concern in wastewater treatment, and treatment is needed before

discharging to receiving water. To remove dye pollutants there are various conventional methods such as adsorption on activated carbon, ultra filtration, reverse osmosis, coagulation by chemical agent etc. The pollutants cannot be completely degraded by given methods, the incapability of conventional methods to effectively remove pollutants leads to discover new, efficient and cost effective methods. Photocatalytic process relies on the activation of semiconductor that gives generation of electrons /holes. These holes can react with water to produce hydroxyl radical which results inseries of redox reaction to destroy the pollutants. ZnO has been demonstrated to be an excellent catalyst.

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LIST OF ABBREVIATIONS

- NPs- nanoparticles
- BET- Brunauer–Emmet–Teller
- FS- fluorescein sodium
- MEMs- micro electro mechanical devices
- PEG- polyethylene glycol
- PL- photoluminescence
- PMMA- polymethylmethacrylate
- PMT- photo multiplier tube
- Rb- rhodamine b
- SAW- surface acoustic waves
- SEM- scanning electron microscopy
- ST- stilbene 420
- TEM- transition electron microscopy
- TFTs- thin film transistors
- UV-vis- ultraviolet –visible spectroscopy
- XRD- X-ray diffraction

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CHAPTER ONE

INTRODUCTION

This chapter deals with luminescence and study of Photoluminescence of various organic dyes A brief discussion to porous material and ZnO as a porous nanoparticle, for the analysis of photocatalysis of organic dye in comparison with catalyst and without catalyst.

1.1 A BRIEF DESCRITION TO THE PRESENT WORK

The aim of this work to fabricate porous nanoparticles (catalyst) for the application of photocatalysis by degrading organic dye. This work explained a detailed study of organic dyes and their photoluminescence properties and on the analysis of their results the particular organic dye is selected to proceed the further work. As this work is based on zinc oxide as catalyst so various methods explored to fabricate porous nanoparticles, this is done by selecting hydrothermal and in comparison with sol-gel method (because of two different shapes).The purpose of a porous nanoparticle was strongly recommended for this study because of their high retention /absorption power due to large surface area, high permeability, high porosity. These all parameters are confirmed by the different techniques used in this work. At last to applicate this catalyst for the application of photocatalysis, these results are compared with catalyst and without catalyst and finally it is concluded that porous structure are more advanced for the photocatalysis as they degrade the dye faster and the application is very useful commercially as well as for human health hazards. It is used for various purposes as for today first need is to protect human by control of hazards. This chapter will give detailed introduction to the luminescence, organic dyes, porous particles and only a brief information of photo degradation techniques.

1.1.1 Luminescence

It is the phenomenon in which emission of light takes place with the absorption of energy from any substance that occurs from electronically excited states. The process in which subsequent emission of light with the absorption of energy is termed as luminescence. Fundamentally it is the emission of light from a material of the black body radiation with the initial absorption of energy from an external source. It is also called as cold emission as unlike blackbody radiation the material need not to be heated. Energy will transfer from the excitation source to the electrons in the materials, therefore electrons get excited from ground states to excited states. Luminescence is closely related with spectroscopy, It is the study of the laws of absorption and emission of radiation.The emission will takes place when an excited electron returns to its ground state. Such phenomena are known as 'phosphor' in those particular material. Those materials are sensitized due to defects created to certain vacancies that generate during synthesis is because of continuous adding some impurity ions to get certain levels for the transfer of energy. It is broadly divided into two categories - fluorescence and phosphorescence, Phosphors are also luminescent materials which emit light when excited by radiation, to provide visible color emission. Excitation with the absorbance of a photon leads to species luminescent which fluoresce or phosphoresce. Fluorescence is a "fast" (ns time scale)on the other hand phosphorescence is "slow" (longer time scale, up to hours or even days). The photoluminescence (PL) can be divided into two categories (1)Large-scale inorganic materials, mainly exhibiting phosphorescence. (2)Small-particle inorganic ("nanomaterials"), which can either fluorescence or phosphorescence. The electronic states of most organic molecules can be divided into singlet states and triplet states; Singlet state: All electrons in the molecule are paired. Triplet state: unpaired one set of electron, as shown below-

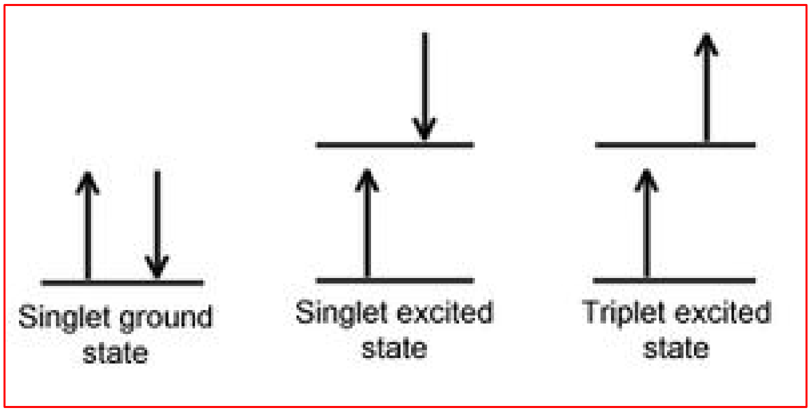

Figure 1.1 Singlet paired and triplet unpaired electrons.

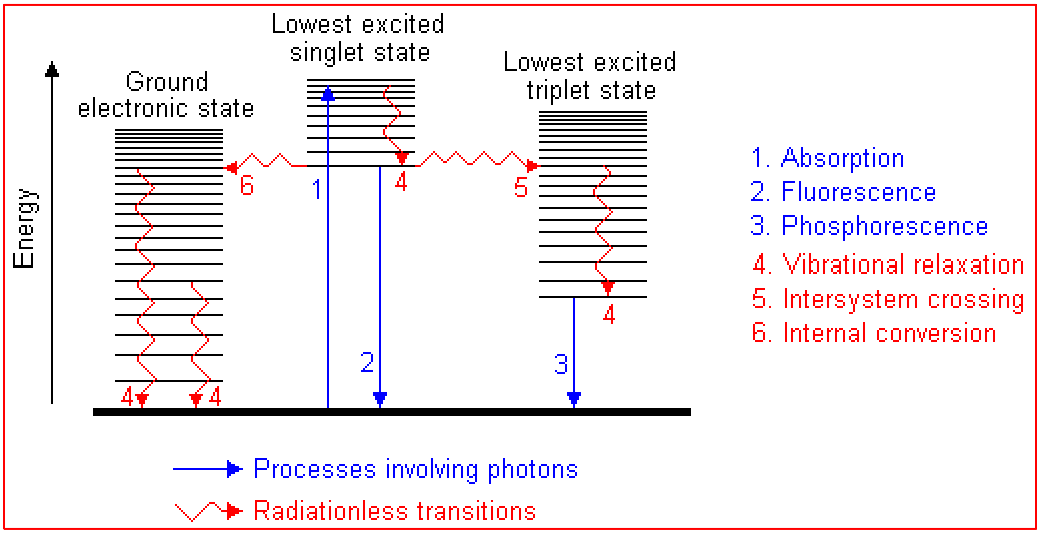

Figure 1.2 Possible physical process following absorption of a photon by a molecule

1.1.2 Intra-molecular redistribution of energy between possible electronic and vibrational states-According to figure-2,the molecule returns to the electronic ground state and the excess energy is converted to vibrational energy (internal conversion), and so the molecule is placed in an extremely high vibrational level of the electronic ground state. This excess vibrational energy is lost by collision with other molecules (vibrational relaxation). The conversion of electronic energy to vibrational energy is helped if the molecule is "loose and floppy", because it can reorient itself in ways which aid the internal transfer of energy. A combination of intra and inter molecular energy redistribution.The spin of an excited electron can be reversed, leaving the molecule in an excited triplet state; this is called intersystem crossing. The triplet state is of a lower electronic energy than the excited singlet state. The probability of this happening is increased if the vibrational levels of these two states overlap. For example, the lowest singlet vibrational level can overlap one of the higher vibrational levels of the triplet state. A molecule in a high vibrational level of the excited triplet state can lose energy in collision with solvent molecules, leaving it at the lowest vibrational level of the triplet state. It can then undergo a second intersystem crossing to a high vibrational level of the electronic ground state. Finally, the molecule returns to the lowest vibrational level of the electronic ground state by vibrational

1.1.3 TYPES OF LUMINESCENCE

Table-1.1 Types of luminescence and their excitation methods.

PHENOMENON	METHOD OF EXCITATION
Photo-Luminescence	Light or photons
Bio-Luminescence	Bio-chemical energy
Sono-Luminescence	Sound waves
Electro- Luminescence	Electric field
Chemi- Luminescence	Chemical energy
Tribo- Luminescence	Mechanical energy
Cathodo- Luminescence	Electrons or Cathode rays
Radio- Luminescence	Nuclear Radiation
Fluoroscence	Uv and visible light,Ionizing Radiations

Phosphorescence	Uv and visible light,Ionizing Radiations
Thermoluminescence	Uv and visible light,Ionizing Radiations

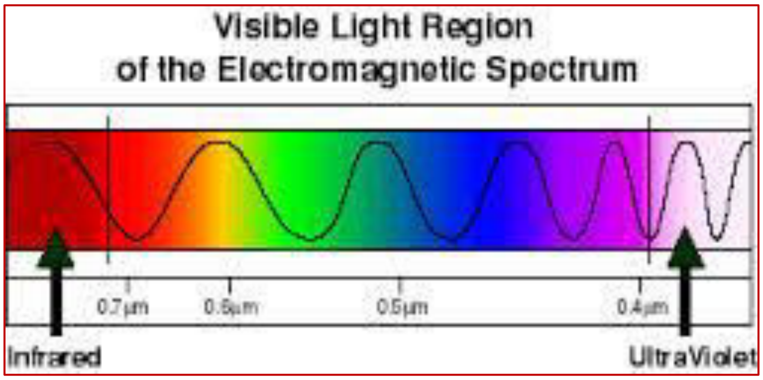

Figure 1.3 visible light spectrum

- Emission wavelength is hc/(E 1-E 2), where E 1 and E 2 are the initial (higher energy) and final (lower energy) states as shown in fig-3
- Visible range: 0.4 – 0.7 µm corresponding to energy of 3.1 – 1.77 Ev,as shown in fig-2

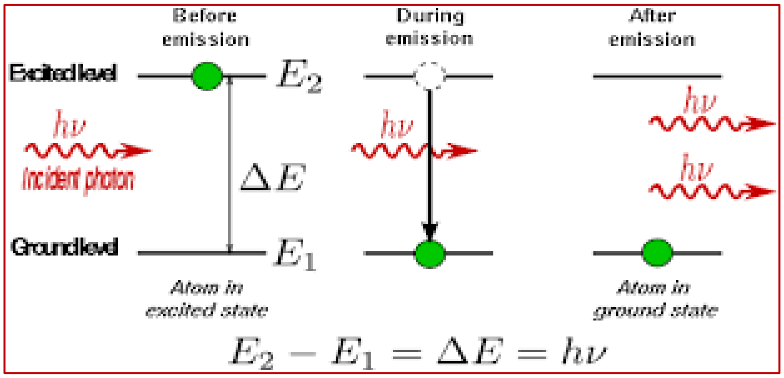

Figure 1.4 Luminescence requires localisation of absorbed energy by discrete states..

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1.1.4 Organic dyes

There are several classes of laser dyes including Polymethines (700 to 1500 nm), Xanthenes also known as Rhodamines (500 to 700 nm) and fluorescein, coumarines (400 to 500 nm) and scintillators (320 to 400 nm) POPOP and PPO. Tuning wavelength ranges of various organic dyes has been presented in Figure-5

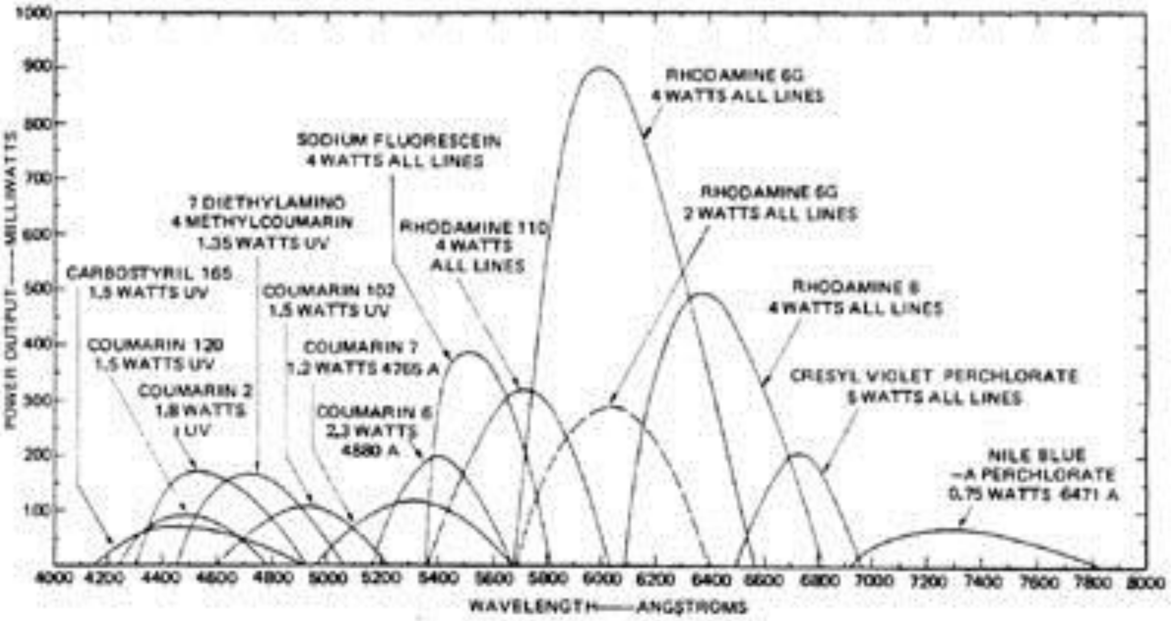


Figure 1.5 Tuning wavelength of various organic dyes.

As shown in the fig-2 the explanation is given as, polymethines dye is this class of dye molecules has a long conjugated methine chain (-CH=CH-). An important use of these dyes has been the color sensitization of photographic films. Cyanine dye molecules form fluorescent photoisomers during excitation in general and their lasing is observed in longer wavelengths. The lasing efficiency of Rhodamine dyes comes from Xanthenes family is very high, and the chemical stability fairly good. The fluorescein dyes also belongs to this family but the lasing wavelengths of fluorescein dyes are shorter than those of Rhodamine dyes, which are typically in the green region. Acriflavin dye come from the family of Acridine dyes. Oxazine dyes are very important materials for dye lasers, especially at longer wavelengths than those of Rhodamine dyes. In the IR region, they compete with cyanine dyes but they are better with regard to chemical stability.

1.1.5 Photoluminescence in organic dyes.

Excitation and Emission Spectra (Figure-5) shows a typical spectrum of the excitation and emission of a fluorochrome. These spectra are generated by an instrument called a spectro-fluorimeter, which comprised two spectrometers: an illuminating spectrometer and an analyzing spectrometer. First, the dye sample is strongly illuminated by a color of light that is found to cause some fluorescence. A spectrum of the fluorescent emission is obtained by scanning with the analyzing spectrometer using this fixed illumination color. The analyzer is then fixed at the brightest emission color, and a spectrum of the excitationis obtained by scanning with the illuminating spectrometer and measuring the variation in emission intensity at the fixed wavelength.

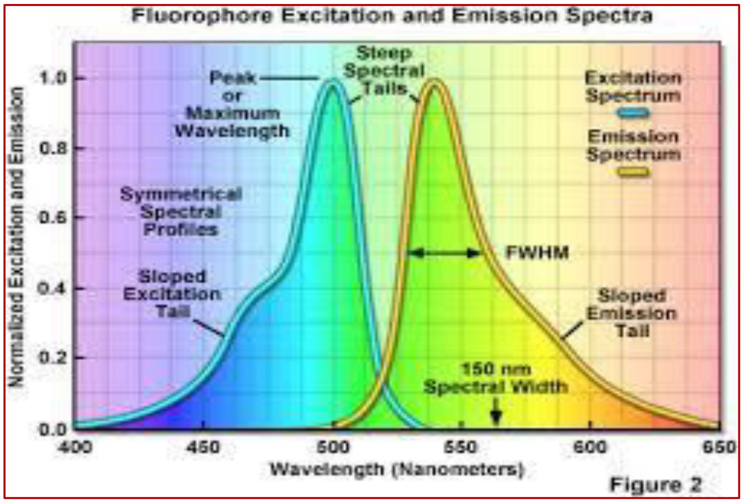


Figure 1.6 Excitation and emission spectra

These color spectra are described quantitatively by wavelength of light. The most common wavelength unit for describing fluorescence spectra is the nanometer (nm).The colors of the visible spectrum can be broken up into the approximate wavelength values.

[Violet and indigo(400−450)nm, Blue and aqua(450−500) nm, Green (500−570) nm, Yellow and orange(570−610) nm, Red (610 to approximately 750) nm]

On the short-wavelength end of the visible spectrum is the near-ultraviolet (near-UV) band from 320 to 400 nm, and on the long-wavelength end is the near-infrared(near-IR) band from 750 to approximately 2,500 nm. The broad band of light from320 to 2,500nm marks the limits of transparency of crown glass and window glass, and this is the band most often used in fluorescence microscopy. Some applications, especially in organic chemistry, utilize excitation light in the mid-ultraviolet band(190–320 nm), but special UV-transparent illumination optics must be used. There are several general characteristics of fluorescence spectra that pertain to fluorescence microscopy and filter design. First, although some substances have very broad spectra of excitation and emission, most fluorochromes have well-defined bands of excitation and emission. The difference in wavelength between the peaks of these bands is referred to as the Stokes shift. In practical applications, phosphors are often excited by cathode rays, X-rays, or UV emission of a gas discharge, which correspond to applications in displays ,medical imaging and lighting, respectively, such as cathode-ray-tube (CRT) color TV, X-ray fluorescent screens, and fluorescent lamps.

1.2 Porous material

Nanoporous particles have attracted interest during the past two decades, due to specific properties and their advantageous applications such as catalysts, gas sensors, as well as electronic devices and biological processes.Synthesis of nanoporous materials which have reported till date focused on template assisted as they are bottom-up processes, including soft templating (chelating agents, surfactants, block copolymers etc.) and hard templating (porous alumina, carbon nanotubes,nanoporous silica and carbon) methods.

Porous materials can be organic materials or polymeric foams. A wide range of inorganic porous materials have been discovered, e.g. for insulation, impact protection, catalysis, construction materials and many other.

- Materials with different pore sizes (from nanometer to millimeter)
- Ordered or irregular pores arrangement.
- Different chemical compositions (metal, oxides…)
- Different methods of preparative approaches.

1.2.1 Porosity of nanoparticles

Porous material- Pores contains (cavities, channels or interstices) are more deeper than their wideness. They are described as either pores or the cell/pore walls.

Accessibility- According to figure-6 they can be closed pores ,open pores ,blind pores (dead-end or saccate) or through pores.

Shape: Pores can be of different sizes and shapes dependin on the material.They are nanorods,nanotubes,nanowires,nanothreads,nanospheres,Cylindrical,funnel shaped, roughness.

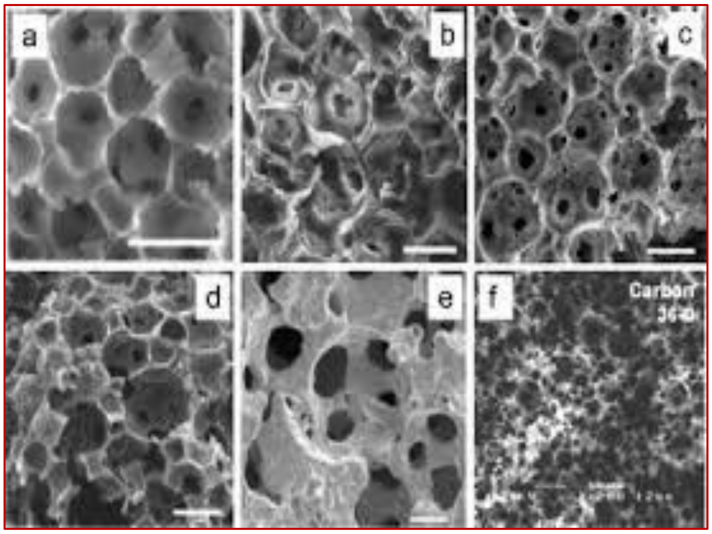


Figure 1.7 Different shapes of porous structures

Measuring porosity-It varies and depends according to the method. Some methods reveals only open pores, e.g. adsorption of molecules.Their accessibility and open pores is then defined by the probe molecule.Or probe may be closed pores, e.g. spectroscopy, diffraction, scattering.

Pore size-Pore size is an important factor for its applications.There are three standard pore size regimes, associated with mechanisms:

•Microporous, smaller than 2 nm

•Mesoporous, between 2 and 50 nm

•Macro porous, larger than 50 nm

1.3 CRYSTAL STRUCTURE OF ZnO

Zinc oxide crystallizes in two main forms first- hexagonal wurtzite and second-cubic zinc blende but there is also a third (B4 type) wurtzite structure which is obtained only at optimum pressure and temperature. For an ideal wurtzite crystal as shown in figure-1.7 having a hexagonal close-packed lattice type, has lattice parameters, a_o= 0.32495 nm and c_o = 0.52069 nm, in the ratio of c_o / a_o =1.602, and which belongs to the space group of P63m*c* and it is characterized by two interconnecting sub lattices of Zn^{2+} and O^{2}- where each of the anion is surrounded by four cations at the corners of a tetrahedron with a typical Sp3 covalent bonding. Among various phases of ZnO, based on the first principle of atomic orbitals theory the wurtzite is the most thermodynamically stable phase. Tetrahedral symmetry is very important for the polarity of ZnO which arises along the hexagonal axis. Spontaneous polarization and piezoelectricity are the direct result of polar symmetry of ZnO along the hexagonal axis. Structure of ZnO given in figure 1.7 has a number of alternating planes composed of tetrahedrally coordinated O^{2-} and Zn^{2+} ions, stacked alternately along the axis.The two oppositely charged ions produced Zn(0001)-positively charged ion and O(0001)-negatively charged ion polar surfaces, resulting in a dipole moment and spontaneous polarization along the c-axis, as well as variation in the surface energy. Polar faces are more stabilised than non polar . It is due to the sensitiveness nature of N-type nature of ZnO that lattice are constants with the presence of structural point defects (vacancies and interstitials) and extended defects (threading/planar dislocations) resulting in a non-stoichiometric compound that are commonly found in ZnO with an excess zinc .These have tendency to function as donor interstitials due to excess energy that give its natural N-type conductivity.The excess zinc in an ionic form exist as Zn+ interstitials that are mobile and tend to occupy special interstitial sites with Miller index (⅓, ⅔, 0.875).These offer passage with special sites routes for zinc interstitials to easily migrate within the ZnO wurtzite structure.

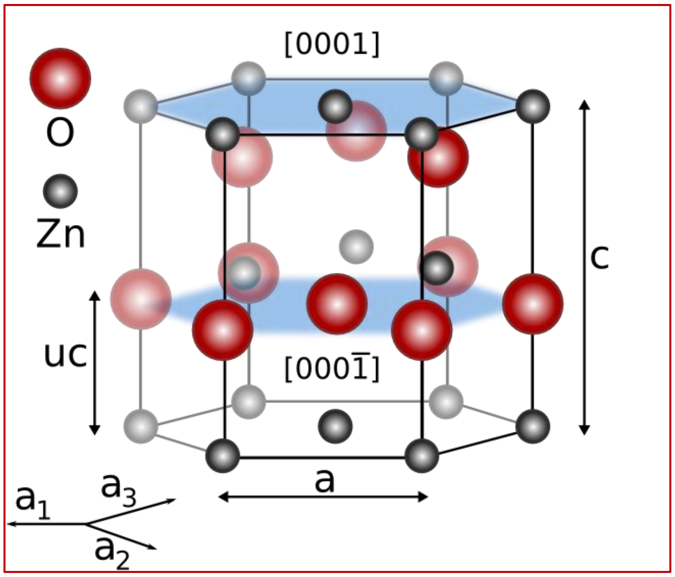


Figure 1.8 The wurtzite structure model of ZnO

1.3.1 OPTOELECTRONIC PROPERTY

To show a better optoelectronic property the most important factor which is responsible is the large exciton binding energy property which is very well posseessed by Zinc oxide having binding energy of 60mev and it could be attended at and above room temperature due to excitonic recombination. Optical absorption and emission have been influenced by bound excitons which are extrinsic transition related to defects or dopants thereby responsible for creating discrete electronic states in the band gap.In general neutral or charged acceptors and donors are the members due to which exciton could be bound with and it depends on the band structure of semiconductor material. Thus exciton because of bound system do not requires traps to localize carriers and recombines with high efficiency. The piezoelectrical field makes deeper exciton of ZnO and stable against field ionization.Doped zinc oxide gives a wide range of sensing spectra within (200-280)nm which makes it to tune for UV and made applicable for numerous fields as ultra high temperature flame detection, solar UV radiation monitoring, and other. Single crystalline made ZnO films shows dependent optical properties because of that it can be applied for modulating UV radiation.With the decrease of nanowire diameter and this reduction in diameter of ZnO nanowire gives quantum size effect and due to which size confinement exciton binding energy is enhanced and PL spectra of ZnO nanowire shows increase of green emission intensity. The excellent emitting power of ZnO has been investigated and line width of excitonic recombination is as narrow as 40 μeV with fine spectroscopic details have been observed. The refractive index of wurtzite ZnO as reported is nw = 2.008 and ne = 2.029.

1.3.2 CHEMICALLY GROWN ZnO

Any material in its nano form is more in demand instead its bulk form because nano level material undergoes a drastic change in its property and has versatile application. Zinc oxide is a multifunctional material which has large direct band gap has enhanced the research on one dimensional nanostructure especially oxide materials. if zinc oxide makes the material eligible exists in various shapes than the properties in the form of nanostructures exhibiting a varieties of properties like UV and visible photoluminescence, piezoelectricity, optical nonlinearity, conductivity, solar cell, , optical transparency and many more. But different processing techniques are responsible for obtaining various shapes of nanostructures that are related to the synthesis of various shapes of zinc oxide nanostructures as these are electrochemical,chemical, hydrothermal process ,thermal vapour deposition laser ablation, vacuum arc deposition. But all these methods reported, require sophisticated equipments and rigorous experimental conditions possesses many complex steps.Thus need arises for a simple synthesis technique and by using it zinc oxide nanostructures can be grown in a laboratory environment and also fabricated such structures for a wide range of applications through repeated modification. Not only the method enable us to fabricate multi-dimensional nanostructures in broad scale while also provides repeated preparation that enables to varying the process conditions for repeatability in the yield an investigational study.Therefore, overall we can conclude that synthesis of ZnO nanostructures by chemical route not only provides a method for large-scale fabrication of ZnO nanostructures with a low cost, but also open a way to the size-controlled fabrication of other materials

1.3.3 ZnO as a mesoporous material

“Zinc Oxide” has a wide gap semiconductor successfully satisfying the required properties. Zinc oxide possessed not only many versatile properties for photoctalysis,UV electronics, spintronic devices and sensor application but also ZnO has been used in its polycrystalline form over a decade in a wide range of applications. It has ignited many research minds all over and creates an enthusiasm to discover proper growth and processing techniques for the synthesis. Zinc oxide has been used in medical treatment and other applications for quite number of years. The research on ZnO has begun from 1950, with a number of reviews on chemical electrical and optical properties like absorption spectra and electroluminescence decay parameter also manufacturing of simpler ZnO devices like ceramic varistors, piezoelectric transducers etc. And a progress in the study of variety of characterization techniques such as cathodluminescence (CL), capacitance – voltage studies(CV), electrical conduction. A new era for research of ZnO begins actually in 1990 with tremendous growth in number of publications related to both characterization and techniques. Growth methods were used such as pulsed laser deposition (PLD) and molecular beam epitaxy (MBE). Commercial ZnO comes to the picture with advanced researches mainly concerned with optimization of different growth parameters and processing techniques. Thus currently researchers main focus is related to the production of high quality, reproducible P-type conducting ZnO for devices application.It has now become one of most studied material as it presents very interesting properties for optoelectronics and sensing applications also in nano range of synthesis.

1.3.4 Methodology Table 1.2 To show different methods to prepare ZnO nano particles

Methods	Precursors	Synthesis condition	Properties
Mechano Chemical process	ZnCl2, Na2CO3, NaCl	Calcination: 2 h, 600 °C,	Hexagonal structure; particles diameter: 21-25nm Hexagonal structure; particles diameter: 18–35 nm Regular shape of particles; diameter ~27 nm, BET: 47 m2/g particles diameter: 27–56 nm particles diameter: ~51 nm, BET: 23 m2/g
Sol-gel	$Zn(CH_3COO)_2$ oxalic acid($C_2H_2O_4$),ethanol	Reaction:50°C,60min; dried of gel 80°C,20h; calcined: under flowing air for 4 h at 650 °C	Hexagonal wurtize structure; uniform, spherically shaped of particles
Solvothermal hydrothermal and microwave technique	$Zn(CH_3COO)_2$, $Zn(NO_3)^2$, LiOH, KOH, NH4OH	Reaction: 5–10 h, 100–200 °C; HMTA concentration: 0–200 ppm	Spherical shape; particles diameter: 55–110 nm
Solvothermal	$Zn(CH_3COO)^2$,	Reaction: 150–180 °C;	Hexagonal (wurtize)structure,

hydrothermal and microwave techniques	$Zn(NO_3)^{2,}$ ethanol, imidazolium tetrafluoroborate ionic liquid	drying: 80 °C in vacuum oven; calcinations: 500 °C	hollow microspheres (2–5µm) consisted nano-sized particles and contained channels(10nm); hollow microspheres consisted of nanorods (~20 nm); flower-like microspheres (2.5 µm)
Precipitation Process	$ZnSO_4$, NH_4HCO_3, ethanol	Drying: Overnight,100°C; Calcination:300–500 °C	wurtize structure; crystallite 20nm
Emulsion	$Zn(CH_3COO)_2$, NaOH and KOH, cyclohexane, non-ionic surfactants	Reaction: Ambient temperature; drying: 24 h, 120 °C	Hexagonal structure; particles morphology: solids (164–955 nm, BET: 8 m2/g),ellipsoids (459–2670 nm, BET: 10.6 m2/g), rods (396–825 nm, BET: 12 m2/g), flakes (220–712 nm, BET: 20 m2/g); crystallites size: 32–77 nm; application: as a photocatalyst

1.4 Photocatalytic degradation of an organic dye.

Dissociation or breakup of the molecules into small pieces by photons is known as photodegradation. It can lead to change the shape of a molecule and irreversibly altered, such as denaturing of proteins.Generally it is reduction and oxidation reaction.It is very helpful to clear or destroy pollutants of drinking water and waste water management. This interesting application of photosensitization with help of appropriate dye,it can extend the power of absorption of a catalyst's toward visible region in spectra. Ability of fluorescence dyes makes this application to absorb the visible light to reach an excited state possible. Dyes has lower redox potential in the excited state than the ground state.The conduction band of photocatalyst has lower redox potential being used, consequently the cationic radicals and conduction band electron are formed when an electron is injected from the excited state into the conduction band.This phenomenon has been already investigated in photoelectrochemical cells, in the absence of molecular dioxygen. While dye itself can undergo an effective degradation in presence of dioxygen. As degradation is desirable when the dye is a target organic pollutant.

1.4.1 Photocatalysis

The acceleration of a photo oxidation reaction in presence of a catalyst,where catalyst can be a semiconductor as ZnO.Absorbtion of U V light by the substrate will be catalyzed to photolysis. In photocatalysis the activity depends on the capability of the catalyst to create electron–hole pairs, which will create free radicals (hydroxyl radicals: ·OH) so they able to undergo secondary reactions. Photocatalysis is an advantageous approach to clean living environments. Also with the modification and further enhancing this technology, we can able to control pollution in air and water. Even we can reduce the spread of infections and diseases such as SARS in hospitals. This new will provide a way of life which would benefit everyone. Photocatalysis consists of two parts:

1-Prefix photo is defined as "light",

2-Catalysis is defined as where a substance take part in modifying the rate of a chemical transformation of the reactants without altering the end product. Substance can be a catalyst which will increase the rate of a chemical reaction by decreasing the activation energy. Thus, photocatalysis is a process in which the reaction uses light to activate a catalyst due to which the rate of a chemical reaction will modified without being present itself.

1.4.2 Photocatalysis is a more advanced technique than conventional organic synthesis due to following reasons

1-Photocatalytic reactions are both oxidation and reduction which occurs simultaneously on the photocatalyst particles while in conventional reactions oxidizing agent and reducing agent are required separately.

2-Photochemical reactions do not need much of solvents as they are expensive and are difficulty to dispose them, generally water is used as solvents. But in conventional reactions various solvents are used depending upon the substance

3-Photochemical reaction is a one way single step reaction, we can get our product just by mixing the reactant and irradiating them but conventional reactions are multi-step reactions.

4-Photocatalytic reactions occur at ambient temperature and pressure so need not to maintain drastic conditions as required in conventional reactions.

1.4.3 Photocatalysts

Industrial and environmental contamination, which is increasing day by day around us or effecting our daily life, is a serious cause which should not to be avoided.Pollution caused by industrial and household wastes caused by air pollutants such as NOx and SOx are best examples of such contamination.The fact that using energy to eliminate such environmental contamination increases emission of CO2 resulting in more global warming, however, change to a dilemma not to use energy to achieve our anti-pollution goal.Under such circumstances, we have come to the conclusion that we need a new material that can gently harmonize the contaminated environment to restore original conditions by using natural energy which is a part of the environment and low-cost energy supplied to our daily home life. One solution to that problem is our proposal, Photo-catalyst.

1.4.4 The function of the photo-catalyst can be divided into five major categories as follows:

1-Water purification

2-Preventing contamination

3-Anti-bacteria

4-Deodorizing

5-Purifying the air (dissolving NOx)

The functions listed above are those which can amplify or accelerate the functions of ultra-violet radiation.It is not strange with regard to zinc oxide as a photo-catalyst from the viewpoint that it works as the catalyst in accelerating the functions of the light.

1.4.5 Photocatalyst has the following advantages over any current air purification technologies-

1-Real destruction of pollutant rather than a simple transfer on a substrate

2-Degradation of pollutant at ambient temperature and pressure

3-Build with easily available materials and by mean of well-known techniques

4-Economical, cheap and low energy consumption

5-Adapted for a large range of pollutant (VOC, bacteria, mold).

1.4.6 Significance of ZnO

ZnO is a white powder known as zinc white or mineral zincite.. Crystalline zinc oxide is thermochromic, changing from white to yellow when heated and in air reverting to white on cooling. Zinc oxide is an amphoteric oxide. It is nearly insoluble in alcohol and water, but it is soluble in most acids, such as hydrochloric acid:

$ZnO + 2\ HCl \rightarrow ZnCl_2 + H_2O$

Bases also degrade the solid to give soluble zincates:

$ZnO + 2\ NaOH + H_2O \rightarrow Na_2(Zn(OH)_4)$

It reacts with hydrogen sulfide to give the sulfide: this reaction is used commercially in removing H_2S using ZnO powder (e.g., as deodorant).

$ZnO + H_2S \rightarrow ZnS + H_2O$

When ointments containing ZnO and water are melted and exposed to ultraviolet light, hydrogen peroxide is produced..

1.4.7 ZnO nanoparticles act as a catalyst

ZnO is Ⅱ-Ⅵ compound semiconductor with wide band gap (3.37 eV) and has been broadly used in photocatalysis.Today, semiconductors are usually selected as photocatalysts, because semiconductors have a narrow gap between the valence and conduction bands. In order for photocatalysis to proceed, the semiconductors need to absorb energy equal to or more than its energy gap. This movement of electrons forms e^-/h^+ or negatively charged electron/positively charged hole pairs. The hole oxidize donar molecules.

1.4.8 Mechanism of photocatalysis

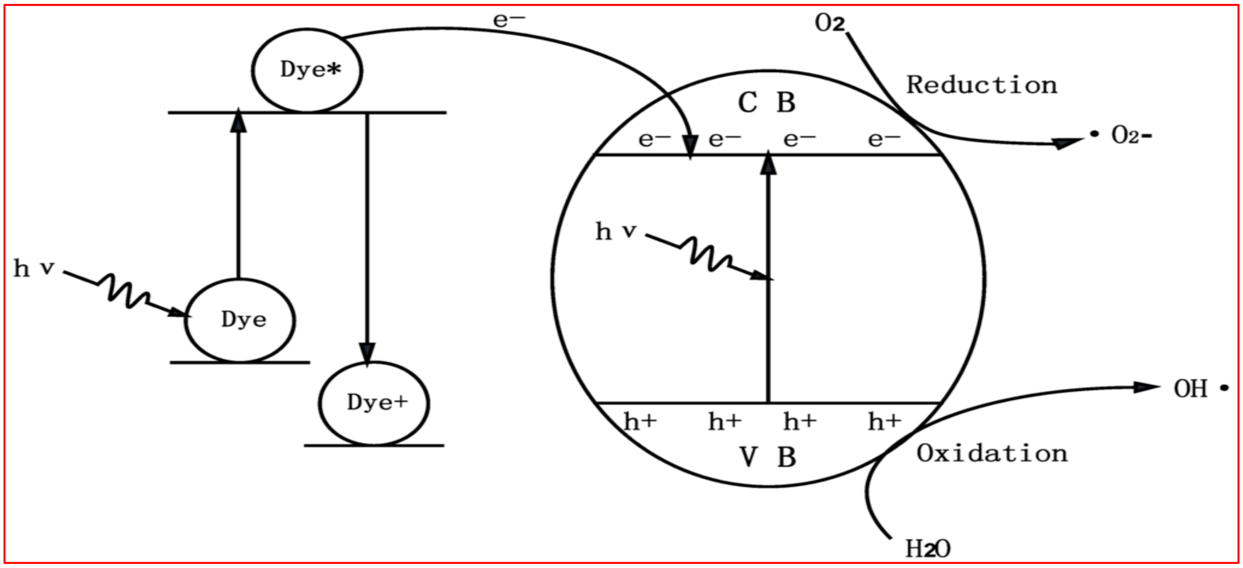


Figure 1.9 Mechanism of potocatalysis.

As given in figure 5.1 when we irradiate ZnO, the electron get excited from valence band to conduction band or can then either drop back down into the valence band resulting in recombination as heat, or it can react with other adsorbed species. Hole will oxidize the adsorbed species, such as organic compounds, water or hydroxyl ions as from mechanism.

$ZnO + hv \rightarrow e^- + h^+$

$e^- + h^+ \rightarrow heat$

All of these produced species are highly reactive. The electrons when combined with oxygen are stopped from dropping back to the valence band and prevent the electron-hole recombination.This means that the hole and the electron have more time to react with species adsorbed to the catalyst. A lack of dissolved oxygen would hinder the reaction as electron-hole recombination would occur far more readily,giving less time for the species.because the oxidation and reduction potential of valence band hole and conduction band electron, respectively, are appropriate for the most of the redox reactions of UV visible analysis.

1.5 Application of ZnO

Various applications of ZnO as described in the chart below figure- 1.8.Pharmaceutical as well as Commercial applications, also various medical purposes regarding human health to prevent from hazards.Photocatalysis is one of the most imp application of ZnO as it covers a wide researchable area.It is used to degrade pollutant externally.Researches are also carried out for various drugs designing due to degrading power of some organic dyes. Cosmetics is also a part of medical application as it is exploring for various purposes and diseases.

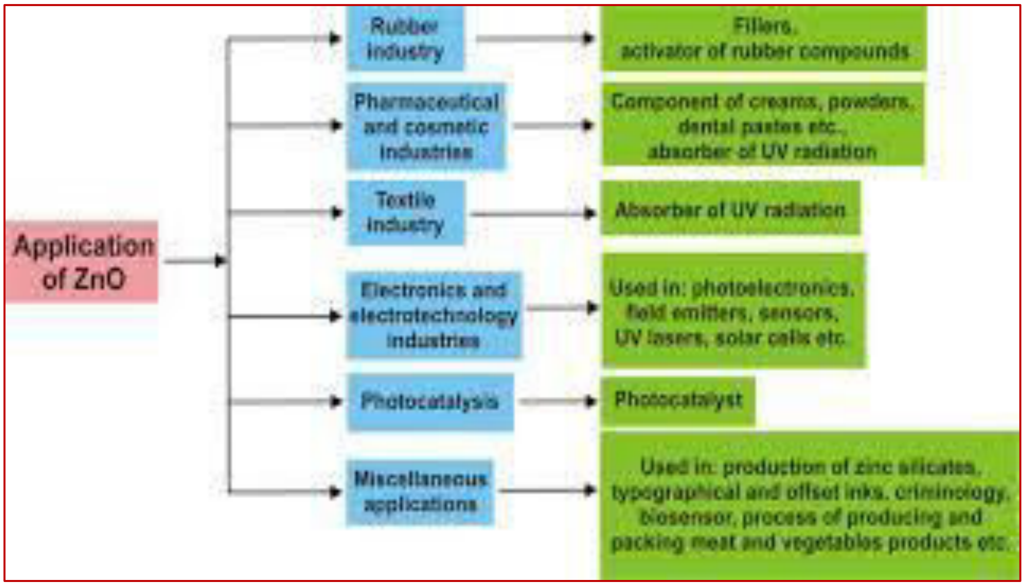


Figure 1.10 Schematic diagram to show applictions of ZnO.

Intensive work has given in recent years on photocatalysis. In this process, by means of oxidation or reduction reactions an electron-hole pair is produced below the intensity of light taking place on the surface of the catalyst. An organic pollutant can be oxidized in the presence of a photocatalyst, directly by means of a photogenerated hole or indirectly via a reaction with characteristic reactive groups as the hydroxyl radical OH produced in solution. ZnO provides less sensitive and superior activity to photocorrosion ZnO was obtained in solution, this being a low-cost method and low-temperature. A sample was placed on a set up containing an aqueous solution of organic dye while being exposed to UV radiation the solution was mixed and stimulated by uv light with or without catalyst. Absorption was measured instinctly after exposure to UV followed at set time intervals, using a UV/Vis spectrometer, ZnO nanospheres were obtained using an electrochemical method at room temperature.The photocatalytic properties of ZnO were determined using the example of degradation with rhodamine (RhB)

CHAPTER TWO

REVIEW OF LITERATURE

Studying ZnO nanostructures which have been synthesized by different methods such as hydrothermal precipitation method and sonochemical method.And their analysis by X-ray diffraction (XRD), scanning electron microscopy (SEM), photoluminescence (PL) techniques and UV–Visible spectroscopy The XRD revealed the hexagonal wurtzite structure of the ZnO nanostructures. And the morphology of the particles was obtained from SEM micrographs. Samples obtained by hydrothermal method were of rice grain shaped and that prepared by precipitation and samples obtained from sonochemical methods were spherical shaped**.** Hydrothermal technique is an important tools for advanced materials processing, owing to its advantages in the processing of nanostructures for a variety of technological applications such as biomedical, electronics, magnetic data storage, optoelectronics, catalysis, ceramics, biophotonics.The technique not only acts as one of the most attractive techniques for processing nano-hybrid and nano composite materials but also helps in processing monodispersed and highly homogeneous nanoparticles. The term ‘hydrothermal’ was first used by the British geologist, Sir Roderick Murchison (1792-1871) to define the action of water at elevated pressure and temperature in bringing about changes in the earth’s crust leading to the formation of various minerals and rocks. It can be defined as any heterogeneous reaction in the presence of aqueous solvents or mineralizes under high temperature and pressure conditions to dissolve and recrystallize (recover) materials that are usually insoluble under normal conditions.The sol-gel method offers controlled consolidation, shape modulation and patterning of the nanostructures. Concentrated ethanolic (ZAH) zinc acetate hydrate suspension when refluxed and distilled forms a transparent solution. Small ZnO nanoparticles of 5 nm can be grown under high concentration conditions by addition of hydroxides..Flower-like structures are very typical of ZnO and can be synthesized using simple hydrothermal methods. The flowers, composed of hexagonal ZnO nanorods, were synthesized at a temperature of 80°C using zinc acetate dehydrate and sodium hydroxide in aqueous solutions. The flowers, with nanorod petals as long as 3–5μm, could be synthesized in just 40 min.Flower-like ZnO nanostructures with nanosheet petals was synthesized through a hydrothermal route using ammonia as the reactants and zinc chloride. The flowers, averaging in size of about 50μm, are composed of sheets of thickness about 180–260 nm. Numerous well distributed nanostructures formed all over the copper plate substrate has reported the growth of cabbage-like nanostructures and flower-like using CTAB as the surfactant in a hydrothermal growth process at temperatures of 130, 160 and 190 °C. CTAB being a cationic surfactant reduces the surface tension and as such inhibits the formation of a new phase. CTAB acts as a transport medium to transport $Zn(OH)_4^{2-}$ growth units which come together to form individual rod-like structures at 120° C,which then self-assemble into the ZnO nanoflowers. Mesoporous and hollow structure have been attracting increasing attention for their special properties and potential applications. However, it is difficult to fabricate mesoporous and hollow structure in a single process. Linear poly (ethylene glycol) (PEG) has been widely used as a template in the synthesis of a series of materials on microscale and nanoscale. Our research group has been interested in exploring the connection of surfactant template, such as PEG,CTAB and oleic acid, with the structure and morphology of the micronanostructure materials New biotinylated silica-coated ZnO quantum dots (QDs)has been developed for improved bioimaging special due to the low cytotoxicity, high luminescence, high stability in aqueous solutions and high sensitivity.Also these materials can be used as advanced fluorescence probes for biological cell-labeling applications.The obtained ZnO nanosheets own the visible yellow-orange emission, allowing the bio-imaging applications and showing the potential prospects in the biomedical fields.ZnO/eugenol based sealers are extensively used in dentistry because of its antiseptic role.Co doped ZnO NPs with the diameter of 50 nm can be obtained via a biomineralization technique in presence of silk as templates.SF-coated Co-ZnO NPs remarkably stimulate the growth of cells when NP concentrations are less than 0.25mg/mL stimulating and the adhesion and proliferation of cell due to the SF peptide coating, indicating that the prepared Co-doped ZnO nano particles. Photocatalysis of methylene blue (MB) was studied for ZnO nanostructures synthesized by different methods. The ZnO nanostructures were further coated with Ag nanoparticles to superior its dye degradation capacity. The Ag coated ZnO nanoparticles will exhibit a higher degradation rate in compared with ZnO nanoparticles. Hence the process of dye degradation is reliable for degradation of dye due to oxidation by highly reactive hydroxyl radicals. Study was conducted on the effect of different parameters on ZnO as reaction ph,amount of catalyst, and concentration of MB dye. Study outlines the synthesis of nanostructured ZnO photocatalyst by hydrothermal, precipitation and sonochemical methods. The rate constant for Ag decorated ZnO photocatalyst is k = 2.109. Degradation kinetics of MB fitted was pseudo first order kinetics. Optimization of parameters was done for pristine and Ag coated ZnO photocatalyst obtained by hydrothermal method. Results were found that that at pH 13; 95 % dye degradation of MB is observed in 7 min for pristine sample and 98 % dye degradation is observed in 6 min for Ag decorated sample. Thus results shows that the nanostructured ZnO photocatalyst exhibits excellent photocatalytic activity and can be considered as a challenging photocatalyst for treatment of dye effluents.Solar photo catalytic technique with semiconductors like, ZnO ,TiO_2 etc are land mark for waste water treatment especially for the removal of dye stuffs and organics..The work deals with the photocatalytic activity of malachite green dye using synthesized ZnO nanoparticles with the Co Precipitation technique.With the variation in experimental conditions, four different samples of ZnO nano particles were obtained and characterized by XRD, SEM and FTIR instrumental method. The IR spectra shows a broad band between 530 and 490 cm-1 with shoulder shape, characteristic of ZnO. The images obtained by SEM of the samples shows plate-like nanoparticles. The ZnO nanoparticles are distributed well within the range of ~ 100nm, a favorable property to exhibit enhanced photo catalytic activity. Size of ZnO nano particle was calculated as 18.33nm, 17.10nm, 12.25nm, and 9.43nm for the four samples. The photocatalytic activity was carried out using different sources of energy like ultra sound radiation ,solar radiation and microwave radiation.Optimum conditions for the maximum degradation of dye was proposed by varying the experimental parameters like dose,ph etc These technique can be used for the treatment of industrial wastes containing dyes.In that places ,where plenty of sunlight, solar radiation can be used for degradation.But in places where don't have enough amount of sunlight than other sources of energy for the photo degradation can be used. A minute gram of (~ 20 mgL-1) of zinc oxide nano particles is used and there will be no harm in mixing this quantity of zinc in water streams, as it is one of the essential trace elements.These are helpful in designing effluent treatment plants in industries. Industrialization and environmental pollution on a global scale is gaining attention for developing new hygienically,friendly purification technologies. Presently wastewater treatment technologies are demanding high capital investment.Many of the problems as high chemical contamination in water, air and soil including high carbon compounds, are responsible to this fast pace of population growth. Human activities have been however disturbed the balance between the natural purification processes leads to a shortage of water. Drinking water and most of the natural resources are found to be contaminated with toxic materials and pathogenic microorganisms. However disinfection of drinking water is currently being carried out through chemical and physical techniques like ozonation, UV treatment and chlorination etc Modern nanotechnology offers opportunities for progress—defeating poverty, starvation and disease and expanding human capacities. It is defined as the ability to control, manipulate, understand matter at the level of individual molecules and atoms as well as at the "supramolecular" level involving clusters of molecules (in the range of about 0.1 to 100 nm), in order to create devices, systems and materials with fundamentally new properties and functions because of their small structure. Nanotechnology that results in improved waste treatment options include removal of the finest contaminants from water (< 300 nm) and "smart" materials or reactive surface coatings with induced specificity to a certain pollutant that destroy or immobilize toxic pathogens and compounds. Photocatalysis is currently a promising technique for water purification in comparison to other conventional methods it breaks the complex long chained organic molecules (toxic) into simpler fragments and also distort cell walls of microbes thereby immobilizing them Photocatalysis can be an attractive way as it is capable of removing chemical as well as biological contaminants. An efficient photocatalyst should absorb light preferably in the visible or near UV part of the electromagnetic spectrum. Photocatalysis applications are also gaining wide spread acceptance in agriculture and microbiology as it is important that the photocatalysts should be biologically inert and non-toxic.As nanostructured photocatalysts provide large surface to volume ratios therefore allowing higher adsorption of the target molecules.The mechanism of photocatalysis is schematically represented in Fig. (**1**). It involves a wide band gap of metal oxide, when irradiation with light of energy will be higher than the band gap energy of the material, electron-hole pairs (excitons) are conduction band while the hole drifts to the bottom of the valence band. Most of these photogenerated charge carriers undergo wasteful recombination, while escape recombination and initiate oxidation reduction reactions in molecules adsorbed at the surface of the photocatalyst and hence degrading them. Photogenerated holes and electrons have been found to degrade almost all types of inorganic , organic and microbial contaminants owing to their high redox potentials The fundamental process during photocatalysis is given by

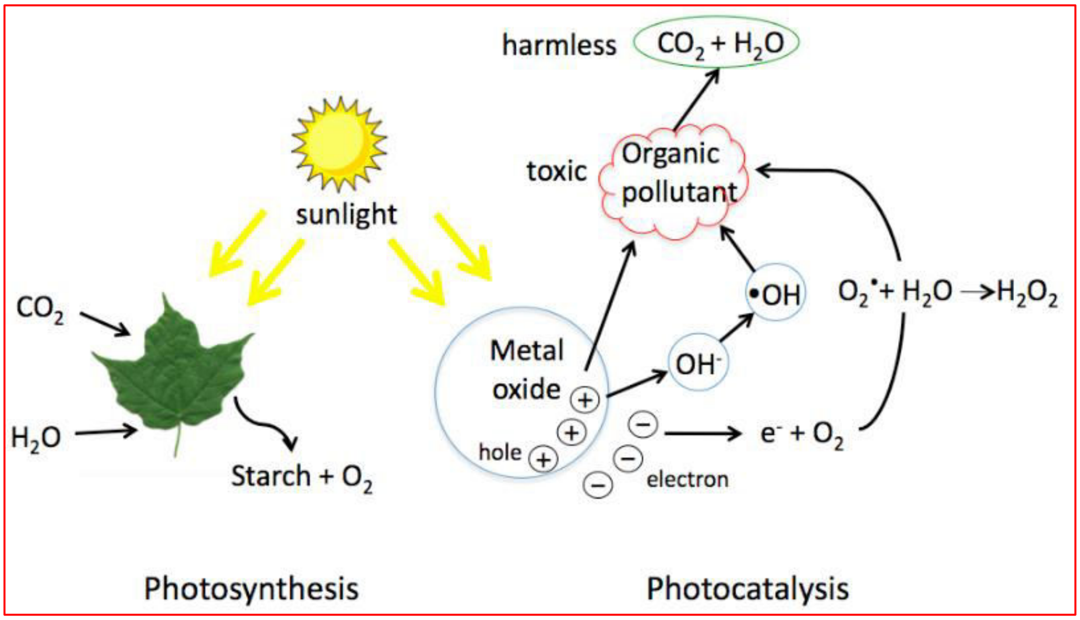


Figure 2.1 Comparison of photosynthesis process in leaves and photocatalysis using metal oxide nanoparticles.In photocatalytic process energy more than the optical bandgap of the semiconductors are generally required (compared to 2.5 eV for photosynthesis process). (Source-Nanoscience & Nanotechnology-Asia, 2012, 2,)

$MO + h\nu \rightarrow MO\ (e^- + h^+)$

where MO represents a metal oxide photocatalyst like TiO2,ZnO etc. Photo-generated electrons lead to the formation of superoxide anions (●O2–), hydrogenperoxide molecules (H2O2), hydroxyl radicals (●OH), hydrogen dioxide anion(HO2–) and the hydroperoxy radicals (●HO2)

MO (e–) + O2 → MO + ●O2–,

MO (e–) + ●O2– +2H+ → MO + H2O2,

MO (e–) + H2O2 → MO + ●OH + OH–,

●O2– + H2O2 → ●OH + OH– + O2,

●O2– + H+ → ●OH2,

MO (e–) + ●OH2 → MO + HO2–,

HO2– + H+ → H2O2,

2●OH2 → O2 + H2O2.

While the oxidation reactions initiated by the photogenerated holes are:

MO (h+) + H2O → MO + ●OH + H+,

MO (h+) + H2O → MO + ●OH + H+,

MO (h+) + OH– → MO + ●OH.

The reactions are terminated as:

●OH + H+ + 2e– → H2O,

1/2 O2 + 2H+ + 2e– → H2O.

Metal oxide nanoparticles when photocatalysed as higher the efficiency of the photocatalytic reactions ,higher the surface area available and more adsorption of the target molecules will be done, with a high surface reactivity owing to large number of active sites, has emerged to be an efficient photocatalyst as compared to TiO2. ZnO is an attractive material for water treatment as it can be tailored to absorb visible light and is capable of ushering in the era of solar photocatalysis. It has an edge over other metal oxides like TiO2 in water purification.But in general further to advanced research, small size ZnO nanoparticles have increased their more numbers of active surface sites and their specific surface area where the photogenerated charge carriers are able to react with absorbed molecules to form hydroxyl and superoxide radicals. Small ZnO nanoparticles with no capping agents can easily form aggregations, leading to the loss of its active sites and photocatalytic efficiency. Moreover, the high electron–hole recombination rate also limits the photo-oxidation rate of organic compounds on ZnO surface, and also aggravates its photo-corrosion in photocatalysis process. To develop a simple and effective technique to overcome the drawbacks of ZnO by enhancing its photocatalytic efficiency while compensating the formation of aggregations. Graphene oxide (GO) with hydroxyl and carboxyl groups, which have excellent solubility and it provides various opportunities for the construction of GO-based hybrid composites. The GO-based hybrids with metal and metal oxide nanoparticles such as ZnO, TiO2, Fe3O4, Pt, Au, Ag have shown potential applications in the areas of catalysts , sensors, optics, electronics. But in all of these, the fabrication of GO-based hybrid catalysts, especially for the photodegradation of organic pollutants, is of the utmost research at current stage. Also GO shows strong positive effect in the stabilization of the photocatalytic nanocrystals and dispersion without the introduction of organic surfactants. Illustrated the unique electronic properties, extremely high specific surface area and locally conjugated aromatic system of GO, making it ideal candidates for catalyst carrier or promoter.

CHAPTER THREE

EXPERIMENTAL TECHNIQUES AND INSTRUMENTS

This chapter gives a detailed information about the techniques that are used in the experimental work. Such as TEM, HRTEM, SEM, XRD, UV Spectroscopy and BET.And instruments that are used during the present work.

3.1 X-Ray Diffraction

English physicists Sir W.H. Bragg developed a relationship in 1913 to explain the cleavage faces of crystals that appear to reflect X-ray beams at certain angles of incidence (theta). This observation is an example of X-ray wave interference (Roentgenstrahlinterferenzen), commonly known as X-ray diffraction (XRD). Diffraction has been developed to study the structure of all states of matter with any beam, Although Bragg's law was used to explain the interference pattern of X-rays scattered by crystals, e.g., ions, electrons, neutrons, and protons, with a wavelength similar to the distance between the atomic or molecular structures of interest.It is a technique used to study periodically ordered structures at atomic scales. The wavelengths of X-rays are in the same order of magnitude as the distance between lattice planes in crystalline materials. When the X-rays enter the material, they get scattered by the electron clouds around the atoms. The periodicity of the lattice planes gives rise to constructive interference of the X-rays shown in figure 2.1and the intensity of the scattered X-rays is plotted against the angle 2θ

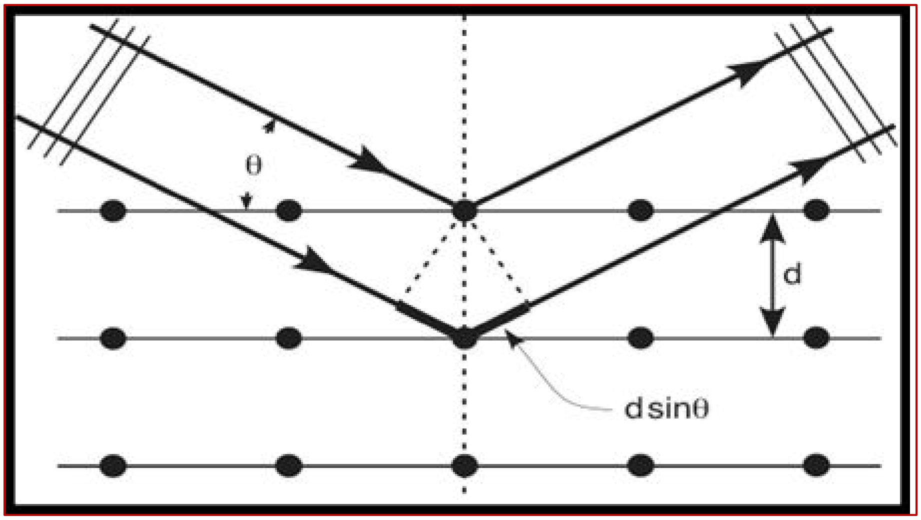


Figure 3.1 Bagg's law pattern

From the plotted peaks the lattice distance can be calculated using Bragg's law as follows:

$$n\lambda = 2d \operatorname{Sin}\theta$$

Where *n* is an integer known as the order of the diffracted beam, λ is the wavelength, *d* is the distance between crystal planes and *θ* is the angle of the diffracted wave. The atomic planes of a crystal cause an incident beam of X-rays to interfere with one another. This phenomenon is called X-ray diffraction.

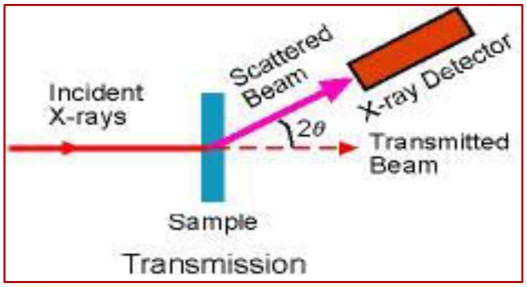


Figure 3.2 Working pattern of XRD

The mesostructure of synthesized nanopartilces has been analyzed by XRD measurement using Cu Kα radiation (λ= 1.54056 Å).A photograph of XRD instrument is shown in Figure-2.3. The accelerating voltage has been set at 40 eV and the current flux has been set at 40 mA. High resolution X–ray diffraction spectra (HRXRD) were recorded on Bruker D8 Discover instrument

Figure 3.3 Photograph of (XRD) taken figure from our laboratory.

Bragg diffraction may be carried out using either light of very short wavelength like X-rays or matter waves like neutrons (and electrons) whose wavelength is of the order of (or much smaller than) the interplanar spacing. The pattern produced gives information of the separation of crystalline planes allowing to give the crystal structure. In terms of the specimens handled, two methods can be identified, namely, the powder method and the single crystal method. In the former, the specimen is a collection of crystallites. Since the fragments are completely randomly oriented, the incident X-ray beam meets with every possible lattice plane, oriented in all the directions. On the other hand, in the single crystal technique, the whole specimen is a single piece, without any discontinuity in the lattice arrangements.

3.1.1 Transmission electron microscopy (TEM)

It is technique in which a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through. An image will be produced formed from the interaction of the electrons transmitted through the specimen; the image will be magnified onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor. TEMs are capable of imaging at a significantly higher resolution, according to the small de Broglie wavelength of electrons. This enables the user to examine fine detail,even as small as a single column of atoms, which is thousands of times smaller than the smallest resolvable object.TEM images contrast is because of absorption of electrons in the material, due to the composition and thickness of the material. At higher magnifications complex wave interactions modulate the intensity of the image, requiring expert analysis of observed images..

Figure 3.4 Tranmission electron microscopy,taken from laboratory.

TEM utilizes a stronger electron beam (~300 kV), and allows for the visualization of pores. TEM is not a substitute for XRD, since only a small sampling is obtained. The magnification achievable by TEM is in the order of 300,000x. TEM gives evidence in support of the powder XRD regarding pore structure and order. The photograph of the TEM instrument is shown in Figure-2.4.The bright field electron micrographs of the samples have been acquired with TECNAI TEM machine (FEI TEM model TECNAI G2 T30, U–TWIN with electron source Tungdten ot LaB6 filament) at the accelerating voltage of 300 keV. To take the measurements, 10 mg of sample was mixed in 1 mL of ethanol and sonicated for 10 min. to achieve uniform dispersion of the particles. A drop of the ethanolic solution was put on carbon coated copper grid and images were taken using TECNAI TEM machine.Mechanism of tem as shown in fig-2.5.

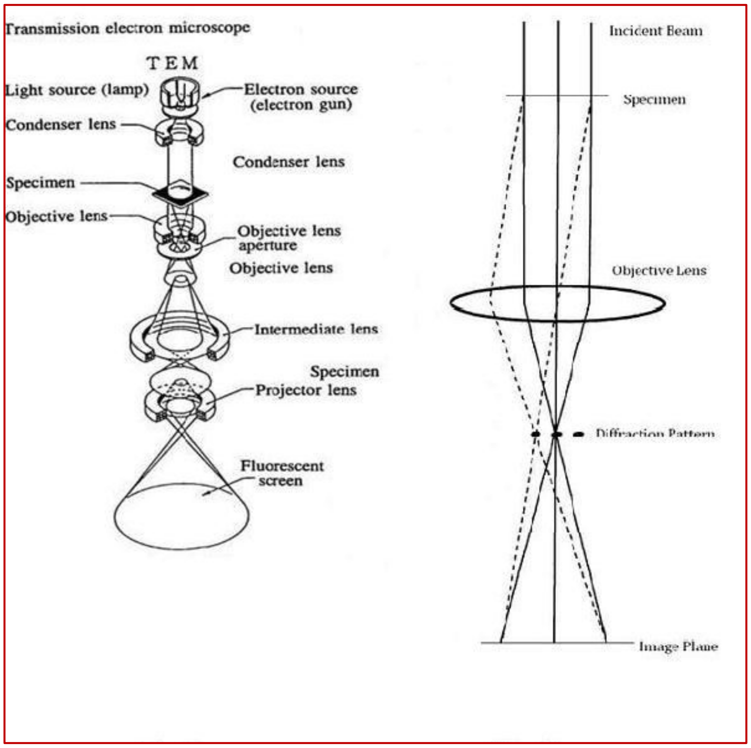


Figure 3.5 Working of TEM

First illumination system will takes the electrons from the gun and transfers them to the specimen giving either a focused beam or a broad beam. In the ray-diagram, above the specimen parts belong to illumination system. The objective lens and stage is the heart of TEM imaging system.It includes the intermediate lens and projector lens. The diffraction pattern and image are formed at the back focus plane and image plane of the objective lens. As TEM works in diffraction mode. If we take the image plane of the objective lens as the objective plane of the intermediate lens and projector lens, we will form image on the screen. It is the image mode.

3.1.2 Scanning electron microscope (SEM)

It utilizes a lower voltage electron beam (<20 kV) and is useful for determining exterior particle morphology to about 50,000x magnification. The shape and size of the nanoparticles are readily observed by SEM. The SEM for morphological investigations has been carried out using field emission scanning electron micrsoscope (FE-SEM) (SEM, JEOL, JSM-6360A) system**.** The sample was deposited on a sample holder with an adhesive carbon foil and sputtered with gold. The photograph of the SEM instrument is shown in Figure 2.6.In SEM, a finely focused beam of energetic (5-30 keV) electrons is scanned across the surface of the specimen to create its magnified image. Since electrons have shorter wavelengths compared to photons, the resolution obtained in SEM is very high compared to that in conventional optical microscopy. Furthermore, the depth of the focus in SEM is much greater along with higher magnification than that achieved in optical microscopy. SEM utilizes the emissive electron-specimen interactions to provide information on the morphology, topography, internal magnetic or ferroelectric domains and compositional variations prevailing in the specimens

Figure 3.6 Scanning electron microscopy,as taken from laboratory.

Briefly, it consists of an electron source, two or more electron lenses also known as condensers, a deflection system and detectors. The electron source produces the beam of electrons that is focused by the condensers. The function of the deflection system is to scan the beam across the specimen surface whereas the detectors record the electron-specimen interactions. The output from a detector is used to modulate the intensity of a cathode ray tube (CRT), which is scanned synchronously with the scan probe on the specimen to produce the image. The magnification is given by the ratio of the CRT scan size to the specimen scan size. The image thus obtained represents the variation in intensity of the signal collected by the detector, as a function of X-Y space on the specimens. SEM images are in fact two-dimensional representations of three-dimensional objects. However, the high depth of the field of SEM lends three-dimensional appearance to the specimen images. Energy Dispersive Specimen (EDS) is a technique used for identifying the elemental composition of the specimen. It is sometimes also referred to as EDAX (Energy Dispersive Analysis of X-rays). During EDS analysis, the specimen is bombarded with a high-energy electron beam. Because of the small size of the electron probe, it is possible to obtain elemental analyses for volumes as small as 1μm in diameter. The incident electron beam can create a vacancy (hole) in the inner-shells of an atom, which leaves the atom as an ion in the excited state. It can relax to its ground state via two competitive processes. One of it involves transitions of outer-shell electrons leading to the emanation of characteristic X-rays. The Auger process is other competitive process. The detection of the characteristic X-rays while performing micro structural investigations by SEM is extremely useful for micro area analysis providing elemental identification and quantification. From the X-ray spectrum emitted by any specimen, two things can be determined; (1) by measuring the energy (wavelength) of each characteristic X-ray that is emitted, elements present in the specimen are identified (qualitative analysis), and (2) by measuring of intensity of X-rays of a given energy, amount of the element present is determined (quantitative analysis) since X-ray intensity can be related to the concentration (i.e., mass or atomic fraction) for each element present. If a light element is not detectable, it is sometimes possible to account for it by difference or by stoichiometry. Insulating materials need to be coated with a conducting layer of C or Au.

3.1.3 UV VISIBLE SPECTROSCOPY

UV spectroscopy is type of absorption spectroscopy in which light of ultra-violet region (200-400 nm.) is absorbed by the molecule. Absorption of the ultra-violet radiations results in the excitation of the electrons from the ground state to higher energy state. The energy of the ultra-violet radiation that are absorbed is equal to the energy difference between the ground state and higher energy states.

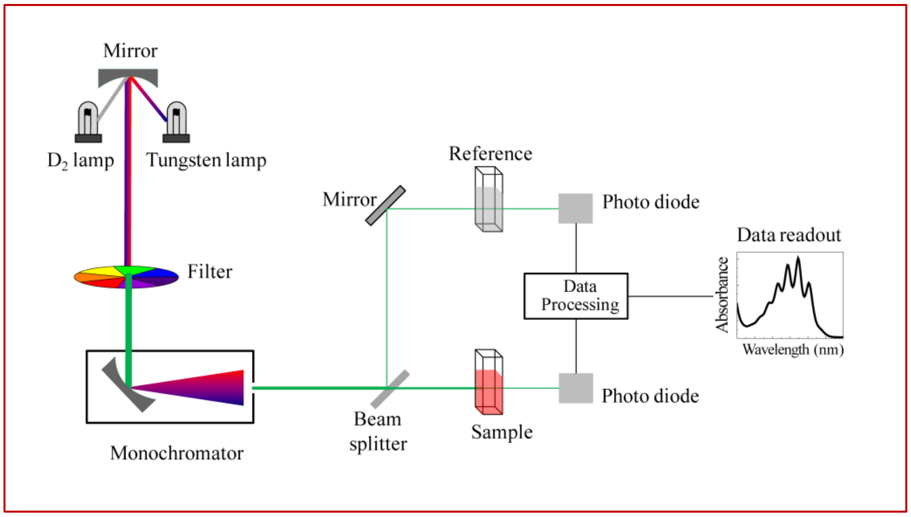


Figure 3.7 working pattern of uv spectrophotometer.

UV spectroscopy obeys the Beer-Lambert law, which states that: when a beam of mono chromatic light is passed through a solution of an absorbing substance, the rate decreases of intensity radiation with thickness of the absorbing solution is proportional to the incident radiation as well as the concentration of the solution. The expression of Beer-Lambert law is-

$$A = \log (I_0/I) = Ecl$$

Where, A = absorbance

I_0 = intensity of light incident upon sample cell

I = intensity of light leaving sample cell

C = molar concentration of solute

L = length of sample cell (cm.)

E = molar absorptivity

From the Beer-Lambert law it is clear that greater the number of molecules capable of absorbing light of a given wavelength, the greater the extent of light absorption

3.1.3.1 Instrumentation and working of the UV spectrometer

Light Source -Tungsten filament lamps and Hydrogen-Deuterium lamps are most widely used and suitable light source as they cover the whole UV region. Tungsten filament lamps are rich in red radiations; more specifically they emit the radiations of 375 nm, while the intensity of Hydrogen-Deuterium lamps falls below 375 nm

Monochromator-are generally composed of prisms and slits.The most of the spectrophotometers are double beam spectrophotometers.

Sample and reference cells-One of the two divided beams is passed through the sample solution and second beam is passé through the reference solution.

Detector-Generally two photocells serve the purpose of detector in UV spectroscopy. One of the photocell receives the beam from sample cell and second detector receives the beam from the reference.This results in the generation of pulsating or alternating currents in the photocells.

Amplifier-The alternating current generated in the photocells is transferred to the amplifier.

Recording devices-Most of the time amplifier is coupled to a pen recorder which is connected to the computer.

Figure 3.8 UV Spectroscopy,taken from chemistry laboratory.

3.1.4 Brunauer Emmett Teller

The most frequently used procedure to determine the surface area of a porous material is the (BET) method.This method has evolved from the Langmuir theory with multilayer corrections.

Figure 3.9 Pore size area analyzer,taken from laboratory.

To calculate the BET surface area the monolayer capacity, nm, of the material is determined from the BET-plot. This is the best linear fit of the adsorption isotherm. BET theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material. The concept of the theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption. The calculation is modeled on the physical adsorption of gas on the surface of the material as a function of pressure. Surface area determinations involve creating the conditions required to adsorb an average monolayer of gas molecules onto a sample. As pressure increases, the amount of gas adsorbed quickly rises due to the capillary condensation in mesopores. This gas condensation occurring in the mesopores allows the fine porous structure of the sample to be evaluated. The pressure is increased until saturation is reached when all mesopores are filled with liquid. The pressure is reduced incrementally, evaporating the condensed gas from the system.

3.1.5 Photoluminescence (PL) spectroscopy

Fluorescence spectrophotometer is a sensitive instrument for the study of fluorescence emission and excitation spectra of compounds. It provides high sensitivity and rapid scanning.This instrument is equipped with a Xenon flash lamp allowing the user to choose the collection mode of choice: as fluorescence, phosphorescence. The instrument has two mono-chromators, excitation and emission, and an extended range photomultiplier tube detector .It is able to scan at the rate of 24000 nm/min without any peak shift. The spectrophotometer are used to record the excitation and emission spectra of liquid as well as powder samples. The photoluminescence spectra are dependent on the excitation and emission wavelength of the samples. The majority of fluorescence assays carried out in solution, and final measurement made upon the sample contained in a cuvette or in a flow cell. Teflon made cuvettes may be squarer rectangular (the latter being uncommon),it must be made of a material that will transmit both the incident and emitted light. The cuvette is placed normal to the incident beam and resulting fluorescence is given off equal in all directions. All fluorescence instruments contain three basic items: a source of light, a sample holder and a detector. For its analytical use, the wavelength of incident radiation should be selectable and the detector signal capable of precise manipulation and presentation .Principle of operation of a fluorescence spectrophotometer is as follows: light from the excitation source is dispersed by the excitation mono-chromator and then incident on the sample. Fluorescent light from the sample is dispersed by a similar mono-chromator incident on the photomultiplier tube. The light is there transformed into a weak electrical and feed to the photometer where it is amplified.Fluorescence emission spectrum is reproduced on the recorder, when the sweep power is connected to the scanning emission mono-chromator, and the emission mono-chromator is set at a wavelength for its maximum wavelength

Figure 3.10 PL Spectrophotometer of laboratory was used for this study.

3.2 Vacuum oven

It is used for drying the material according to the temperature needed for that particular sample. But material can be dried at max 200 °C ,lowest it can be 20 °C or 50 °C or depends..

Figure 3.11 Vacuum oven (source-In laboratory)

3.2.1 Autoclave

Autoclaves used in this work are made of stainless steel with tight fitting of nuts. Inside this white Teflon is used of beaker shape in which sample is to be kept but it can not be filled to full volume only 75% of the total volume of the capacity of that autoclave can be filled and most important is handling of autoclave because it creates pressure inside so nuts and bolts should be air tight and check before placing in the vacuum for a definite temperature.

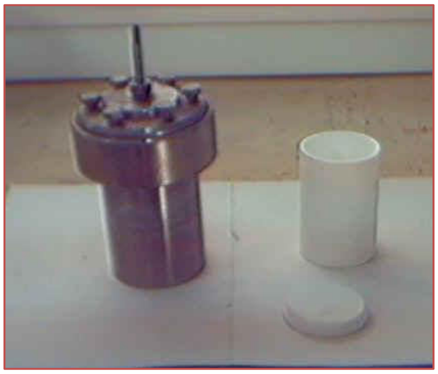


Figure 3.12 Autoclave with Teflon lining(source-In laboratory)

3.2.2 Furnace

A muffle furnace is (usually) a front-loading box-type oven or kiln for high-temperature applications such as fusing glass, creating enamel coatings, ceramics and soldering and brazing articles. Solid dried material can be placed at high temperature but below its melting point. Furnaces are usually heated to desired temperatures by connvection, conduction,or blackbody radiation from electrical resistence elements.

Figure 3.13 Muffle furnace(source-In laboratory)

3.2.3 Reflux

A liquid/solution reaction mixture is placed in a round flask that have two or three neck top most is to fix condenser other two for thermometer and sometimes third for adding drop wise solution. This vessel is connected to a condenser, such that any vapors given off are cooled back to liquid, and fall back into the reaction vessel therefore it has a inlet and a outlet ,connected by the tap water through inlet. The vessel is then heated vigorously for any course of time of reaction at particular temperature. The purpose is to thermally accelerate the reaction by conducting it at an elevated temperature. The advantage of this technique is that it can be left for a long period of time without the need to add more solvent or fear of the reaction vessel boiling dry as any vapour is immediately condensed in the condenser. In addition, as a given solvent will always boil at a certain temperature, one can be sure that the reaction will proceed at a constant temperature. One can control the temperature by careful choice of solvent within a very narrow range. The continuously mixing of the solution serves the constant boiling action. Whereas a magnetic stirring mechanism is also used to achieve a uniform solution The technique is very useful for performing reactions that will work under controlled conditions which require substantial time for completion. This method will provide high and improved yield of particles, uniformity, less reaction time, short time, small and reduced size of particles, well dispersed and enhanced particles.

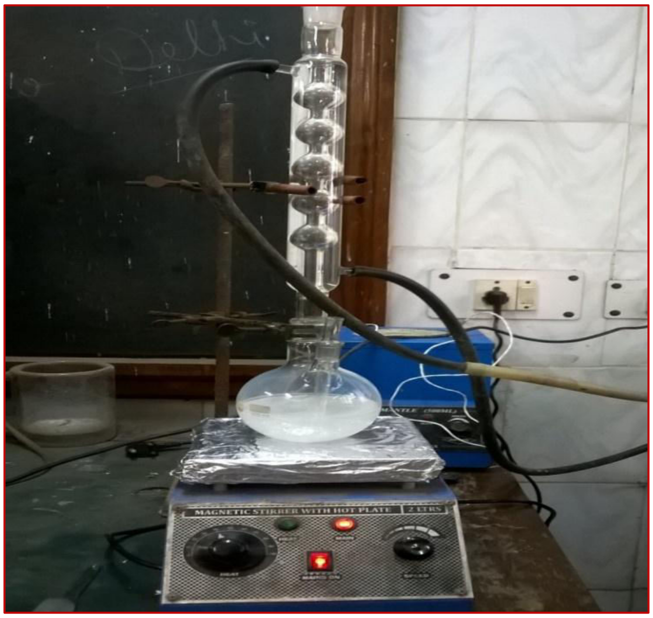


Figure 3.14 Refluxing setup (source-In laboratory)

CHAPTER FOUR

EXPERIMENTAL AND SYNTHESIS

The chapter experimental and synthesis has been divided in two parts

(A) To prepare solution of organic dyes at different molar concentration.

(B) Preparation and synthesis of ZnO mesoporous particles.

PART-A

In this chapter firstly preparation of organic dye solution used in the laboratory for this study has been discussed. The method and the parameters which are used in the preparation are given in detail. Fluorescence quantum yields of different organic dye solution have been studied by recording photoluminescence spectra. The PL studies of the dyes with solutions having some radical species produced by dissolving aqueous ammonia also studied in order to find the possibility of estimating their concentration. It was analyzed that the PL intensities of the solution get sensitized/ quenched with the concentration of the foreign radicals. Thus, there exists a possibility of using these solutions as an active medium for detecting such toxic gases.

4.1 TO PREPARE ORGANIC DYE SOLUTION

4.1.1 Solvents of organic dyes

For the preparation usually very small quantity of organic dye is to be taken, A typical dye concentration is 10^{-2}M to 10^{-5} M. Due to which the solvent in which the dye is to be dissolved plays very important role for defining physical properties and potential hazards. Lasing wavelength and energy are very sensitive to the choice of solvent. There are so many dyes which have polar molecules and with the excitation to their lowest lying singlet state gives an increment to the dipole moment. So the solvent polarity plays very important role in shifting of the wavelength. Most of the time the gain of curve will shift toward longer wavelength and it will lead to increase solvent polarity. Even in some polar dyes, the shift can be as high as 20-60 nm. But in some cases due to vibrational overtones that interfere with the lasing process ,solvent cannot be used with longer wavelength. Solvents can be like water, ethanol, methanol but it will depend largely to the physical and chemical property of the dye as they play most important role for deciding the solvent and handling to these dyes is also very important as some dyes are toxic and some are not. Before working to the particular dye its properties, character and behavior should be read properly. It is clearly given for each dye that in which solvent they will dissolve properly. As for most of the dyes will dissolve in water. But they are often not useful solvents for near IR and therefore IR dyes due to the presence of hydroxyl group overtones in this spectral range. Accordingly, the solvent DMSO or polychlorinated aromatics, which lack hydroxyl resonances, are commonly used for dyes that lase in the near-IR and IR regions of the spectrum. But these solvents are toxic and can harm to the body indirectly by entering through skin which in contact while working or handling. So, it is strongly advice to handle all organic dyes with lots of care needed and solutions containing organic dyes should be placed in well ventilated environment.

. 4.1.2 Stock solution

Particular dye should be weighed according to their molar mass and transfer it to a beaker or flask of 250ml/500ml.Because direct exposure of light can effect dye or dye solution by degrading it so brown bottles are frequently used to avoid direct light. It will make sure that entire dye is transferred to the bottle and be care full while pouring to the bottles ,most of the errors occur while transferring for different molar concentration. Adding 5% more or less solvent does not affect the operation because it can be stored as stock solution but molars should be accurate. Stock solution are recommended when any circumstances occur because of any fault or error. The solution may be ultrasonicated for 10-20 min or depending upon the dissolving power of that particular dye, most of dyes frequently dissolves with their respective solvents. In this section specifications of different organic dyes used in the laboratory has been discussed.

Figure 4.1 Prepared stock solution of different dyes in our laboratory.(a) Congo- red(b) Malachite green(c) Fluoroscein sodium(d) Rhodamine b.

4.1.3 EXPERIMENTAL

For studying the quantum yield of different dyes, Malachite green and Rhodamine B were procured from spectro chem India ltd and used without any further purification. Distilled water was used as a solvent. Cary Eclipse Spectro fluorometer was used to record the Photoluminescence spectra of dyes under investigation. Excitation and emission slits were fixed at 2.5 and 2.5 nm respectively. Scan rate was at 600nm/min with data interval of 1 nm throughout the experiment, average time was 0.1 sec. For all the organic dyes, the dye solutions concentration in distilled water were varied from 10^{-3} to 10^{-6} M and corresponding emission spectra were recorded at fixed excitation wavelength.

A Rhodamine b dye

With 479.02 molecular weight of dye 0.023951 g is weighed for 50ml,it is 10^{-3}M.After removing 1ml and adding 10 ml water to the other bottle it will make 10^{-4}M. As like this $^{10-5}$M and 10^{-6}M concentration will be prepared with stock solution.Rhodamine-b is pink in colour and easily dissolves in water The solubility of Rhodamine B in water is ~15 g/L Chlorinated tap water decomposes rhodamine B. Its solution absorbs plastics and should be kept in glass.Its chemical formula is $C_{28}H_{31}ClN_2O_3$ and molar mass 479.02 it fluoresce and thus can be detected easily and inexpensively with instruments called fluorometers. The photograph of prepared dye solution in the laboratory is shown in Figure 4.1. The dye solutions of different concentration starting with 10^{-3} to 10^{-6} M concentration have been in the laboratory using different solvent with ultrasonic bath.

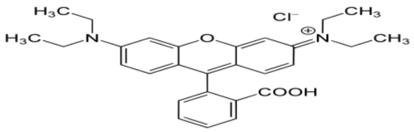
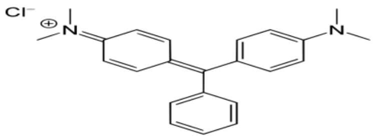
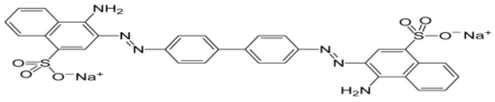
B Malachite green dye

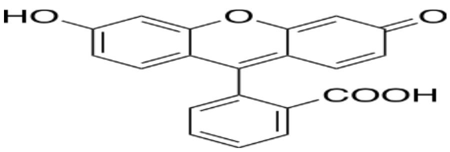
With 927.03 molecular weight of dye 0.0463515g of MG is weighed for 50 ml, it is 10^{-3}M.In the same procedure as above mentioned 10^{-4}M, 10^{-5}M, 10^{-6}M were prepared with stock solution and give ultrasonic bath for 20 min to the solution. Figure 4.2 depicts image of prepared different molar concentration with their stock solutions.

Figure 4.2 Variation in different molar concentration of malachite green as prepared in laboratory

Not all dyes fluoresce, only some organic compounds that exhibit fluorescence when dissolved in solids or solutions. Strong fluorescence is one of the most important conditions for laser action to occur from organic compounds. Many atoms and molecules emit absorbed light as fluorescence in gas phase. The absorption and reemission of light from molecules is not a simple process. Several non-radiative processes precede and/or compete with the reemission process. Often, the entire energy of an absorbed photon is converted into heat. Conversion of absorbed light into re emission of photons from organic compounds called luminescence, consists of two parts called fluorescence and phosphorescence.

Table 4.1 The Physicochemical data of different organic dyes that used in the present study is given below in the Table.

Organic dyes	Formula	Structure	Properties
Rhodamine	$C_{28}H_{31}ClN_2O_3$		Molar mass=479.02 Soluble in water
Malachite Green	$C_{23}H_{25}ClN_2$ (chloride)		Molar mass=364.911 g/mol (chloride Soluble in water
Congo Red	$C_{32}H_{22}N_6Na_2O_6S_2$		Molar mass=696.665

Fluoroscein	$C_{20}H_{12}O_5$		Soluble in water Molar mass=332.31 g·mol^{-}
Stilbene-420	$C_{28}H_{20}O_6S_2$.2Na		Molar mass=562.56

4.1.4 ORGANIC DYES IN SOLUTION

Two dyes has been reported for its laser activity, as malachite green and Rhodamine b are popular classes of organic dyes emitting orange and red region in the spectrum respectively. Rhodamine b and its derivatives are known molecules for investigations in biochemistry and biophysics. External and Internal interaction processes like, intra-molecular transfer of charge, light induced cis-trans photo isomerization multiple electronic states with their complex structure giving pathways for excitation energy, high sensitivity on internal electronic interactions by substituted groups and also external electrostatic interactions with solvent molecules, all these phenomena makes these two dyes among the most intensively investigated compounds in photochemical and biophysical investigations. The unique spectral-luminescence properties of rhodamine b dyes are widely used as markers and probes in studies of various objects including biological systems in sensors including those based on Langmuir-Blodgett films in supra-molecular chemistry and in studies of nano objects prepared by the sol- gel method. In this study we have taken two important dyes. The first dye is Malachite green and the second dye is Rhodamine b. The physical properties and chemical data of these dyes is as given in Table 4.1. The Lasing efficiency of these dyes is very high and the chemical stability is also good. We have chosen the solvent distilled water as both can dissolve efficiently. These two have very high sensitivity for detection even fluorescence sensing of chemical and biochemical analytes can be achieved by high sensitivity detection. These are most sensitive technique because of the different ways of measuring absorbance and fluorescence. Since absorbance of light is measured with the difference in intensity between light passing through the reference and sample. But in fluorescence the intensity is measured directly, without comparisons with the reference beam. This technique can also detect even a very small concentration of an analyte.

4.1.5 Interaction of aqueous ammonia to the organic dye solution

For luminescence studies of toxic gases as formally experimented with aqueous ammonia added to these dyes, the amount of ammonia solution to be added is in micro at each reading For luminescence study photoluminescence excitation and emission spectra are recorded..This results in the quenching of the fluorescence spectra of the organic dye. This principle can be used for the sensor development (proposed study). In this section objective is to explain the mechanism of fluorescence quenching/fluorescence sensitization of organic dyes in presence of aquous ammonia a toxic gas. Ammonia (NH_3) is a primary hazardous air pollutant. It is a common naturally occurring substance. Ammonia with direct exposure to human can lead to irritation to nose or skin even eyes. It is a health hazardous at high concentration it can lead to serious harm to human health, adversely affecting the biotic nature of water resources especially aquatic life. It may also be present in dissolved form in other wastes. Major sources of ammonia are natural as decaying of plants and animals and from human wastes also from man made sources such as extensive use of fertilizers and pesticides and waste of industrial sites. The toxicity of ammonia is well recognized. Concentrations of 5–10 ppm in air are recommended threshold limits for human exposure and 2 ppm is the recommended limit for working environments. However, much more concentrations of NH_3 could be found in atmosphere, especially, during high traffic hours and near industries, causing biohazards and hazards to human health. Excess levels of NH_3 may cause sensory and breathing problems such as, broncho-constriction (airway narrowing) and unconsciousness. Therefore, the monitoring of ammonia in air is of special importance for pollution control and efforts to develop methods of analysis and sensors to carry out this task are required. There is a rapid need for, sensitive, extensive and reliable sensor for the precise detection and monitoring of NH_3 as in liquid (dissolved in a solvent) state, also a need for finding new indicators, that could be, reliable, reusable and sensitive. It has been demonstrated that the fluorescence quenching the decrement of intensity due to the presence of NH_3 in the solution could be used to detect and monitor the dissolved NH_3 in aqueous solutions. The presence of NH_3 in gaseous form can also be monitored and detected continuously by passing air consisting of traces of NH_3 through the dye solution and measuring the intensity of the sensitized fluorescence emission spectra. Quantitative data on the fluorescence quenching of aqueous ammonia with solution is reported here. Another advantage of quenching is that the decrease in the fluorescence emission intensity on addition of the quencher NH_3 reduces the signal to noise ratio. Thus an efficient sensor or NH_3 could be constructed. Fluorescence quenching refers to any process which decreases the fluorescence intensity of a certain fluorophore. A variety of processes can result in such a decrease in intensity such as collisional or dynamical quenching, static quenching etc. dynamic quenching results with collision between fluorophore in its excited state and quenching molecule. The fluorophore returns to ground state without emission of light. On the other hand in static quenching, a non-fluorescent complex is formed between the fluorophore and the quencher. Usually only a fluorophore which is not complex can exhibit fluorescence. As in both the cases, the fluorescence intensity is related to the concentration of the quencher. The MG dye is the most effective and useful material in the orange region. It is superior to the known Coumarin dyes with respect to their threshold ,slope efficiency and its photochemical stability, as the yellow-orange emission is in the most sensitive region of the common photomultiplier tubes, it is very sensitive and suitable for many applications Malachite green and rhodamine are chosen as fluorophore for studying quenching in the presence of aqueous ammonia because of its stability against structural changes with a change in environment temperature, solvent, concentration etc.

PART B

4.2 SYNTHESIS OF ZnO

4.2.1 Materials

Zinc nitrate hexa hydrate have been purchased from spectro chem India Ltd.Urea also from spectro chem India ltd. Cetyltrimethylammonium bromide (CTAB, AR Grade), Sodium Hydroxide (NaOH, AR Grade) and Mesitylene have been purchased from Sigma Aldrich and used as it is. Methanol and Concentrated HCL have been purchased from Merk India Limited. The double distilled water has been used as an aqueous medium throughout the experiment.

4.2.2 Methodology

4.2.2.1 ZnO prepared by hydrothermal method

With the help of hydrothermal method, the given synthesis is worked out.0.002mol CTAB and 0.003mol of zinc nitrite hexahydrate, $Zn(NO)_3.6H2O$ taken as precursor materials .These two were added to 10ml deionised water and 40 ml anhydrous ethanol with 10 min ultrasonic treatment. Then 0.015 mol of urea, $CO(NH)_2$ will be added to that solution under vigorous stirring. Stirring is continued for 6 hours with 60^0C provided temperature. Then the sample will poured to a round neck flask for refluxing with condenser provided at top fitted with the neck of flask this will continued for 6 hours, this is done to provide uniformity to the particles in the solution. After this the prepared solution will be transferred to a Teflon-coated autoclave of 80 ml capacity for 24 hr at

150^0C. After cooling to room temperature, white powder obtained was collected and washed several times with distilled water and ethanol to remove impurities, then brown power dried at low temperature 80^0C for 6 hour in vacuum. For Post-annealing treatment of obtained pre-cursors was carried out at 673K for 2 hr in a temp-programmed Muffle furnace.

4.2.2.2 ZnO prepared by Sol-gel Method

This method differs from the hydrothermal as it does not required to put sample for the autoclave. The synthesis follows as 2.7mmol of CTAB dissolved in sol of 480 ml water along with Zinc acetate dehydrate as precursor then Mesitylene (48.8mmol) added to solution with vigorously at magnetically stirrer at 80 °C for 2 hr then 3.5ml of 2M NaOH (aq) added drop wise at rate of 1ml/min to solution reaction mixture stirred vigorously at 80 °C for 6 hours by refluxing method**.** Resulting white precipitate which is isolated by centrifuging/filter paper After collecting white precipitate it washed with abundant ethanol and dried under vacuum at 100 °C for 12 hr The Structure templating CTAB and mesitylene molecules were removed from composite material by acidic medium .A suspension of the synthesized material was stirred for 6 hr at 50 °C in a 100 ml ethanol sol with 0.75 ml conc. HCl**.** Template removed from solid product was then isolated by filtration and dried again under vacuum at room temp for 12 hr at 80 °C and finally dried material was put into muffle furnace at 800 °C for 4 hour, and collected the final output.

4.3 Photocatalytic Performance

ZnO as a catalyst was used to study the photocatalytic degradation kinetics of Rhodamine B (RhB) in aqueous solutions. In the experiment, 75 mg of the catalyst were dispersed in

100 ml of solution and under continuous stirring it will mixes with the solvent in the reaction. Before exposure to the UV light it will be left for 45 min and observe without catalyst reaction to abtain an adsorption/desorption equilibrium. Once on reaching equilibrium the solution was exposed to UV light.At given time intervals, 5 ml aliquots were sampled, centrifuged to remove the particles and measured by UV-visible spectroscopy

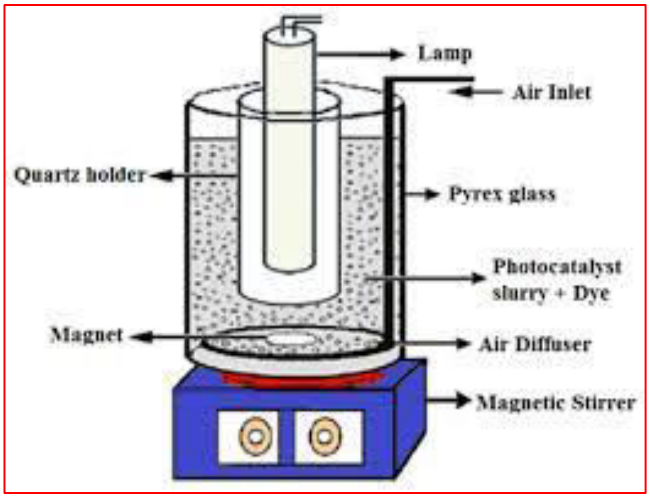


Figure 4.3 Photocatalysis set up with uv light

The rate of Rhb decomposition catalyzed by ZnO-NPs is assumed to be fitted by a first-order rate law. Rhb dye shows the prominent peak at 664 nm.A basic mechanism of photocatalytic reaction on the generation of electron-hole pair and its destination is as follows: when a photocatalyst is illuminated by the light stronger than its band gap energy, than immediately electron-hole pairs will diffuse out to the surface of the photocatalyst and participate in the chemical reaction with the electron acceptor and donor. Those free holes and electrons transform the surrounding oxygen or water molecules into OH+ free radicals with super strong oxidation.

CHAPTER FIVE

RESULT AND DISCUSION

PART A

5.1 Structural Characterization To study and analysis of the ZnO sample prepared for its structure and morphology character and various other factors, It is characterized with some techniques and also comparison of the two ZnO particles prepared with two different methods as obtained different shapes**.**

5.1.1 XRD of ZnO nanoflower shape prepared by hydrothermal method

Spectra of the sample after post annealing treatment are presented in Figure.5.1.All peaks can be indexed well to the known hexagonal ZnO with a wurtzite structure. The ZnO phase is well crystallized. No other diffraction peaks were detected, shows that no impurity exist and the hydrozincite have completely transformed into the ZnO phase.

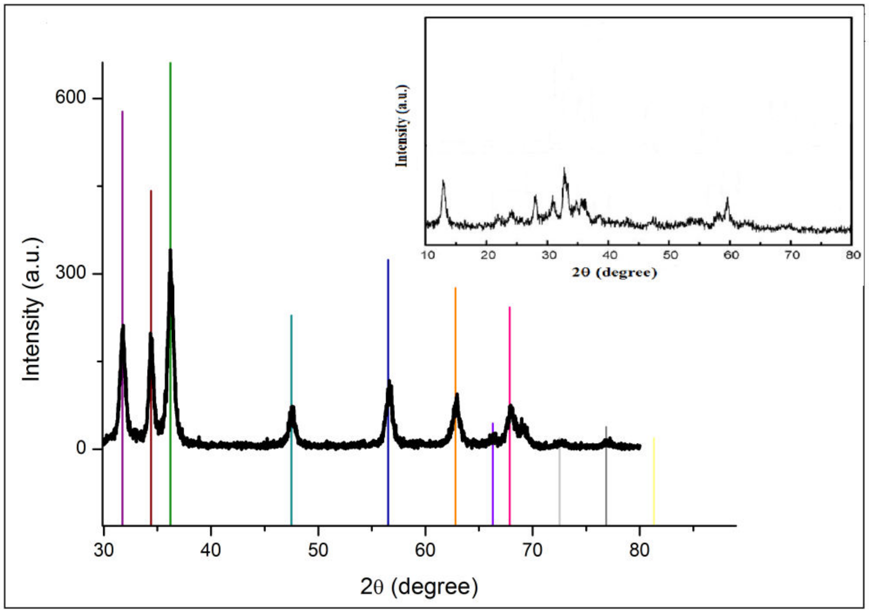


Figure 5.1 XRD of ZnO

5.1.2 SEM (Scanning Electron Microscope)

SEM images of ZnO nanoflower particle shows that it has a rough but porous external surface.It looks like a cabbage with petals covering all over the particle providing porous external surface with particle size 400-500nm in Figure-5.2, a) dispersed images at 5um b) more focused at 2um c) interestingly giving flower structure at 2um d) focusing towards the petals at 1um.

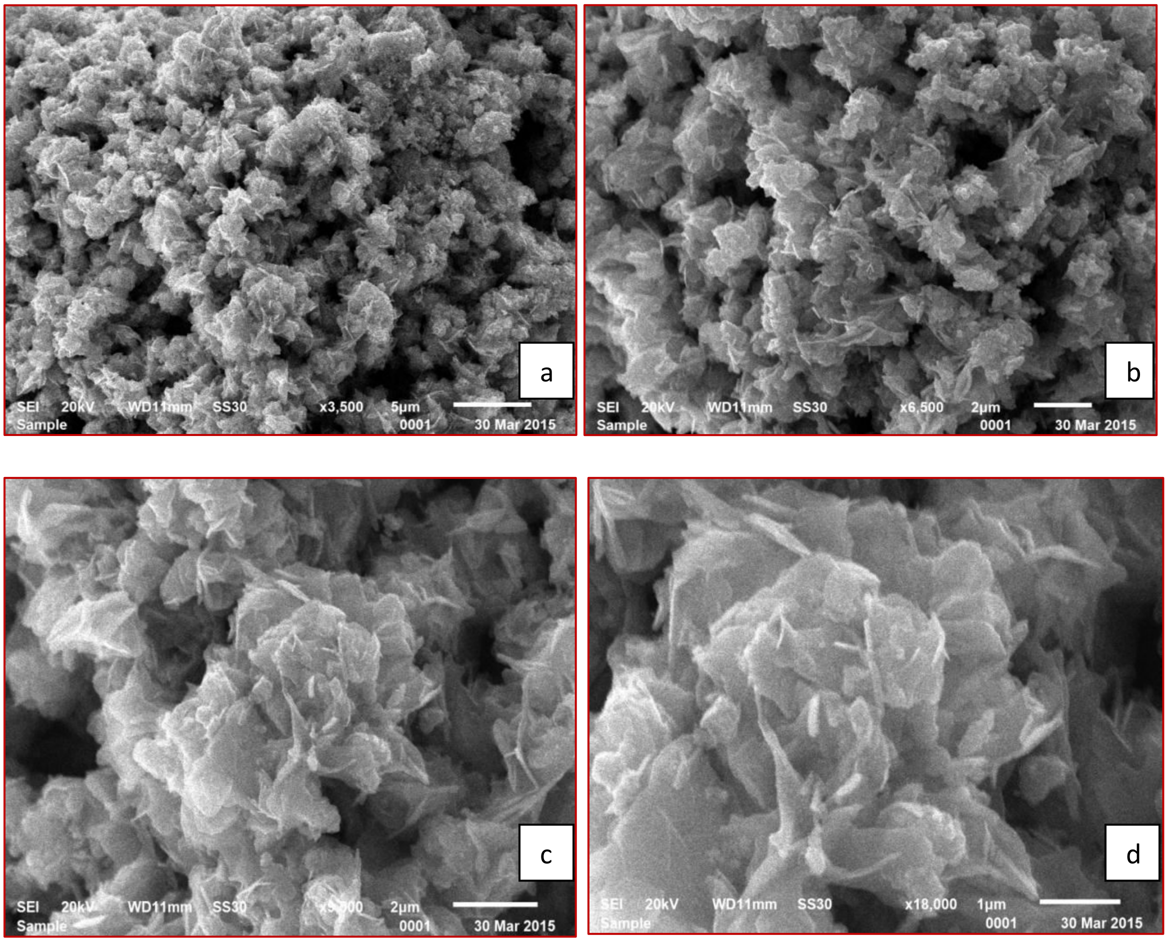


Figure 5.2 SEM images of ZnO nanoflower particle.

5.1.3 TEM

When the nanopieces are provided with pores and to study about the structural porosity of the particle,a high magnification is needed which is given by TEM. As TEM images of an individual ZnO nanoparticle is shown in Figure 5.3. A further magnified image of the fringe of ZnO nanoparticle, nano-building blocks is shown in Figure 5.3(b).The orderly and clear lattice fringes, paralleled to each other, shows that the particles are well crystallized. Although the ZnO nano-piece building block is a single crystal, it is interesting that the ZnO nano-piece seems flexible from the SEM observations (Figure 5.2). The flexibility of ZnO nano-piece may be favors its great potential application in piezoelectric properties.

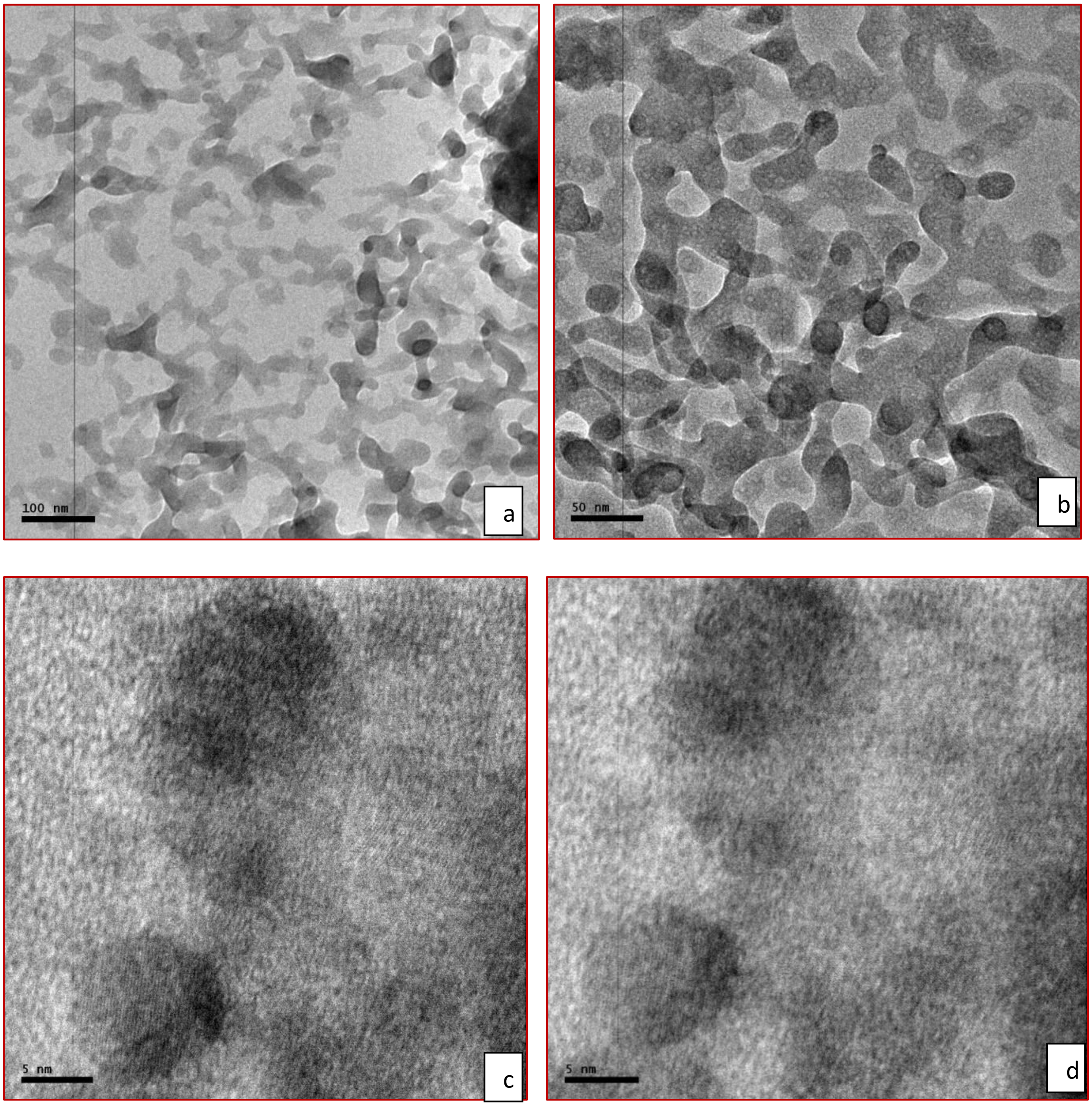


Figure 5.3 TEM (a) at 100nm to (b) at 50 nm, HRTEM at 5 nm.

5.1.3 Brunauer Emmett and Teller

Pore size analyser is used to measure surface area and pore size to volume ratio. ZnO can inherit well the size of LHZC crystals as well as morphology in the thermal decomposition process. ZnO nano-pieces calculated by the BET measurements as the results of the surface area shows that as-obtained ZnO perfectly inherits the structure of Zn5$(CO_3)_2(OH)_6$ precursor. The specific surface area of the synthesized ZnO is approximately 50.317 m^2/g, which is larger than that of commercial ZnO powders (4–5m^2/g). Below is the adsorption isotherm graph of ZnO (Figure 5.4).

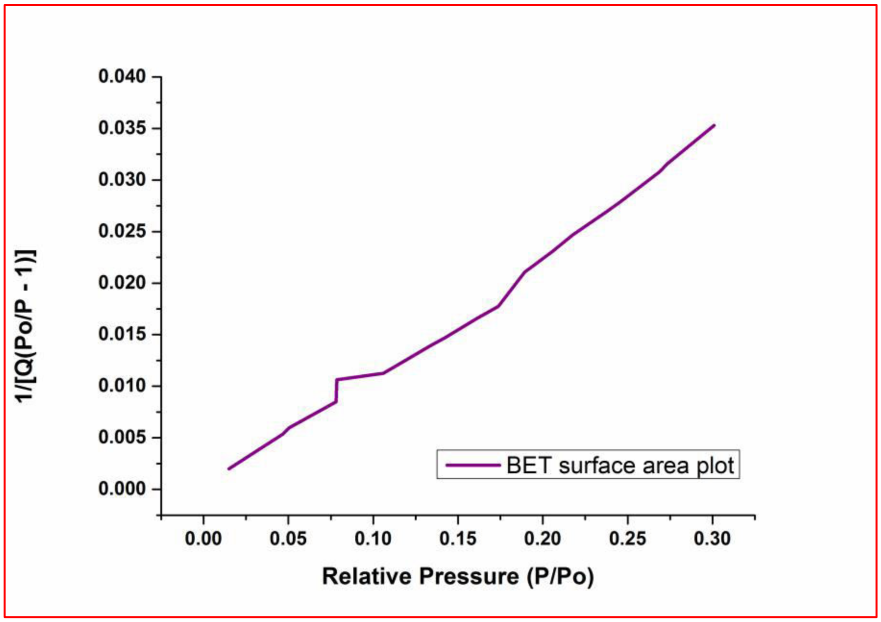


Figure 5.4-Adsorption graph of BET

5.1.4 STRUCTURAL MECHANISM OF THE ZnO NANO-PIECES

For the understanding of the formation mechanism of the hydrozincites nano-pieces, the time-dependent experiments were followed at the same reaction temperature. At reaction time of 0.5 hr, a few piece-like structures were obtained, and these pieces are linked up edge by edge. Upon increasing the reaction time to 1.5 h, the small pieces continue to grow and contact with each other under the control of growth kinetics, and eventually form the primary building blocks of ZnO nano-pieces based structures, which further grow and connect into a larger loop. The LHZC crystals with the absolute morphology can be obtained, as the reaction time reaches more than 5 h. As from the above results and discussion, the most credible mechanism that destined the formation of nano-piece is proposed upon the growth nature of LHZC crystals in aqueous solution and the reasonable mechanism of secondary nucleation and growth. First, The urea used in above method slowly begins in the solution to hydrolysis to release hydroxyl anions and carbonate anions with the elevated temperature. Then the finalized soluble species, $(Zn(OH)_4)_2$, causes a suitable level of super-saturation of the solution, that results in the homogeneous nucleation of LHZC crystals. It is well established that crystal growth of the LHZC in the solutions is two-dimensional and the resultant particles have plate-like or piece-like shapes, thus the piece-like LHZC crystals are formed at the primary stage of the reaction. At this level, the CTAB molecule which play a role of surfactant(for controlled growth of nano-pieces), interacts with the surface of nano-pieces to limit their further growth and agglomeration. After homogenous nucleation in solution, secondary nucleation of the LHZC crystalline preferentially happen at the edge of each nano-piece, which forms the newborn crystals grow and assembly along the edge of neighboring pieces. Based on the growth trend, the clusters of the nano-pieces gradually form the closed random flower like structures, which nano-pieces are eventually shaped. We can conclude that it is the origin of a porous part. However, no matter what way they applied, the nano-pieces assembly of the the secondary nucleation and growth are decisive in the formation of LHZC micro-particles.

5.1.5 Discussion of modified shape of the particle

The work reported as a facile and cheap method to the fabrication of ZnO nanoflower by the hydrothermal and post-calcinations treatment approach. The as-obtained ZnO nano-pieces with a diameter of 15mm inherited well the size and morphology of LHZC crystals during the thermal decomposition process. The time dependent experiments revealed its unique growth process, the reasonable mechanism of secondary nucleation for the assembly of ZnO mesoporous particles into nanoflower was proposed. The particles and specific nanostructure are constructed by the adjacent nano-piece led to high surface area and high utilizing efficiency of the UV light, which was responsible for superior photo-catalytic activity of the mesoporous ZnO particles.

5.2 Results and Analysis of ZnO Prepared by Sol-gel method

5.2.1 XRD

Figure 5.5 represents the X-ray diffraction pattern of ZnO. The diffraction peaks have been keenly indexed as hexagonal wurtzite phase of and further it also confirms the synthesized ZnO powder was free of impurities as it does not contain any characteristics XRD peaks other than ZnO peaks.

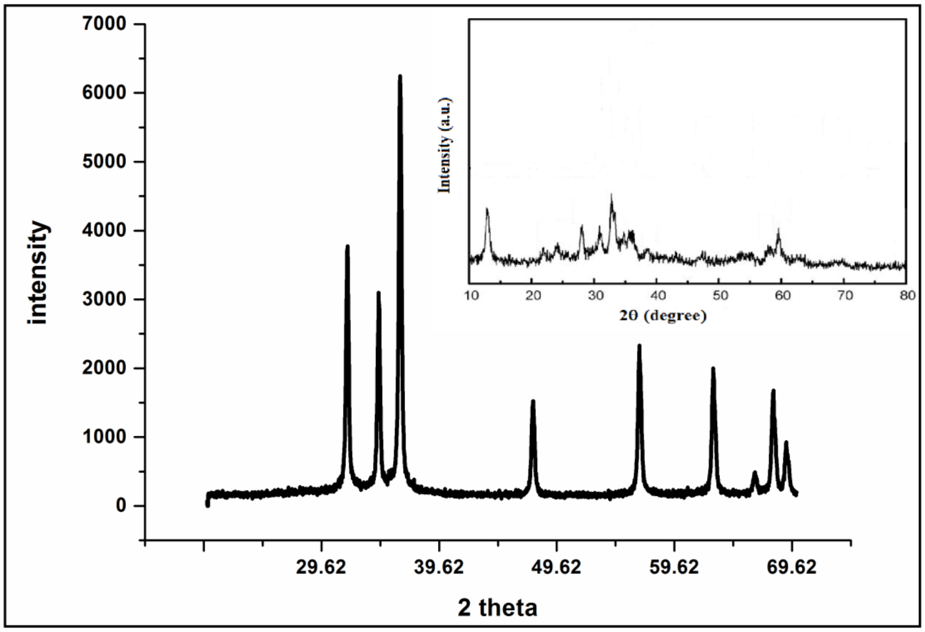


Figure 5.5 XRD of ZnO.

5.2.2 SEM (Scanning Electron Microscope)

SEM images of a well-dispersed state of ZnO microspheres with a narrow size distribution have a uniform morphology and size, the average diameter of microspheres is ca. 20 mm. To our surprise ,from the observation of the magnified SEM image of Figure 5.6(a), we can clearly see the surface of the intact ZnO microspheres is porous, which seem to be interweaved with the innumerable ZnO nano-pieces. The interweaved nano-pieces of ZnO sphere is very similar to the bird's nest which is shown in the inset of Figure 5(b). Figure 5.6(c) further confirms that ZnO spheres are irregularly constructed by the pieces like units as the elementary building blocks, interestingly, the hatch in the sphere is similar to the entrance of the bird's nest. Figure 5.6(d) shows a typical magnified top view SEM image of the ZnO sphere.

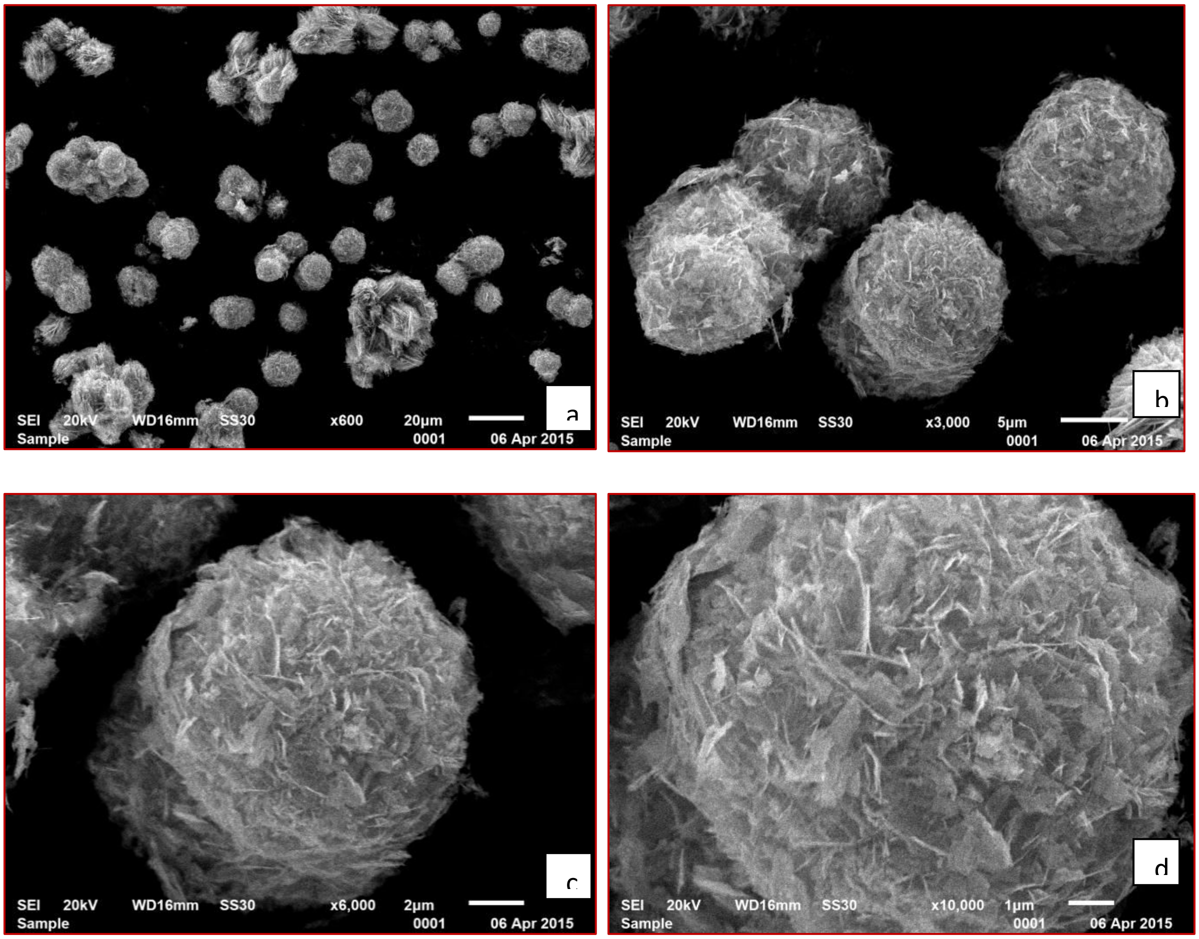


Figure 5.6-(a) Spherical Particles(b) Showing nest like spindle in micro spheres(c) Intertwined microsphere(d) Intertwined fibers showing pores .

5.2.3-TEM (Transmission Electron Micro-Scope)

ZnO spheres building blocks, the high-resolution transmission electron microscopy is employed. Many scattered are observed in nano-pieces, which makes the nano-pieces present a porous feature. The images were taken using TECNAI TEM instrument (FEI TEM model TECNAI G2 T30,TWIN) at 300kV. TEM images of the particles is as shown in Figure 5.7.

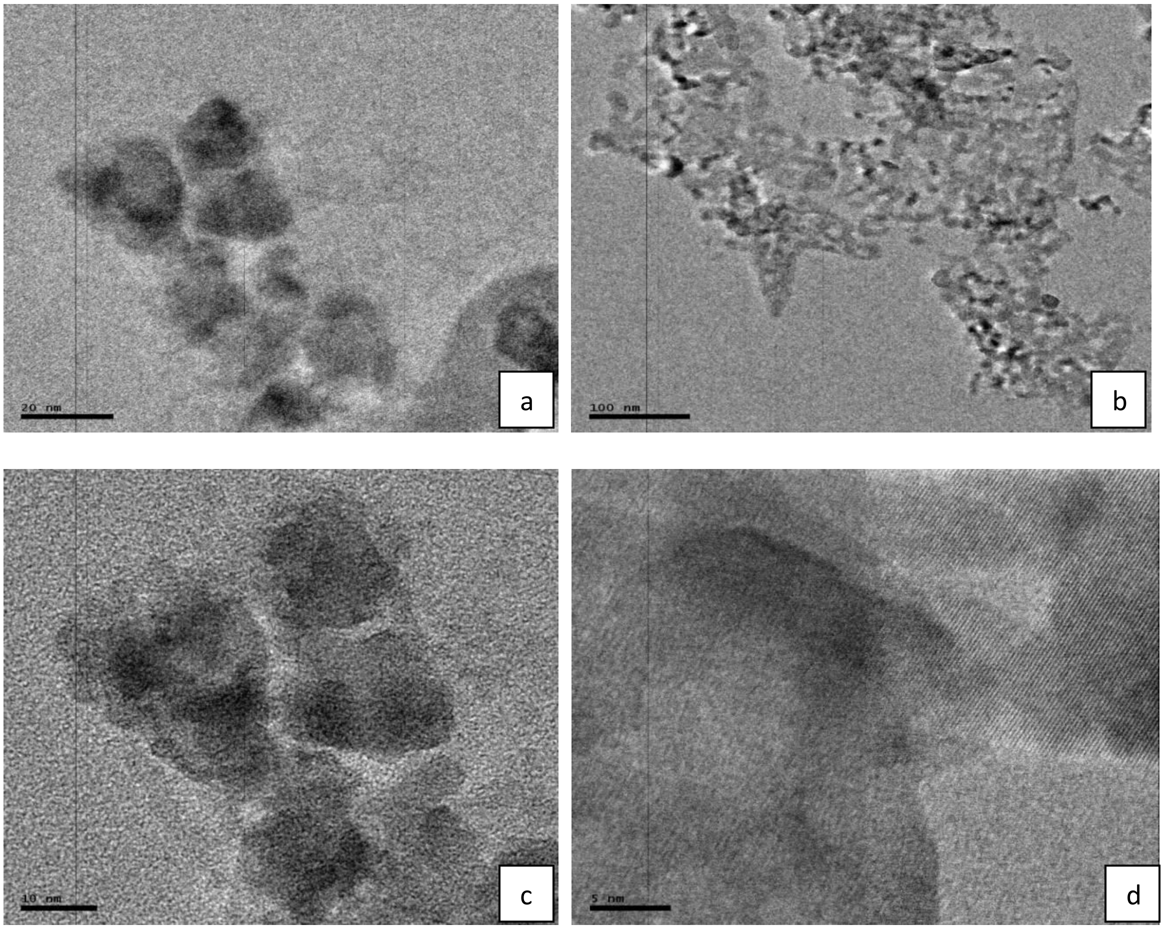


Figure 5.7 TEM images of spherical ZnO

5.2.4 Brunauer Emmett Teller

Surface area of the zinc oxide particles were measured using BET method. Surface area analysis was done using Micr-meritics surface analyzer tri-star 3000. Measurements were carried out by nitrogen adsorption at liquid nitrogen temperature The results of the surface area show that as-obtained ZnO perfectly inherits the structure of $Zn5(CO_3)_2(OH)_6$ precursor. The specific surface area of the as synthesized ZnO is approximately 42.752m^2/g, which is larger than that of commercial ZnO powders (4–5m^2/g).Figure 5.8 is the adsorption isotherm plot.

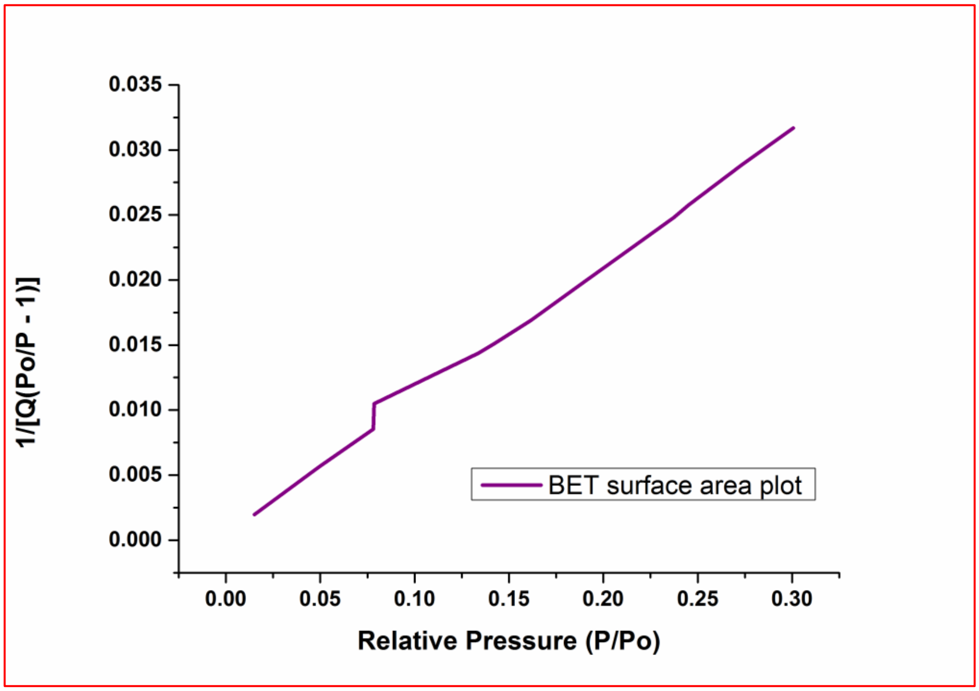


Figure-5.8-Adsorption of spherical ZnO

Table5.1 Comparitive data of bet analysis of both ZnO nanoparticle.

Particle name	Surface Area(m^2/g)	Pore Volume (cm^3/g)	Mean Pore Size(nm)
ZnO flower shape	50.317	0.02	2.06
ZnO spherical shape	42.752	0.22	6.04

5.2.5 DISCUSSION

As discussed in above experiments, work is different in methods and their characteristics. As prepared ZnO nanoflower particle has 50.317 m^2/g specific area in comparison to spherical shape which has 42.752 m^2/g specific area. Also spherical ZnO has 20nm diameter in comparison to flower ZnO has 15nm diameter. This modification in the method is to be carried to determine the comparative study for photocatalytic study and to analyze the degradation rate of both catalysts with respect to the commercial ZnO and without catalyst. Usually the synthesized porous catalyst will absorb rapid and degrade the dye in comparison with commercial particle. This happens because the catalyst which has more specific surface area which is available in form of porous structure to the catalyst, so it will absorb more readily the dye and it will increase the degradation rate of the solution.

PART B

OPTICAL RESULTS

5.3 Photoluminescence of rhodamine b

Changes in maximum emission wavelengths were noted with respect to the change in concentration of the organic dye at fixed excitation for the organic dyes solutions in distilled water as solvent. Maximum efficiency of rhodamine-b dye solution in water was obtained at 10^{-4} M concentration of dye solution. For Rhodamine-B dye solution, the excitation peak are found at 356 nm (shown in Figure 5.9 and figure 5.10) emission spectra with excitation wavelength 356 and excitation spectra with emission wavelength at 590 nm. were plotted for its concentrations.

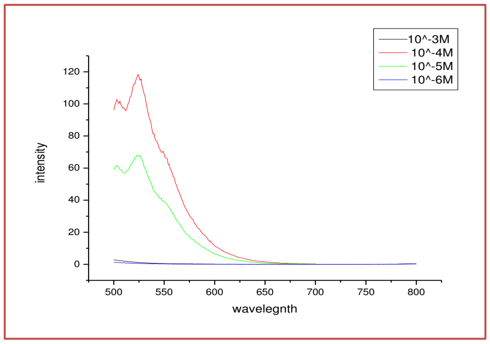


Figure 5.9 Emission spectra of rhodamine at 10^{-4}M max intensity, exication 356nm, slit width 5

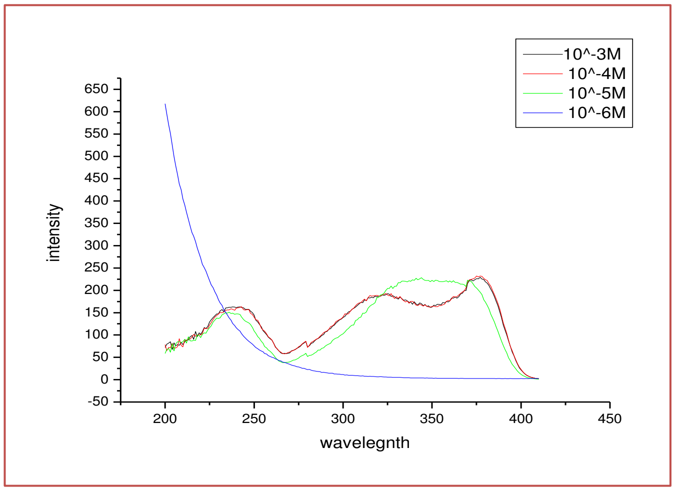


Figure-5.10 Excitation spectra at emission-590nm

5.3.1 Photoluminescence of rhodamineB dye solution with aqeous ammonia 10^{-4}M stock solution in water was prepared by dissolving the appropriate amount of the dye (5.63 mg) in a given volume (100 ml) of water. The dye solution concentration was kept as low as 10^{-4} M to avoid self-quenching or the inner filter effect. For studying quenching, the desired quantities of the aqueous ammonia solution were mixed in micro liters as a quencher in 4ml of the 10^{-4} M dye solution in a quartz cuvette closed with a Teflon lid to record excitation/emission spectra

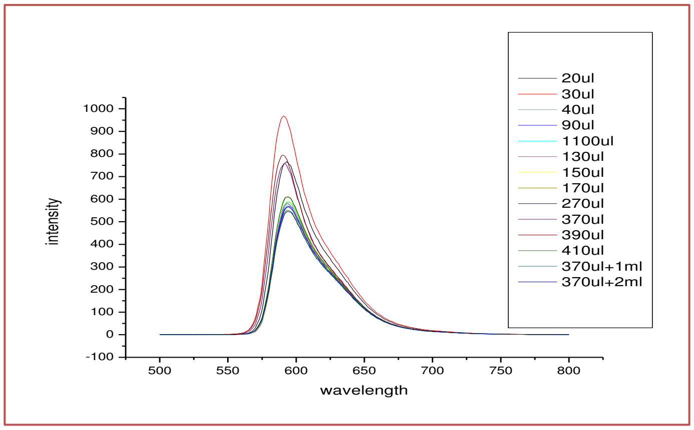
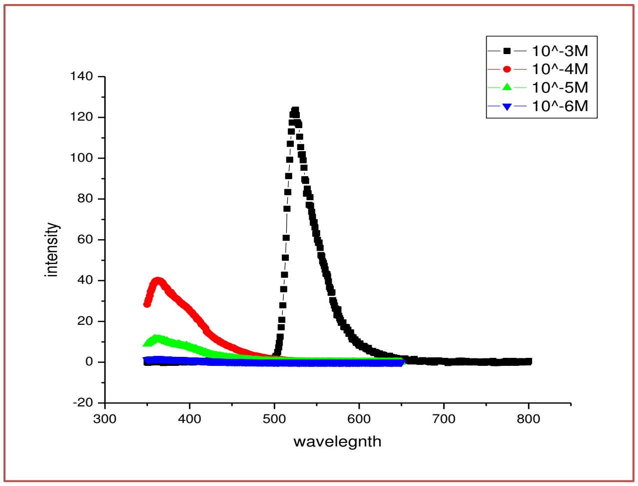


Figure 5.11-Rhodamine b on interaction with ammonia(toxic gas)-adding ammonia in micro-liter and check the point at which dye shows variation with increasing intensity.

5.3.2 Photoluminescence of Malachite green organic dye solution emission and excitation in malachite green are given below at fixed excitation at 350nm. Its maximum intensity is at 10^3M,will be taken when it will interact with aqueous ammonia so that a change can be noticed in the aqueous ammonia.



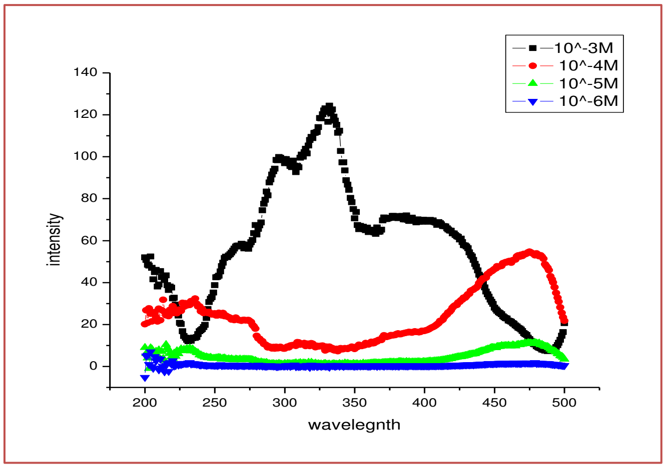


Figure5.12 Emission spectra

Figure5.13 Excitation spectra

5.3.3 Photoluminescence on interaction of Malachite green dye solution with aqueous ammonia

Malachite Green dye is chosen as a fluorophore for studying the changes in its fluorescence emission/excitation spectra in the presence of aqueous ammonia because of its stability against structural changes with a change in solvent, concentration, environment temperature, etc. It is also readily available. The choice of water as a solvent was governed by the fact that the dye easily dissolves in this solvent and detection time would also be very fast (milliseconds, if needed to detect the intensity at the peak position) due to non-viscous dye solution. Another consideration for choosing water as solvent was again the stability of the dye molecules in water than in other solvents. The excitation maxima were found to be at around 350 nm. Therefore, the excitation wavelength was selected at around the same wavelength for recording all the emission spectra.

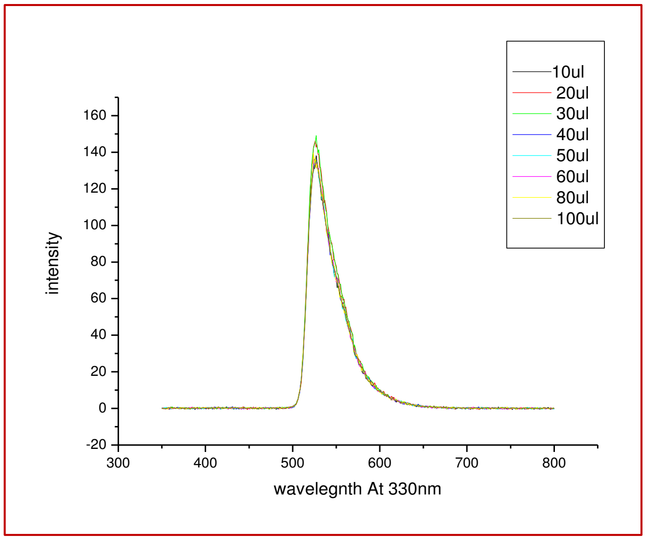


Figure-5.12 Emission spectra of Malachite green when interaction with ammonia

The emission spectra of the MG dye solution with varying aqueous ammonia concentrations are as shown in Figure 5.12. The excitation wavelength was kept at 350 nm as the excitation spectrum shows a band of maximum intensity around this wave length. It could also be observed, that the nature of the spectra remains almost unaltered in the presence of the aqueous ammonia except the intensity which increases on increasing the aqueous ammonia concentration. It is also observed that there is no appreciable change in the spectra of the dye solution with the aqueous ammonia concentration increasing. This shows that there is no possibility of forming a complex with the dye molecules and the sensitization may be due to collisions. The spectra could remain unaltered even after formation of the complex.

5.4 Photoctalytic Tests

Figure 5.4 and Figure 5.5 shows the degradation of the organic dyes Rhb in the presence of catalysts, for comparison with ZnO commercial powder. This results demonstrates that the ZnO nanoflower particle is more affective to degrade organic dyes as compared to spherical ZnO. This is attributed to the larger specific surface area of the flower's porous structure which is about 50.317 m^2/g as compared ZnO spherical particle has 42.752 m^2/g. The larger the surface area that the catalyst possesses, the more reactants(e.g., O2, OH- , and organic molecules) that should be adsorbed on its surface due to an increase in the number of active sites, thus leading to higher catalytic activity. Moreover, the main process of the degradation of the dye is adsorption–oxidation–desorption mechanism.Theses free radicals will cause the destructive oxidation of the organic dye.These catalytic degradation follows the pseudo-first-order reaction with respect to the dyes.This indicates that for dyes the degradation rates follow the order of ZnO flower > ZnO spheres > ZnO commercial powder. After demonstration of the catalytic activity of the ZnO nanoparticles their reusability was checked, and it confirms that these particles are useful for many cycles. All these results conclude that as prepared ZnO nanoparticles could work as an effective and reusable catalyst at room temperature without using any specific light source.

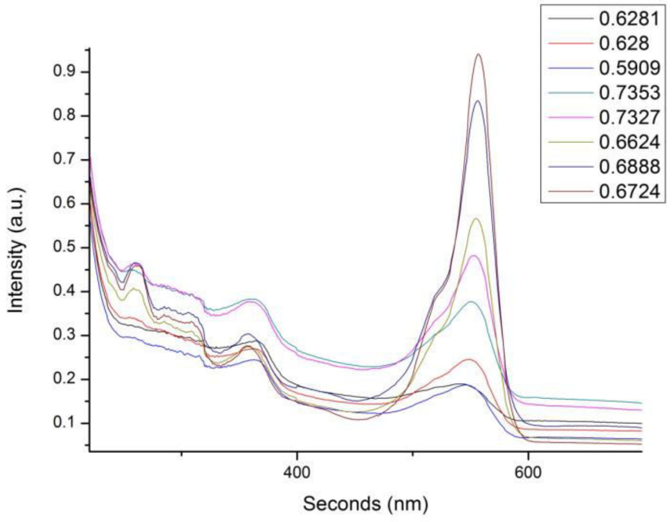


Figure 5.13 Absorption of Rhodamine b when sensitized with ZnO nanoflower particles.

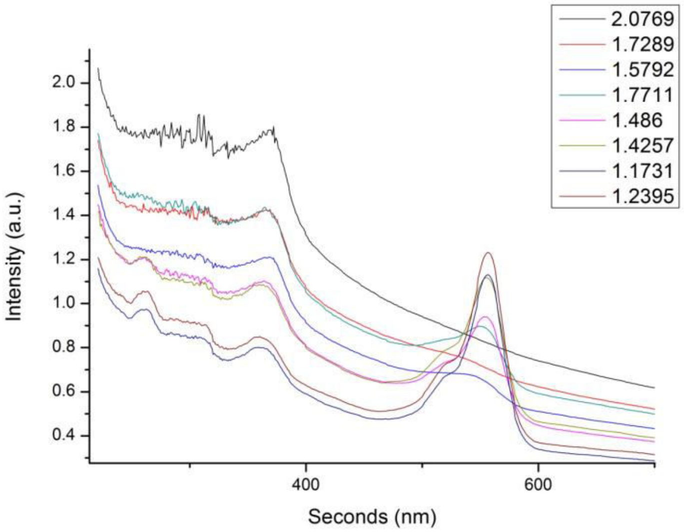


Figure 5.14 Absorption of Rhodamine b in presence of spherical ZnO nanoparticles

Figure 5.13 and Figure 5.14 demonstrates the above results by presenting the spectrum of rhodamine b following sensitized degradation under visible light by ZnO, traces have the same absorbance at 554 nm .Plotting the absorbance at the center of the absorption peak of a dye is no doubt the easiest way to describe the decoloration kinetics.While we have our reservations as for the validity of these values in describing the so-called "activity" of the semiconductor.

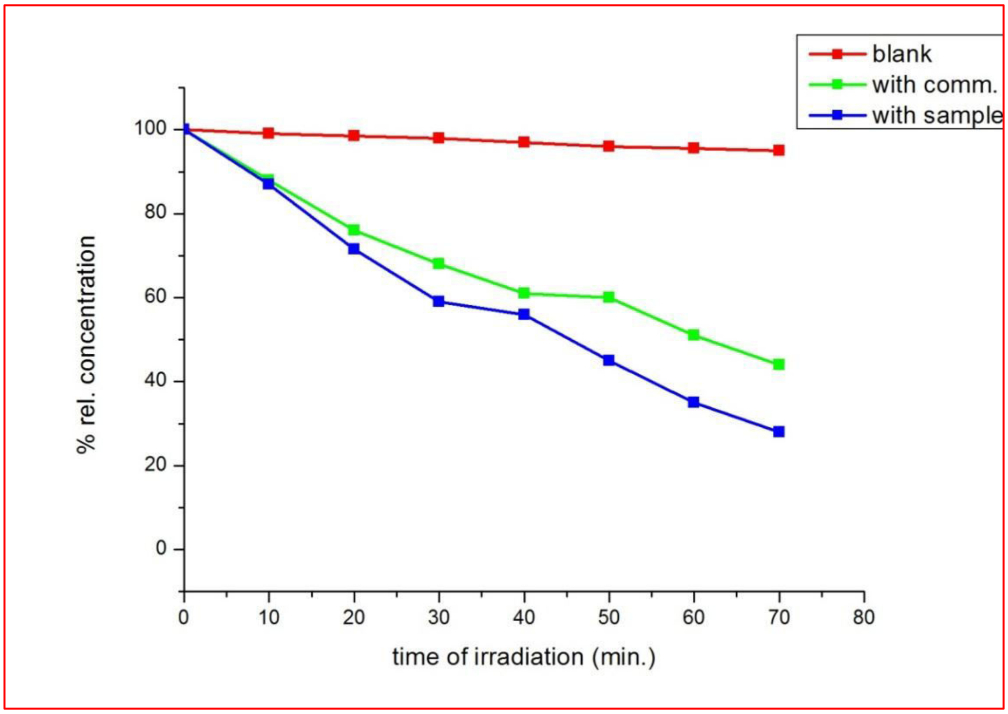


Figure-5.15 Photocatalysis of ZnO as catalyst(sample) and without catalyst(blank) on comparison with commercial ZnO

The synthesised ZnO particles have been investigated for the application in photocatalytic with rhodamine b dye. Figure 5.13 is the image of absorption spectra of aqueous solutions of rhodamineB (initial concentration of 10^{-3} to 10^{-5} M in 100 ml) in the presence of the porous ZnO particles (75 mg) irradiated under a UV light (80 W) for the different time intervals. To define the photocatalytic experiment of the novel structural ZnO nanopieces has been improved, a series of relative experiments performed to the solution firstly without any catalyst then comparative readings at regular interval in the presence of catalyst(ZnO): (1) In absence of ZnO but with UV light irradiation; (2) with commercial ZnO nanopowders(the average diameter is 20 nm)and UV light; (3) Lastly in presence of ZnO nanopieces with UV light. The relative results are carried out in the form of the degradation rate of rhodamine b, which is converted from the data of UV absorption spectrum, are presented in figure 5.15 From the experimental results curve 1, the photocatalytic efficiency for degradation of rhodamine is very low, only 5% decrease of the rhodamine b concentration can be detected after 70 min. The ZnO nanopowder shows an excellent photocatalytic activity in degradating rhodamineB, the degradation rate reach to 50% after 70 min irradiation (curve 2). It should be noted that photocatalysis have been great enhanced in the case of condition (3), if the as-obtained porous ZnO nanoparticles flower based particles is used as photocatalyst,the curve (3) indicated that the degradation rate of rhodamine b was faster and thorough, at which degradation rate achieve 75% in the same period (70 min). The comparative results implies that self assembly of nanopieces-based ZnO nanoparticles has outstanding catalytic performance.The highly photocatalytic performence of as-obtained ZnO is mainly attributed to the high specific surface area, high permeability and high porosity. First, for the assembly building units of ZnO nanopieces from the precursor of LHZC, the unique layered and porous nanopieces with a nano-scale thickness can improve the area density of zinc ions to a great extent, and improve reaction contact surface and catalytic activity sites, which is also in favor of photocatalytic reaction. The surface of nanopieces can be easily coordinated by hydroxide anions in the alkaline solution, the highly reactive hydroxyl radicals (OH^-), a powerful oxidation agent, generated on the surfaces of ZnO crystals in the presence of the valence-band holes. Second, for the subtle structure of ZnO nanopieces constructed particles, it can be considered as a micro-reactor in the photocatalytic process. High porosity provides ideal channels for effective diffusion and absorption of the dye molecules into the inner of ZnO particles , besides, the UV light can easily enter into the thin nanopiece-based internal space, while it is difficult to go out due to the frequent internal reflection and refraction, which significantly increases the utilizing efficiency of the UV light. The main advantage is the ability to use UV-vis spectroscopy, a non-expensive, easy to use technique, to measure the kinetics of their photocatalytic degradation, as they are appropriate to be used with uv-light.

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CHAPTER SIX

CONCLUSION

The work concluded with the study and analysis of photoluminescence of organic dyes to understand the changes and properties of different dyes for the identification of a particular dye chosen for photocatalytic activity. Synthesis and experimental work of ZnO shows that porous nanoparticles are best to deal with photocatalytic activity because of their more surface area and increased porosity also highly permeable to take less time to degrade a particular dye.And finally a successfull study of photoctalytic degradation of orgnic dye which shows results without catalyst and with catalyst comparison and from the data obtained it can say that this application is very useful in biochemistry and biologically in cosmetics and in drug delivery.The results obtained in the present study shows the efficiency of photocatalysis in degraing dyes, which resists other conventional treatment processes.Photo oxidative degradation appears to be a promising technology that has many applications in environmental clean up systems, waste water management, biologically to degrade particular drug effectively in presence of organic dye. A detailed feasibile study has been carried out on photo catalytic degradation of Rhb using ZnO powder as a photo catalyst under UV radiation. The current study shows the green approach for fabrication of ZnO nanoparticles and it is responsible for significant photocatalytic and antioxidant activity.The formed ZnO-NPs are highly stable and exhibited more than 60% degradation of Rhb. Heterogeneous photocatalysis process is an eco-friendly way to reduce the pollution load of wastewater. The Results of the study indicates that ZnO is very effective

& suitable. The best reaction dosage of ZnO catalyst is about 50 mg/750ml.The maximum degradation efficiency of dye was achieved with the combination of UV+ ZnO.The maximum decolorisation occurred in less than or equal to 70 min. The photo degradation of RhB is 99.99%. It follows the first order kinetics, in comparison of the catalyst which have more surface are takes less time (70 min) to degrade whole dye.

CHAPTER SEVEN

FUTURE SCOPE

This present study can be further extened by giving more research to this application,as this work presents only nanoflower shape ZnO particles as modified structure but other shape of structure can be synthesized with the variation at different optimized condition and particle size can be reduced which is needed for nanoporous. Various shapes of mesoporous zno can be synthesized with suitable methods. By changing the precursor and its concentration to different morphological shapes like sphere, rod, and tube like nano materials can be formed. These ZnO nanoparticles have a great advancement in biomedical application. ZnO particles have a good cytocompatibility and a potential in several biomedical applicationsAnd with the fabrication of a sensor cell,this work can be most likely applicable to a biosensor Metal oxide semiconductor gas sensors supply good advantages with respect to other gas sensor devices because their operation is at elevated temperatures and in harsh environments, they are mechanically robust and relatively inexpensive and offer exquisite sensing capabilities.124 Since the gas sensing includes the adsorption and catalytic reactions on a surface, the main parameter to tailor the sensitivity of a semiconductor sensor material is the surface area For this purpose, ordered mesoporous oxides have been synthesized for their potential applications as sensors (ZnO).Incorporation of mesoporous nanoparticle with a particular dye and then using that pellets in the sensor cell,with the help of bubbling of any toxic gas will read out the quenching effect.Due to this effect we can study the toxicity of that particular toxic gas.And some measures can be understand to reduce toxicity.As toxic gas like ammonia is present environmentally allaround and some times it also effects human health in breathing or irritation to the skin or eyes.This study can be further used for biological and sensor applications. The sensor can monitor the total ammonia and ammonium concentration in dialysate. The sensor has an optical indicator, such as an ammonia sensitive membrane, positioned in direct contact with the dialysate fluid when in use. The ammonia sensitive membrane has a variable optical indication, such as a variable color change, in relation to the concentration of ammonia in the dialysate. An optical reader reads the color change of the membrane to measurethe total ammonia and ammonium concentration in the dialysate. The sensor can be used in the dialysis system to monitor the effectiveness of sorbants which remove ammonia/ammonium which is produced from an enzyme reaction with urea, the urea being removed from a patient during dialysis treatment.This work has a very wide scope in many field as well as in biomedical as this is a never ending research work with various applications.

CHAPTER EIGHT

REFRENCES

1-A. Monnier, F. Schuth, Q. Huo, D. Kumar, D. Margolese, R. S. Maxwell, G. D. Stucky, M.Krishnamurty, P. Petroff, A. Firouzi, M. Janicke, B. F. Chmelka, Science 1993, 261, 1299.

2-African Journal of Basic & Applied Sciences 2 (5-6): 161-166, 2010 ISSN 2079-2034

3-Agnieszka Kołodziejczak-Radzimska*and Teofil Jesionowski Institute of Chemical Technology and Engineering, Faculty of Chemical Technology,

4-Azizi S., Sehili T., Djebbar K., Comparative Study of Phototransformation of Isoproturon Aqueous Solution by UV/H2O2 Treatment, Fenton's Reagent,Photo-Fenton and Photocatalytic Processes J. Env. Eng. Tech. 2 (1) (2013)17-24

5-Bhatkhande, D. S., Pangarkar, V.G., Beenackers, AA. CM., Photocatalytic degradation for environmental applications:a review J. Chem. Tech. Bio. 77(2011) 102-116.

6-Biomaterials 21 (2000) 121}130 Young Jin Kim!, Inn-Kyu Kang!,*, Man Woo Huh", Sung-Chul Yoon#

7-Chong, M. N., B. Jin, et al., Recent developments in photocatalytic water treatment technology: a review Water Res.44 (10) (2010) 2997-3027.

8-College of Chemistry and 1944-3994/1944-3986 © 2011 Desalination Publications. All rights reserved doi: 10/5004/dwt.2011.2159 Environmental Science, Henan Normal University, Xinxiang, Henan 453007, P.R. China

9-D. Y. Zhao, Q. S. Huo, J. L. Feng, B. F. Chmelka, G. D. Stucky, J. Am. Chem. Soc. 1998,

10-Disposable Potentiometric Ammonia Gas Sensors for Estimation of Ammonia in Blood

11-F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, Angew. Chem. Int. Ed. 2006, 45, 3216.

12-Fang, Z. Rapid production of micro- and nano-particles using supercritical water Eng. Mat. 30(2011) 11-27.

13-J Nanopart Res (2013) 15:1505 DOI 10.1007/s11051-013-1505-9 Haja Bava Bakrudeen • John Tsibouklis Boreddy S. R. Reddy

14-J. Reichman, Handbook of Optical Filters for Fluorescence Microscopy (Chroma Technology, Brattleboro, 2010)

15-Liu, X. Y.; Tian, B. Z.; Yu, C. Z.; Gao, F.; Xie, S. H.; Tu, B.; Che, R. C.;

16-Maghrabi M, Karali T, Townsend P D, Lakshmanan A R. J. Phys. D - Appl. Phys. 33 (2000)

17-Mathur V K, Lewandowski A C, Guardala N A, Price J L. Radiat. Measur. 30(1999) 735

18-Moharnm ad Omar and Howard H Patterson, Luminescence theory -Encyclopedia of Spectroscopy. Academic Press New York (1999).

19-Nair B S K, Sundar D, Tomita A, Hoffmann W, Lakshmanan A R J. Lurnin.86 (2000) 67

20-National Centre for Plasma Science and Technology (NCPST), School of Physical Sciences

21-P. Bamfield, M.G. Hutchings, Chromic Phenomena Technological Applications of Colour Chemistry, 2nd edn. (The Royal Society of Chemistry, Cambridge, 2010)

22-Samira Bagheri, Chandrappa K. G.* and Sharifah Bee Abd Hamid Nanotechnology & Catalysis Research Centre (NANOCAT), IPS Building, University of Malaya,50603 Kuala Lumpur, Malaysia 2013, 5(3):265-270

23-Sarika D. Shinde, G. E. Patil, D. D. Kajale, D. V. Ahire, V. B. Gaikwad and G. H.Jain,Synthesis of ZnO nanorods by hydrothermal method for gas sensor applications(2012)

24-Sci. Technol. Adv. Mater. 10 (2009) 013001 (18pp)

25-Sheng Xu and Zhong Lin Wang (□)School of Materials Science and Engineeri © Tsinghua University Press and Springer-Verlag Berlin Heidelberg 2011ng, Georgia Institute of Technology, Atlanta, Georgia 30332-0245, USA

26-T. Senthil, S. Anandhan / Journal of Colloid and Interface Science 432 (2014) 285–296

27-Y. Meng, D. Gu, F. Zhang, Y. Shi, H. Yang, Z. Li, C. Yu, B. Tu, D. Zhao, Angew. Chem. Int.

28-Y. Meng, D. Gu, F. Zhang, Y. Shi, L. Cheng, D. Feng, Z. Wu, Z. Chen, Y. Wan, A. Stein, D.

29-Poznan University of Technology, M. Sklodowskiej-Curie 2, PL-60965 Poznan, Poland Materials 2014, *7*, 2833-2881; doi:10.3390/ma7042833

30-Vij. D.R. Luminescence of solids Plenum Press NewYork (1998)

31-M.Inada,J.J.Phys.,17(1978)1-10.

32-G.Heiland,E.Mollwo,F.Stockmann,Solid State Phys.,8(1959)193-196

33-S.K.Tiku,C.K.Lau,K.M.Lakin,App.Phys.Lett.,35(1980)318-320.

34-P.R. Emtage,J.App.Phys.,48(1977)4372-4384.

35-F.S.Hickerne,J.App.Phys.,44(1973),1061-1071.

36-J.R.Haynes,Phys.Rev.Lett.,17(1966)16.

37-A.R. Hutson,Phys.Rev.,108(1957)222-230.

38-Prokic M Appl. Rad. Isotopes, 52 (2000) 97

39-T.Damen,S.P.S Porto,B.Tell,Phys.Rev.,142(1966)2.

40-Y.S.Park et al,Phys.Rev.,143(1966)2.

41-M.Matsuoka,J.J.App.Phys.,10(1971)736.

42-Enzyme and Microbial Technology 48 (2011) 427–437

43-1S.C. Singh, 2D.P. Singh, 3J. Singh, 3P.K. Dubey, 3R.S. Tiwari and 3O.N. Srivastava

44-Ammonia and ammonium sensors United States Patent Application 20030113931

45-Flodstrom, K.; Alfredsson, V.; Kallrot, N. J. Am. Chem. Soc. 2003, 125,4402.

46-Kim, T. W.; Kleitz, F.; Paul, B.; Ryoo, R. J. Am. Chem. Soc. 2005, 127,7601.

47-Journal of Nanoscience and Nanotechnology Vol. 12, 1–7, 2012

48-Materials Research Bulletin 45 (2010) 2024–2030 Qiyong Zhu a,b, Jie Chen a, Qing Zhu a,

49-Yuming Cui a, Lei Liu a, Bo Li a, Xingfu Zhou a,* Yumin Liu*, Lv Hua, Shuangqing Li, Guoxi

50-Ren, Y.; Jiao, F.; Bruce, P. G. Micropor. Mesopor. Mat. 2009, 121, 90.

51-G. S. Attard, J. C. Glyde, C. G. Göltner, Nature 1995, 378, 366.

52-Maghrabi M, Townsend P D. J. Phys. - Cond. Matter 13(2001) 5817

53-Kleitz, F.; Choi, S. H.; Ryoo, R. Chem. Commun. 2003, 2136.

54-Peng, L. M.; Zhao, D. Y. Angew. Chem. Int. Ed. 2002, 41, 3876.

55-Zhao, Chem. Mater. 2006, 18, 4447 Ed. 2005, 44, 7053.