B. TECH. PROJECT REPORT

On

Synthesis of Silver Nanoparticles

BY

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DISCIPLINE OF ELECTRICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY INDORE
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Synthesis of Silver Nanoparticles

A PROJECT REPORT

Submitted in partial fulfillment of the
requirements for the award of the degrees

of
BACHELOR OF TECHNOLOGY
in
ELECTRICAL ENGINEERING

Submitted by:
ANIL YADAV

Guided by:
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INDIAN INSTITUTE OF TECHNOLOGY INDORE
December 2017

CANDIDATE'S DECLARATION

I hereby declare that the project entitled **"Synthesis of Silver Nanoparticles"** submitted in partial fulfillment for the award of the degree of Bachelor of Technology in 'Electrical Engineering' completed under the supervision of **Dr. Vipul Singh, Associate Professor, Electrical Engineering,** IIT Indore is an authentic work.

Further, I declare that I have not submitted this work for the award of any other degree elsewhere.

Anil Yadav

(140002007)

CERTIFICATE by BTP Guide(s)

It is certified that the above statement made by the student is correct to the best of my knowledge.

Dr. Vipul Singh,

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Preface

This report on “Synthesis of Silver Nanoparticles" is prepared under the guidance of

Dr. Vipul Singh.

Through this report, I have tried to give a detailed description of Silver nanoparticles and ZnO nanostructures. I have deposited Silver nanoparticles on ZnO nanostructures and studied the effect of Ag-NP’s on PL spectra, DRS etc. of Zno nanostructure.

I have studied the effect of UV irradiation for different time intervals. Also studied the effect of concentration of Silver Nitrate in precursor solution on photo-generated Silver Nanoparticles and observed the effect of ethanol and concentrated $AgNO_3$ separately on PL Spectra.

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Abstract

These days Nanoparticles and Nanostructures have been a focal point of a lot of researchers because of its wide applications in the field of OLEDs, Solar cells, Photodetectors, Biosensors etc. The modification of semiconductors with noble metals has attracted significant attention especially in heterogeneous photocatalysis. Incorporating silver in ZnO is now an exciting area in research for developing electronic applications. In addition, silver modification is found to be effective for the fabrication of *p*- type ZnO, as the naturally occurring ZnO displays *n*- type conductivity due to its native defects such as zinc interstitials and oxygen vacancies. The modification with silver has influenced the photocatalytic activity of nanocrystalline photocatalysts because of its optical and electronic properties.

We successfully prepared Silver nanoparticles decorated on ZnO nanostructures through photochemical reduction process. Here, we observed the changes in the PL spectra of ZnO when a solution of $AgNO_3$ and ethanol was dispersed under UV illumination for different time intervals. We also observed the effect of $AgNO_3$ and ethanol separately on ZnO seed layer PL spectra. Then ZnO nanostructures were grown on ZnO seed layer through hydrothermal process. Again, we observed the changes in PL spectra of ZnO nanostructures when silver nanoparticles were deposited. Also, we observed the absorptance spectra when UV light was illuminated for 1 minutes, 2 minutes and 3 minutes.

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List of Abbreviations

Ag-NPs	Silver Nanoparticles
SERS	Surface Enhanced Raman Scattering
MOCVD	Molecular Organic Chemical Vapor Deposition
HMTA	Hexamethylenetetraammine
SEM	Scanning Electron Microscope
DRS	Diffuse Reflectance Spectroscopy
LSPR	Localized Surface Plasmon Resonance
OLEDs	Organic Light Emitting Diodes
UV	Ultraviolet - Visible
PL	Photoluminescence

Chapter 1 – Introduction

1.1 Nanotechnology

Nanotechnology is an interdisciplinary field of science concerning the design, synthesis, characterization and application of nanomaterials and nanostructures. Materials in the micrometer scale mostly exhibit physical properties the same as that of bulk form; however, materials in the nanometer scale may exhibit physical properties distinctively different from that of bulk. Crystals in the nanometer scale have a low melting point and reduced lattice constants, since the number of surface atoms or ions becomes a significant fraction of the total number of atoms or ions and the surface energy plays a significant role in the thermal stability.

In general, nanotechnology can be understood as a technology of design, fabrication, and applications of nanostructures and nanomaterials. In order to explore novel physical properties and phenomena and realize potential applications of nanostructures and nanomaterials, the ability to fabricate and process nanomaterials and nanostructures is the first corner stone in nanotechnology. Nanostructured materials are those with at least one dimension falling in nanometer scale, and include nanoparticles (including quantum dots, when exhibiting quantum effects), nanorods and nanowires, thin films, and bulk materials made of nanoscale building blocks or consisted of nanoscale structures. Many technologies have been explored to fabricate nanostructures and nanomaterials.

1.2 Silver nanoparticles and its applications:

Silver nanoparticles have been the focal point of researchers because of its potential applications in the field of biomedical and optoelectronics. As it is non-toxic to the environment, which is the biggest concern these days. Silver nanoparticles (AgNPs) are one of the most vital and fascinating nanomaterials among several metallic nanoparticles that are involved in biomedical applications. AgNPs play an important role in nanoscience and nanotechnology, particularly in nanomedicine. Although several noble metals have been used for various purposes, AgNPs have been focused on potential applications in cancer diagnosis and therapy. Following are the main applications of silver nanoparticles:

- **Diagnostic Applications:** Silver nanoparticles are used in biosensors and numerous assays where the silver nanoparticle materials can be used as biological tags for quantitative detection.
- **Antibacterial Applications:** Silver nanoparticles are incorporated in apparel, footwear, paints, wound dressings, appliances, cosmetics, and plastics for their antibacterial properties.

- **Conductive Applications:** Silver nanoparticles are used in conductive inks and integrated into composites to enhance thermal and electrical conductivity.
- **Optical Applications:** Silver nanoparticles are used to efficiently harvest light and for enhanced optical spectroscopies including metal-enhanced fluorescence (MEF) and surface-enhanced Raman scattering (SERS).

1.3 Zinc Oxide nanostructures and its applications:

Zinc oxide (ZnO) has been known as the next most important material for the fabrication of efficient nanodevices and nanosystems because of its versatile properties such as semiconducting, piezoelectric, and pyroelectric multiple properties. ZnO is also an attractive material for short-wavelength optoelectronic applications owing to its wide band gap of 3.37 eV, large bond strength, and large exciton binding energy (60 meV). Therefore, it is suitable for efficient excitonic emission at room-temperature and solid-state blue to UV optoelectronics, including laser developments. ZnO has a wide morphological diversity in nanostructures such as nanowires, nanorods, nanotubes, nanowalls. The key characteristics of ZnO and its suitability for use in distributed device active layers and discrete devices are heavily dependent on nanostructure morphology, and, hence, they require parameter tuning for optimal performance.

The variety of ZnO nanostructures is dependent on growth mechanism, growth method, synthetic condition, kind of substrate and so on. The nanostructures include nanorods, nanowires, nanocolumns, nanotubes, nanobelts, nano-rings, nanoribbons, nanosheet networks, hollow micro- and nano-spheres, nanoflowers, and nano-combs. With reduction in size, novel electrical, mechanical, chemical and optical properties are introduced resulting from surface and quantum confinement effects. ZnO is a significant technological material. The absence of a center of symmetry in its wurtzite structure, along with large electromechanical coupling, results in strong piezoelectric and pyroelectric properties. ZnO is therefore widely used in mechanical actuators and piezoelectric sensors.

1.4 Crystal Structure of ZnO:

The ZnO crystal is hexagonal wurtzite and exhibits partial polar characteristics with lattice parameters a=0.3296 and c= 0.52065 nm.

The structure of ZnO can be described as a number of alternating planes composed of tetrahedrally coordinated O^{2-} and Zn^{2+} stacked alternately along the *c*-axis, as shown in figure 1.1. The tetrahedral coordination in ZnO results in piezoelectric and pyroelectric properties due to the absence of inversion symmetry. Another important characteristic of ZnO is polar surfaces. The most common polar surface is the basal plane (0001). One end of the basal polar plane terminates with partially positive Zn lattice sites and the other end terminates in partially negative oxygen lattice sites. The oppositely charged ions produce positively charged Zn-(0001) and negatively charged O-($000\bar{1}$) surfaces, resulting in a normal dipole moment and spontaneous polarization along the *c*-axis as well as a variance in surface energy. To maintain a stable structure, the polar surfaces generally have facets or exhibit massive surface reconstructions, but ZnO± (0001) surfaces are exceptions: they are atomically flat, stable and exhibit no reconstruction. Efforts to understand the superior stability of the ZnO±(0001) polar surfaces are at the forefront of research in today's surface physics. The other two most commonly observed facets for ZnO are $\{2\bar{1}\bar{1}0\}$and $\{01\bar{1}0\}$, which are non-polar and have lower energy than the {0001} facets.

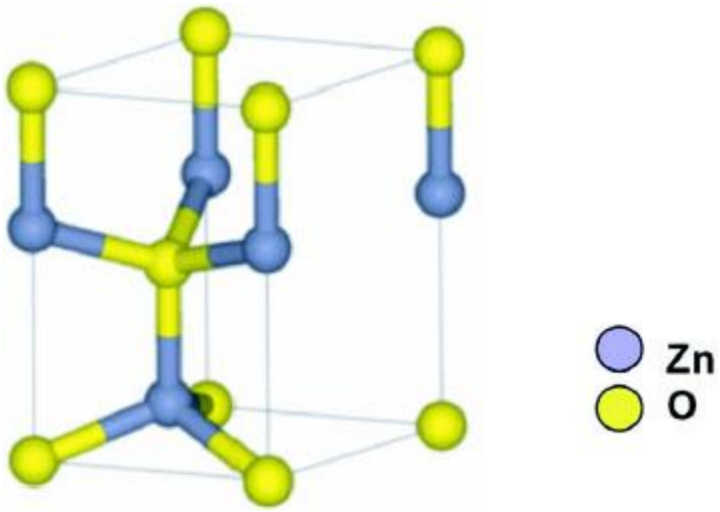

Figure 1.1. Wurtzite structure model of ZnO.

1.5 Defect States in ZnO nanostructures:

At room temperature, ZnO typically exhibits one emission peak in the UV region due to the recombination of free excitons, and possibly one or more peaks in the visible spectral range which are attributed to defect emissions, but the origin of defect emissions is still not fully clear. In addition to experimental studies of the defect emissions, energy levels of different defects and their formation energies have been calculated. However, the origins of different defect emissions are still not fully understood, and controversial hypotheses have been proposed to explain the different defect emissions.

It is known that different types of defects are responsible for green, yellow and orange-red emissions, but the chemical natures of the defects responsible for these emissions have not been conclusively established. The most commonly observed is the green defect emission, for which various hypotheses have been proposed.

Yellow and orange-red emissions may involve similar deep levels but different initial states, and they were also found to exhibit different dependences on the excitation wavelength. The yellow emission is commonly attributed to oxygen interstitial defects. In addition to this common hypothesis, the possible presence of $Zn(OH)_2$ at the surface was identified as a possible reason for the weak UV and the strong visible (broad yellow and green) emission. The orange-red emission centered at ~640–650 nm is also commonly attributed to the presence of excess oxygen in the samples, such as oxygen interstitial defects. Other hypotheses include surface dislocations and zinc interstitials.

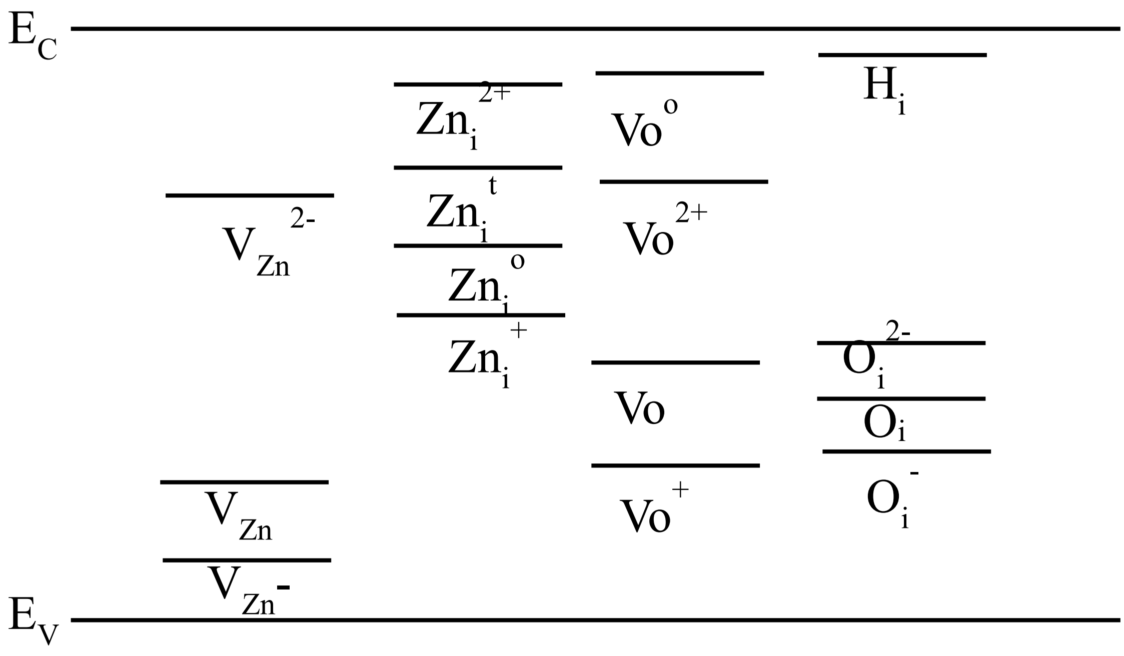

Figure 1.2. Defects in ZnO nanostructures.

Figure 2 shows calculated energy levels of different defects in ZnO from different studies in the literature. All the levels are referred to the conduction-band minimum (CBM). V_{Zn}, V^{-}_{Zn} and V^{2-}_{Zn} denote neutral, singly charged, and doubly charged zinc vacancy respectively. Zn^{o}_{i} and Zn^{t}_{i} indicate neutral octahedral zinc interstitial and neutral tetrahedral zinc interstitial while Zn^{+}_{i} and Zn^{2+}_{i} indicate singly charged and doubly charged zinc interstitial. V_o denote neutral oxygen vacancy while V^{+}_{o} and V^{2+}_{o} denotes singly charged and doubly charged oxygen vacancy. H_i and O_i represent oxygen and hydrogen interstitial respectively.

1.6 Hybrid Ag-ZnO nanostructures:

Semiconductor-based heterostructures with the desired composition and morphology could modulate the properties of the materials and find a potential application in nanodevices. For example, control over the composition and size of the semiconductors allows for the tuning of their band gaps, which determines the absorption and emission characteristics of the optoelectronic devices. Stimulated by the potential applications in biomedicine, photocatalysis, and nanodevices, significant advances have been made in recent years to design various kinds of semiconductor-based heterostructures.

Chapter 2 – Synthesis Processes and Characterization Techniques

Among the various methods that have been developed for the shape and size-controlled synthesis of Ag nanocrystals, the photochemical method has many advantages including low processing temperature, low cost, and controllable size of the Ag nanocrystals. In addition, the photochemical method is also applicable to the synthesis of diverse metallic nanocrystals on semiconductor substrates rather than ZnO. In addition, the absence of organic capping agents in the synthesis processes makes this photochemical approach particularly suitable for preparing metal/semiconductor hybrid materials with surfactant less clean metal/semiconductor interfaces which are critically important for application in plasmon-assisted photocatalysis and photovoltaics.

2.1 Synthesis processes for ZnO nanostructures:

One-dimensional (1D) ZnO nanostructures have been synthesized by a wide range of techniques, such as wet chemical methods, physical vapor deposition, metal–organic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE), pulsed laser deposition, sputtering, flux methods, electrospinning, and even top-down approaches by etching. Among those techniques, physical vapor deposition and flux methods usually require high temperature, and can easily incorporate catalysts or impurities into the ZnO nanostructures. Therefore, they are less likely to be able to integrate with flexible organic substrates for future foldable and portable electronics. MOCVD and MBE can yield high quality ZnO nanowire arrays, but usually suffer from the poor deposition uniformity, low product yield, and limited choices of substrate. Also, the experimental cost is usually very high, so they have been less widely adopted. Pulsed laser deposition, sputtering and top down approaches have less controllability and reproducibility compared with other techniques.

Wet chemical methods are attractive for several reasons: they are low cost, less hazardous, and thus capable of easy scaling up; the growth occurs at a relatively low temperature. In addition, there are a variety of parameters that can be tuned to effectively control the morphology and properties of the final product. Wet chemical methods have been demonstrated as a very powerful and versatile technique for growing 1D ZnO nanostructures.

2.2 Hydrothermal Growth:

Hydrothermal process is successfully used for the controlled fabrication of ZnO nanostructures on glass and Si substrates by the thermal decomposition of methenamine and zinc nitrate. To initiate the growth from the substrate, a thin layer of ZnO nanoparticles was grown on the substrate. Methenamine, also known as hexamethylenetetramine (HMT) or hexamine is a highly water soluble, non-ionic tetradentate cyclic tertiary amine. Thermal degradation of HMT releases hydroxyl ions which react with Zn^{2+} ions to form ZnO. This can be summarized in the following equations:

$$(CH_2)_6N_4 + 6H_2O \longleftrightarrow 6HCHO + 4NH_3$$

$$NH_3 + H_2O \longleftrightarrow NH_4^+ + OH^-$$

$$Zn^{2+} + 2OH^- \longleftrightarrow Zn(OH)_2 \longleftrightarrow ZnO + H_2O$$

It is a general acceptance that the role of HMT is to supply the hydroxyl ions to drive the precipitation reaction. Apart from that, some also opine that HMT acts as a buffer as the rate of its hydrolysis decreases with increasing pH and vice versa. The rate of decomposition of HMT is independent of the reaction that yields ZnO indicating that HMT does act as a kinetic buffer. In oxide formation, the phase that is thermodynamically less stable will precipitate out faster. In the initial growth stage, the pH and the concentration of Zn^{2+} ions is such that the ZnO growth will be through $Zn(OH)_2$. With the gradual increase in the pH and the decrease in the concentration of the Zn ions, $Zn(OH)_2$ becomes thermodynamically unstable and the $Zn(OH)_2$ formed on the substrate will start dissolving. Further growth of the nanostructures will have to be through direct deposition of ZnO.

2.3 Synthesis processes for Ag nanoparticles:

Ag-NPs are generally prepared by either thermal reduction, microwave reduction, sonochemical reduction, chemical reduction, or photoreduction of silver cations (Ag^+) in solution. Thermal treatment is a classical way to prepare Ag-NPs: the solution containing silver cations is heated in the presence of a reducing agent such as H_2 or CO, introduced directly into the reaction mixture. Microwave-assisted reduction presents several advantages like a more homogeneous heating, a shorter reaction time, and an easier nucleation of Ag-NPs. The sonochemical process is used for the preparation of Ag-NPs when the particle size strongly depends on the type of reducing agent applied. Using sodium borohydride, a strong reducing agent, results in spherical Ag-NPs 10 nm in size, while with a weak reducing agent, such as sodium citrate, the formation of Ag-NPs ~3 nm in size is observed. Moreover, chemical treatment is an efficient process for preparing Ag-NPs in solution with good control of their size and shape. The key to a rational design is to find the proper combination of silver precursors, a reducing agent, stabilizers, and reaction conditions (rate and pH). The drawback of these methods is the use of relatively large amounts of reducing agents and their subsequent elimination in an additional step. Furthermore, Ag-NPs are generally sensitive to heat and oxygen; the addition of capping and stabilizing agents is usually recommended to preserve their structure and prevent their aggregation in solution.

2.4 Photochemical Reduction:

Photochemical reduction of the cations of some metals (for example, Ag, Au, Cu, Pt, Pd, Cd, etc.) induced by semiconductor nanostructures (TiO_2, ZnO, SnO_2, CdS, ZnS, etc.) are of great interest not only as model processes for the investigation of photocatalytic properties of ultra dispersed semiconductors, but also as one of the methods of the preparation of nanostructured metal–semiconductor composites. An advantage of this method lies in the opportunity to control the composition of metal–semiconductor nanostructures through variations in the conditions of photochemical reaction. UV light was irradiated on the sample dispersed with precursor solution, electron- hole pairs were generated in semiconductor nanostructures and electrons were taken by metal ions and reduced to metal/semiconductor hybrid nanostructures.

2.5 Scanning Electron Microscope:

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm).

Accelerated electrons in an SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathodoluminescence–CL), and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination). X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete orbitals (shells) of atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element). Thus, characteristic X-rays are produced for each element in a mineral that is "excited" by the electron beam. SEM analysis is considered to be "non-destructive"; that is, x-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly.

2.6 Diffuse Reflectance Spectroscopy:

The optical phenomenon known as diffuse reflectance is commonly used in UV-visible, near infrared and mid infrared regions to obtain molecular spectroscopic information. It is usually used to obtain spectra of powders with minimum sample preparation. A reflectance is obtained by the collection and analysis of surface reflected electromagnetic radiation as a function of frequency or wavelength. Two different type of reflections can occur; regular reflection usually associated with reflection from plane surfaces, and diffuse reflection associated with reflection from dull surfaces textured like powders. Techniques such as external reflectance and total internal reflectance spectroscopy uses the phenomenon of diffuse or specular reflection to obtain spectroscopic information.

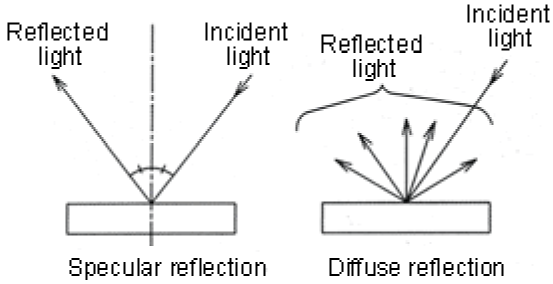

Figure 2.1 Types of Diffraction

2.7 Materials and Chemicals Used:

The following materials have been used for the synthesis of silver nanoparticles:

Substrate: Glass

Chemicals:

Zinc acetate ($Zn(CH_3COO)_2$), Ethanolamine ($OHCH_2CH_2NH_2$), 2-methoxyethanol ($CH_3OCH_2CH_2OH$), Zinc nitrate hexahydrate ($Zn(NO_3).6H_2O$), Hexamethylenetetraamine ($(CH_2)_6N_4$, HMTA), Silver nitrate ($AgNO_3$), Ethanol (CH_3CH_2OH).

Chapter 3 – Experimental Procedure

This chapter presents the various experimental methods used for the synthesis of Silver nanoparticles. The general steps involved in the synthesis of Silver nanoparticles has been given in the form of a flow diagram in the beginning of this chapter. A brief description of various methods involved in the fabrication of thin films and device has also been discussed.

(Caution: Some of the materials used in the lab can be corrosive or harmful to your body. Make sure that you use safety goggles, rubber gloves, and masks whenever necessary to ensure your safety.)

The following steps were taken for making thin films:

Fig 3.1 Flow diagram showing steps involved in deposition of ZnO seed layer

The following steps were taken for synthesis of Silver nanoparticles:

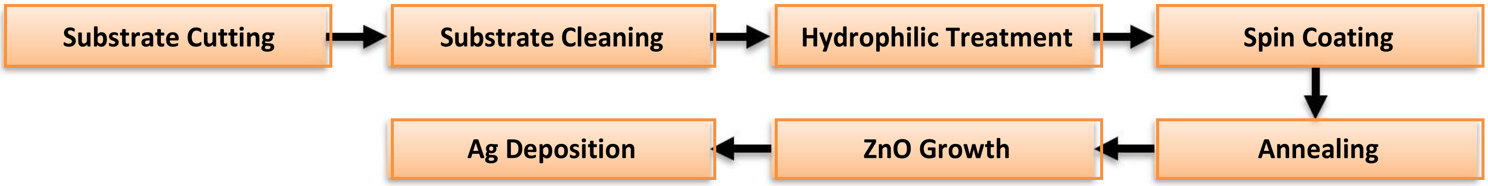

Fig 3.2 Flow diagram of steps involved in synthesis of Ag-ZnO nanostructures.

3.1 Substrate cutting

The glass substrates of required dimensions were cut with the help of diamond cutter. The dimension of glass substrates were different for different characterization, but for most of them 1.2cm × 1.2cm glass substrate were required.

3.2 Cleaning procedure:

The next stage involves cleaning the substrates. The substrates were cleaned for inorganic impurities clinging to the surface of these substrates by using the ultrasonic bath. First, substrates were ultrasonicated for 15 mins in acetone and then taken out and dried. In second step, substrates were ultrasonicated in Isopropyl alcohol for 15 mins and then dried. In third step, substrates were ultrasonicated in DI water for 5 mins. All these steps should be sequential followed by hydrophilic treatment.

3.3 Hydrophilic Treatment

To ensure good adhesion between seed solution and substrate, hydrophilic treatment on glass substrate is usually required to make the surface more hydrophilic.

Take a petridish, pour NH_4OH : H_2O_2 : DI water in 1:1:5 ratio. Put glass samples in the petridish and heat for 20 mins at around 60^oC.

Generally, the glass and SiO_2 surfaces are hydrophilic in nature and seed solution (Zinc acetate, ethanolamine and 2-methoxyethane) is also hydrophilic in nature but to reduce the surface energy mismatch between substrate surface and ZnO seed layer and thereby improving the smoothness of thin film we make the surface more hydrophilic.

3.4 Spin Coating:

Spin Coating is done to make thin layer on glass substrate. Thickness of the layer can be varied by varying the speed of the spin coater. A seed layer of ZnO was coated on glass substrate using spin coater. An equimolar colloidal solution of Zinc acetate(2M) and ethanolamine(2M) was prepared in 2-methoxyethanol. This solution was dispersed on glass substrate and left untouched for 5 minutes to make a good adhesion between glass and solution, and then spin coated at 3000 rpm for 30 seconds followed by annealing.

3.5 Annealing:

Annealing is a heat treatment, done on the spin coated substrate to eliminate the solvent from the solution on substrate. Also, it modifies the surface morphology and changes physical parameters. Here, substrate was heated at 330°C for 5 minutes. A fine seed layer was formed and will act as nucleation sites for the further growth process.

3.6 Growth Process:

A precursor solution was prepared by mixing $Zn(NO_3).6H_2O$ (0.1M) with equimolar hexamethylenetetraamine ($(CH_2)_6N_4$, HMTA) in a borosilicate glass beaker. The seed layer was immersed in precursor solution and reaction was carried out in seal tight beaker at 110°C for 4 hours. A high quality ZnO nanorods were synthesized through the hydrothermal growth process. Following reactions were involved in hydrothermal growth process:

$$(CH_2)_6N_4 + 6H_2O \longleftrightarrow 6HCHO + 4NH_3$$

$$NH_3 + H_2O \longleftrightarrow NH_4^+ + OH^-$$

$$2OH^- + Zn^{2+} \longleftrightarrow Zn(OH)_2 \longleftrightarrow 2H^+ + ZnO_2^{2-} \longleftrightarrow ZnO + H_2O$$

3.7 Silver Deposition:

Silver nanoparticles were deposited on ZnO nanostructures by dispersing precursor solution of 80% $AgNO_3$ and 20% ethanol on ZnO nanostructures under UV illumination, electron-hole pairs were created in ZnO nanostructures and Ag^+ ions were reduced to Ag and Ag nanoparticles were deposited on ZnO nanostructures. This method has many advantages over other methods that were discussed in previous sections.

3.8 Photochemical Process:

As band gap of ZnO is 3.37 eV, when UV light was illuminated, electron-hole pairs were generated and electrons in conduction band acts as reducing agent and holes in valence band acts as oxidising agent. Here following reactions were involved in this process:

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

$$Ag^+ + e- \rightarrow Ag$$

After all these steps, the final samples look as shown in the below:

Fig 3.4 Final Prepared samples

Chapter 4 – Analysis, Discussion and Results

4.1 Light absorption in ZnO and Ag nanostructures:

When light either in the visible or ultraviolet is absorbed by the valence electrons in ZnO and silver nanostrctures, and these electrons are then promoted from their normal ground states to the higher energy states. Transition energy levels are known to vary with the size and geometry of the active structure and precise structural manipulation has become possible in the wake of nanotechnology and nanoscience hereby allowing fine tuning of transition energy levels. With this stance, all new construction concepts may be employed to quantum transforming devices. The optical excitation of plasmon resonances in SNPs represents the most efficient mechanism by which light interacts with matter. By varying the particle size, shape, and surrounding dielectric medium the plasmon resonance can be tuned across the near-UV, visible, and near-infrared spectral range. The high efficiency for interaction with light, tunability of the optical resonance, as well as photochemical robustness makes SNPs attractive for applications in optical filters, plasmonic waveguides, substrates for surface-enhanced spectroscopies, and biosensors.

4.2 Spectroscopy

Spectroscopy usually means experimental charting of the energy level structure of physical systems. It is often used for the analysis of various types of radiation, electromagnetic or particle emission. Spectroscopic investigations can be of fundamental or an applied nature. Most fundamental spectroscopic techniques can be used to determine energy levels, transition probabilities etc., experimentally. Spectroscopic methods are also employed for understanding of the studied systems using adequate theory and models. Usually, certain primary quantities viz. wavelength, intensities, etc. are measured in spectroscopic investigations.

The spectroscopic information can be used for various kinds of analysis for instance, optical absorption and emission spectroscopy is used for both qualitative and quantitative chemical analysis. It can also be used to determine the electronic arrangement of various materials. Thus, spectroscopic techniques are one of the most powerful tools for a great variety of molecular structure studies.

4.3 Absorption Spectroscopy

The nature of excited state and the processes of absorption and emission of light are central ideas in the modern spectroscopy. Absorption spectroscopy refers to the interaction (absorption) of electromagnetic radiation (160 to 780nm) by matter. The collective oscillation of the conduction electrons, known as localized surface plasmon resonances (LSPRs), which depends on the shape and size of the particle and on the refractive index of the surroundings.

4.4 Photoluminescence spectroscopy

Photoluminescence (PL) is the spontaneous emission of light from materials under optical excitation. The excitation energy and intensity are chosen to probe different regions and excitation concentrations in the sample. PL based investigations can be used to characterize a variety of material parameters. PL spectroscopy is a selective and extremely sensitive probe of discrete electronic states and its emission spectra can be used to identify surfaces, interfaces and impurity levels. It is a nondestructive technique that requires minimal sample manipulation and since the technique is based on optical excitation, highly resistive materials pose no practical difficulty. Although there is a fundamental limitation of PL analysis and it relies on radiative events therefore, materials with poor radiative efficiency, such as low quality indirect band gap semiconductors are difficult to study via ordinary PL. The principle of PL measurement can be described as follows. When a light of sufficient energy is incident on a material, photons are absorbed and electronic excitations are created. These excitations or quasiparticles are the bound state of an electron and its quasiparticle hole, usually occurring in an insulator or semiconductor. Since, they are bounded coulombically therefore their energy is less than that of free electron hole pairs. These excitons provide a means to transport energy without transporting the net charge. Eventually these excitons relax to the ground state and if the relaxation (recombination) is radiative it results in PL emission. This emitted light can be collected and analyzed to yield a wealth of information about the photo excited material. PL spectrum is indicative of transition energies, which in turn determine the electronic energy levels. The PL intensity gives a measure of the relative rates of radiative and nonradiative recombination.

4.5 Explanation of UV & PL Spectra

There are many observations we can make from DRS Spectra and PL Spectra.

The following below parameters are of our primary interest:

1. Red-shift and blue-shift
2. PL intensity

3. Absorption intensity
4. Defect related emission
5. Narrow/ Broader Spectrum

Red shifted spectra refer to spectra which is shifted towards longer wavelength and less energetic. Blue shifted spectra refer to spectra which is shifted towards shorter wavelength and more energetic.

In PL spectra of ZnO and Silver deposited ZnO, two peaks were observed. One is in UV region called Near Band Edge emission and other is defect related emission in Visible region known as Deep-Level emission. NBE is due to transition of electrons from edge of conduction band to edge of valence band. DL emission is due to energy states introduced in forbidden energy gap because of surface defects and defects related to vacancy created and interstitial position gained by different atoms or ions in crystal structure which is described in section 1.5.

In Normalized PL spectra of hybrid Ag-ZnO nanostructures, defect related emission in visible region is enhanced with increase in UV illumination time, and that may be due to increase in density of defects related to oxygen vacancies in crystal structure. Broadening of NBE emission peak is also observed, which can also be due to defect states introduced because of Zn^{2+} interstitial positions. Blue shift is also observed in hybrid Ag-ZnO nanostructures, which can be due to Quantum Confinement effect and due to transition of electrons from higher energy levels as band-edge energy levels may be blocked.

In PL spectra of Ag deposited ZnO nanostructures, we observed, quenching in NBE emission intensity, may be electrons are transferring from ZnO to silver that can be a reason for low intensity in NBE emission.

In DRS spectra of Ag-ZnO hybrid nanostructures, two peaks are observed, one is in UV region at around 370nm to 380nm corresponding to ZnO and other is in Visible region at around 420nm corresponding to Silver which confirmed the deposition of Ag on ZnO. From DRS spectra increase in absorption can be observed with increase in UV illumination time. There may be increase in density of silver nanoparticles that can be a reason for increase in absorption intensity. We observed red-shift in both the peaks corresponding to ZnO and Ag. For ZnO peak red-shift may be due to transfer of electrons from ZnO to Ag and red-shift in peak corresponding to Ag may be due to increase in size of Silver nanoparticles.

4.6 SEM IMAGES:

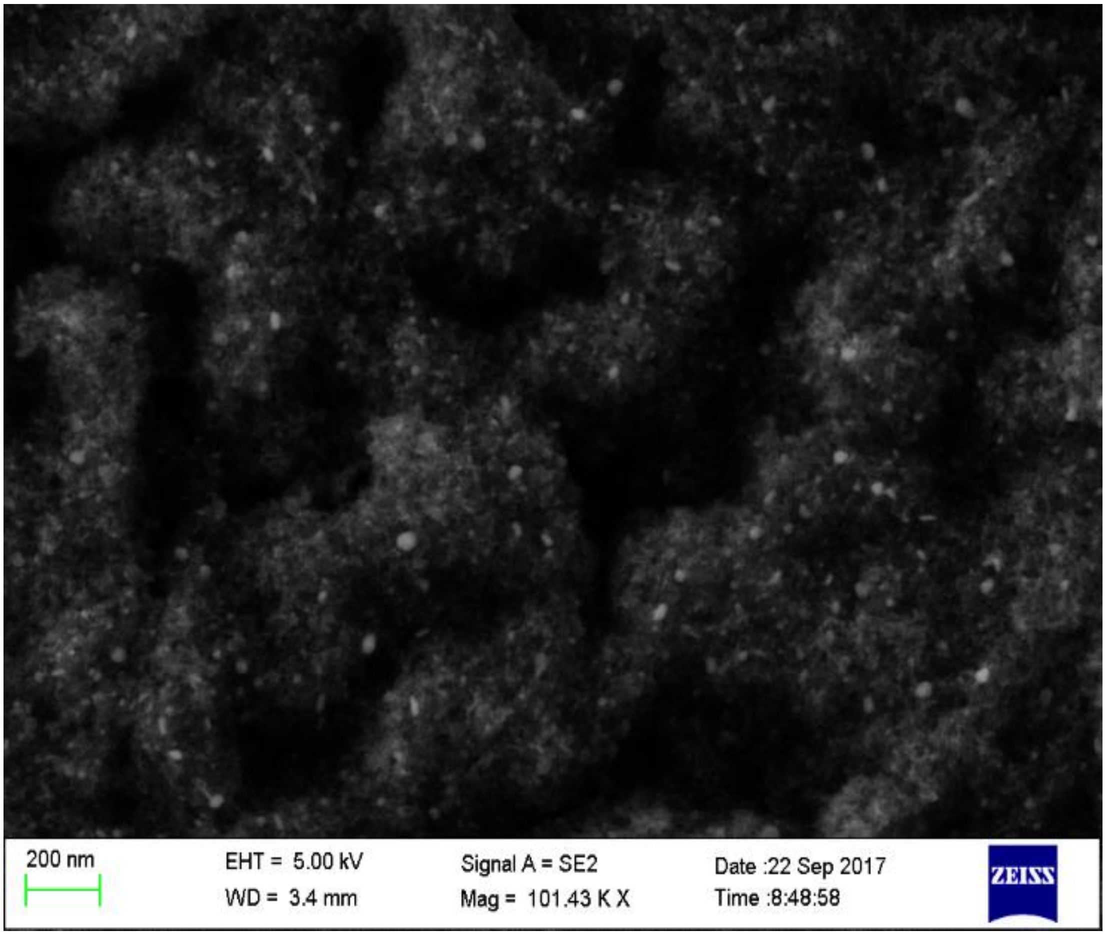

Figure 4.1 SEM image

4.7 DRS and PL Spectra:

A) DRS Spectra

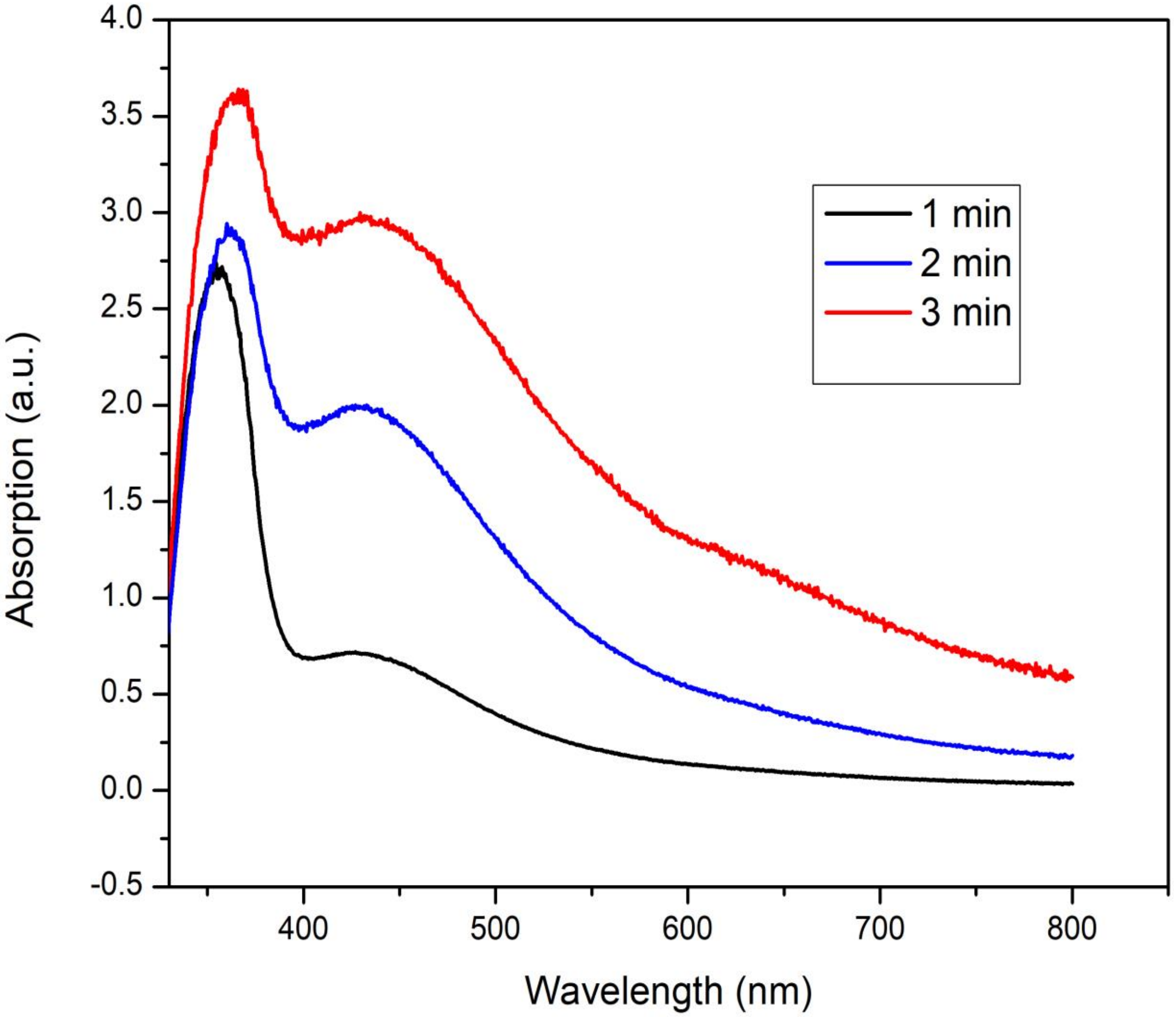

Figure 4.2 DRS spectra of Ag-ZnO nanostructures when UV light was illuminated for 1 minute, 2 minutes and 3 minutes.

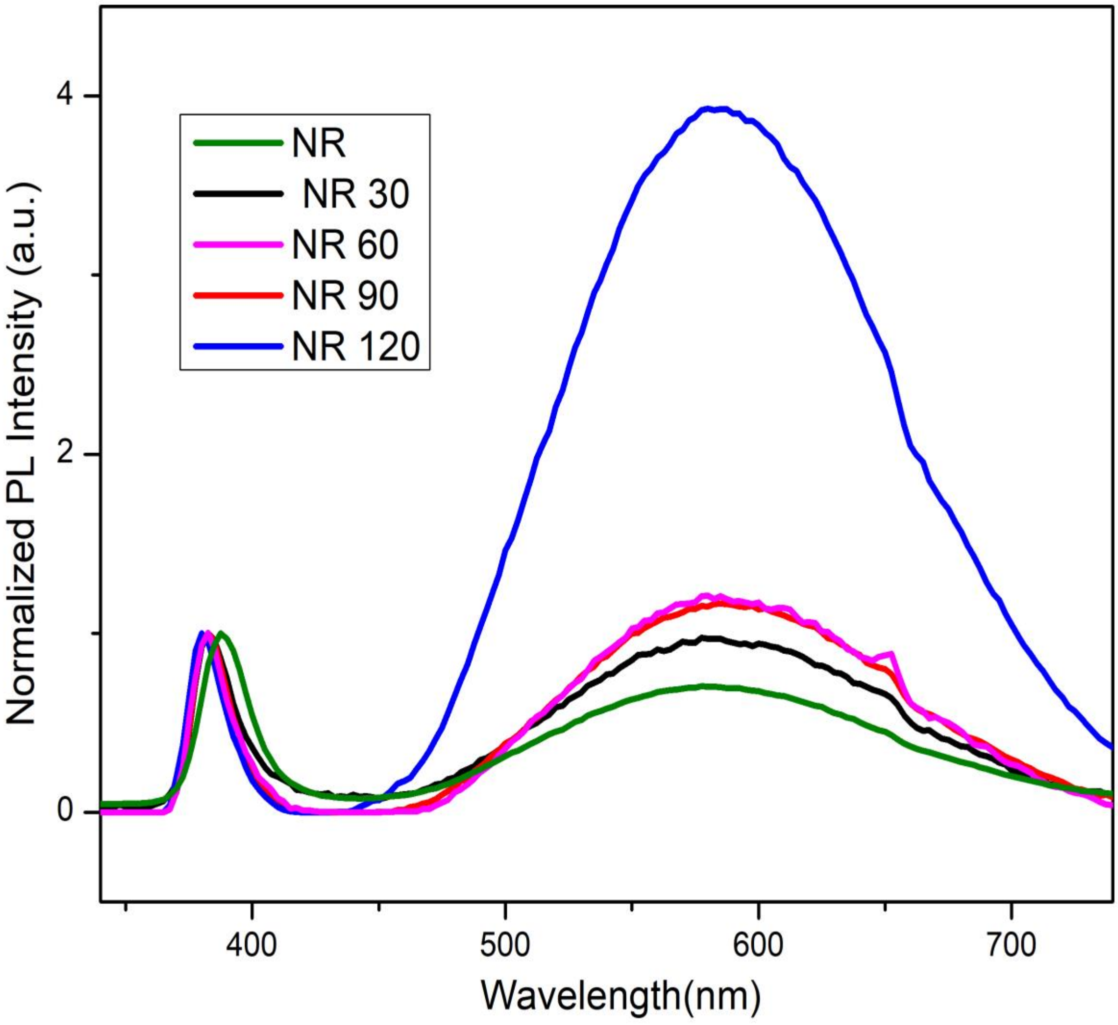

Figure 4.3 Normalized PL spectra of ZnO nanorods and Ag-ZnO nanostructures when UV light was illuminated for 30 seconds, 60 seconds, 90 seconds and 120 seconds.

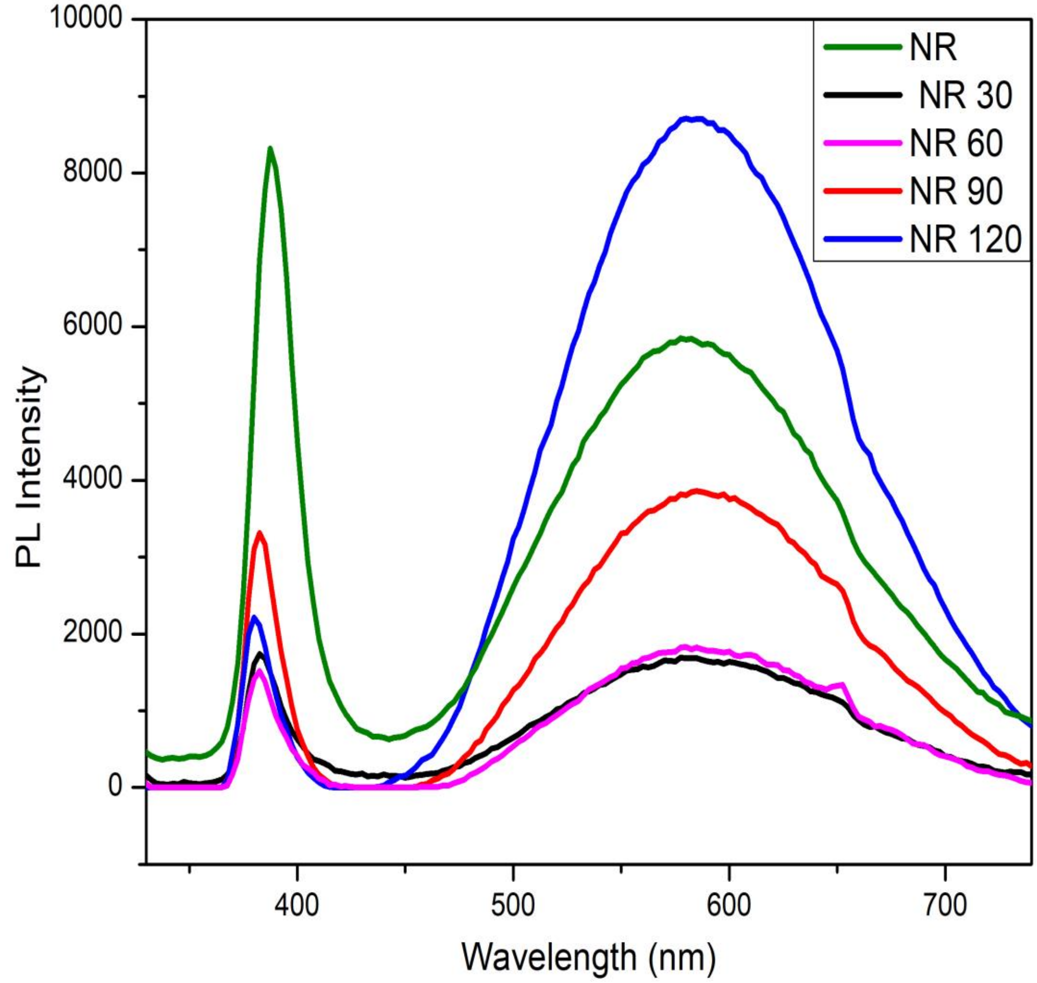

Figure 4.4 PL Spectra of ZnO nanorods and Ag-ZnO nanostructures when a solution of 20% $AgNO_3$ and 80% ethanol was dispersed under UV light was illuminated for 30 seconds, 60 seconds, 90 seconds, and 120 seconds.

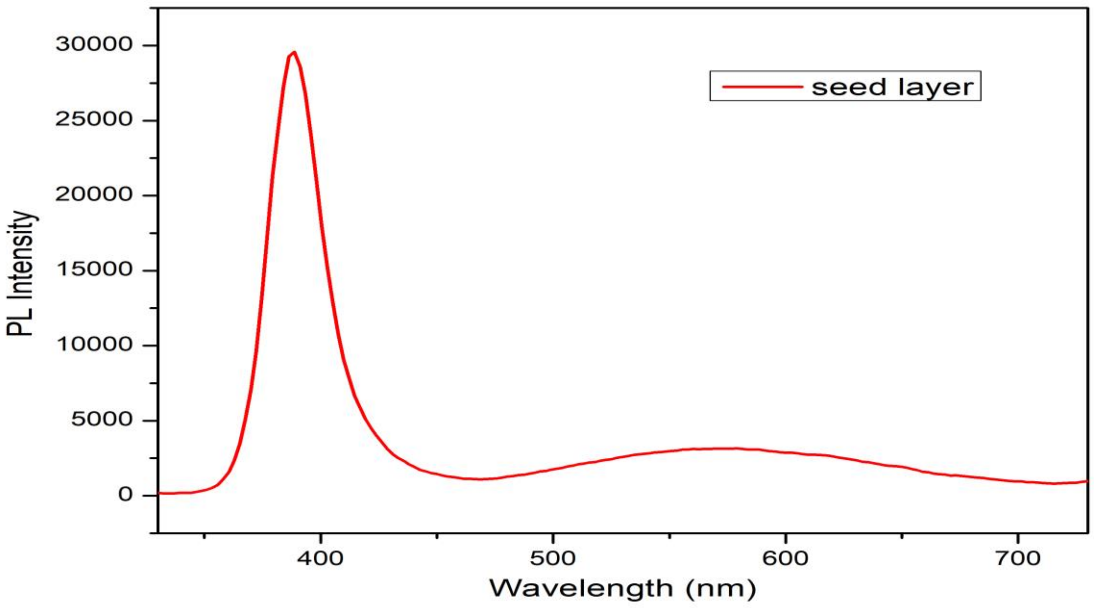

Figure 4.5 PL spectra of ZnO seed layer

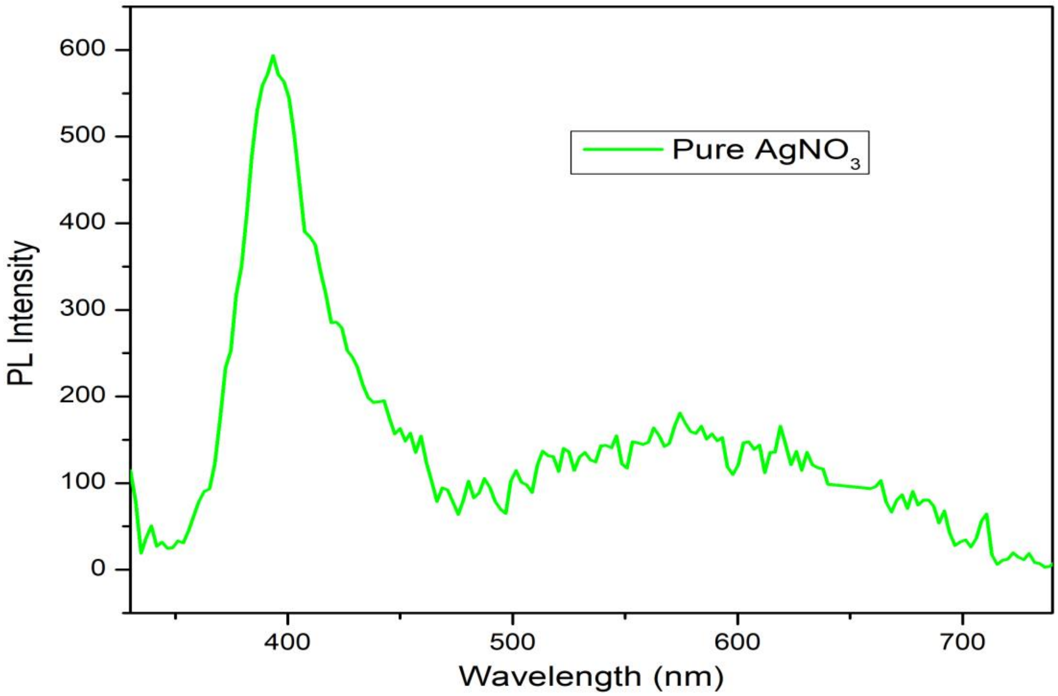

Figure 4.6 PL spectra of Ag-ZnO nanostructures when pure $AgNO_3$ was dispersed under UV illumination.

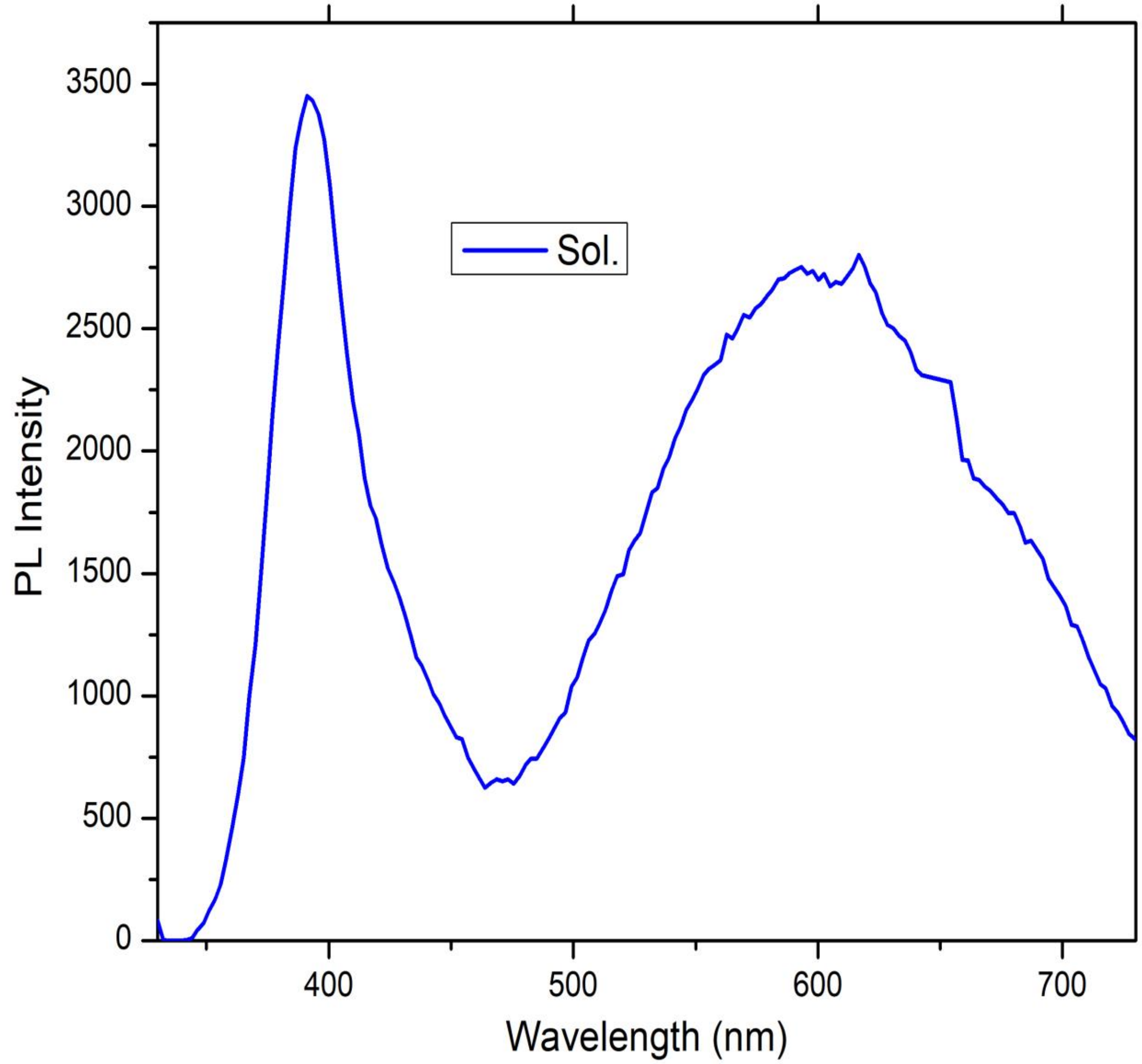

Figure 4.7 PL Intensity of Ag-ZnO nanostructures when a solution of 80% $AgNO_3$ and 20% ethanol was dispersed on seed layer on ZnO seed layer and sample was illuminated with UV light.

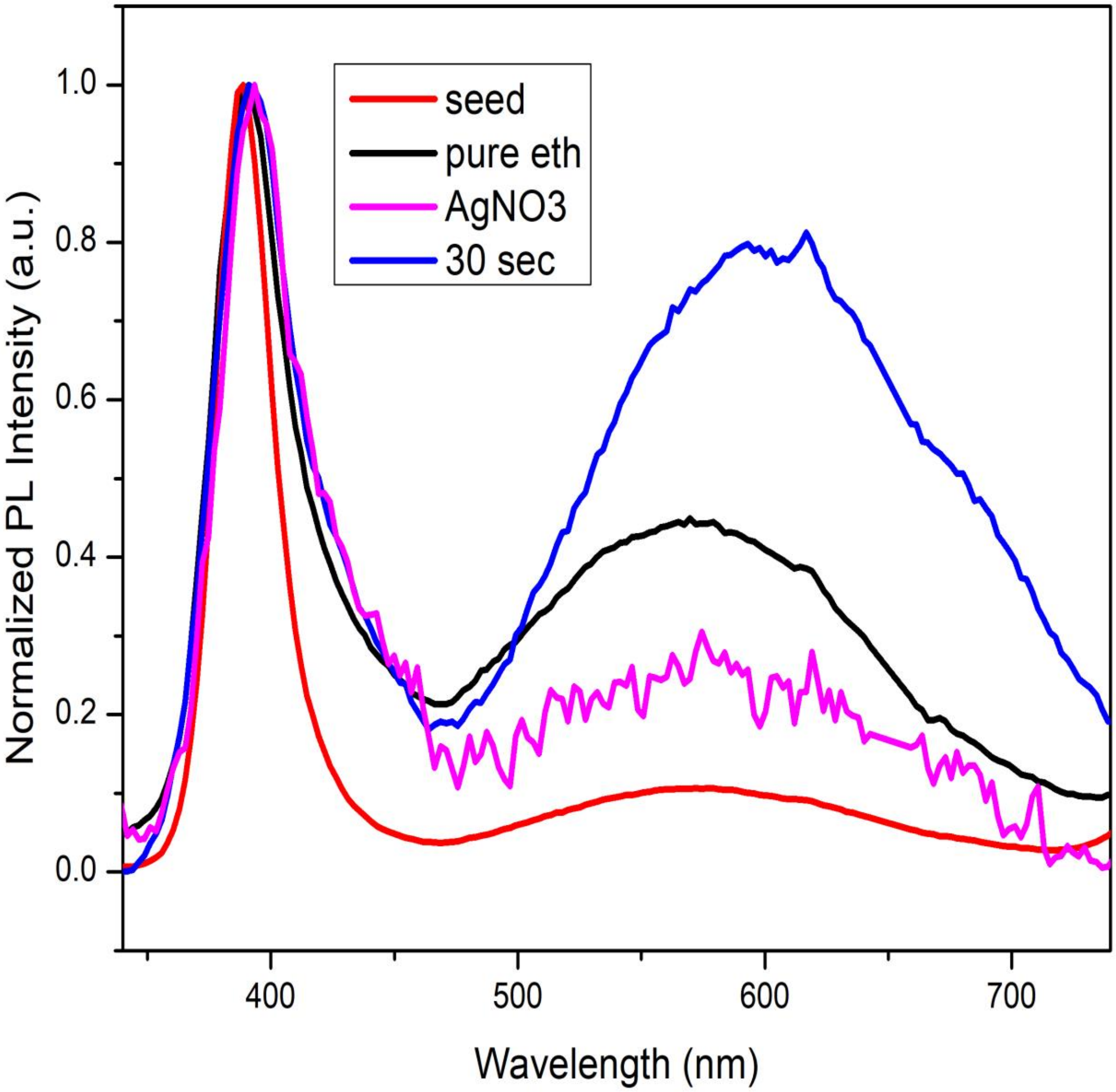

Figure 4.8 Normalized PL Spectra of ZnO seed layer and when $AgNO_3$ and ethanol were dispersed on seed layer under UV illumination

Chapter 5 – Conclusions and Future Scope

We have successfully prepared silver nanoparticles through Photochemical reduction process. For reduction process we have used ZnO nanostructures on which Silver nanoparticles were deposited upon UV illumination with precursor solution dispersed on ZnO nanostructures. And also, we have synthesized ZnO nanorods through hydrothermal growth process.

In this work Ag-ZnO nanostructures were prepared and studied the effect of Ag nanoparticles on ZnO nanostructures. We have also seen, how size of Ag nanoparticles is affecting the properties of ZnO nanostructures. As plasmonic properties depend on the shape, size and density of nanoparticles, we can get desired the absorption frequency by tuning the shape, size and density of nanostructures.

These days environmental problems are of the biggest concerns. Fresh air and fresh water is the basic need for all. But as industrialization is increasing rapidly and so the pollution. The hybrid Ag-ZnO nanostructures prepared here can be used for environmental remediation. Organic dyes can be reduced or oxidized by photochemical process using these nanostructures. We will study the affect size, shape and density of Silver nanostructures on ZnO nanostructures for their photochemical activities.

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