Synthesis and characterization of gold-silver Nanostructure with controlled optical properties

By

Ambreen Akram

(320-FBAS/MSPHY/F-14)

Supervisor

Dr. Shaista Shahzada

Asistant professor

Department of physics, FBAS, IIUI

Co-Supervisor

Dr. Amjad Nisar

Pakistan Institute of Nuclear Science and Technology

PINSTECH, Islamabad

Department of Physics

Faculty of Basic and Applied Sciences
International Islamic University, Islamabad
(2017)

Nanotechnology
X-ray Spectroscopy
Nanoparticles

International Islamic University Islamabad,

Faculty of Basic and Applied Sciences,

Department of physics

Synthesis and characterization of gold-silver Nanostructure with controlled optical properties

By

Ambreen Akram

(320-FBAS/MSPHY/F-14)

Thesis submitted to

Department of Physics

International Islamic University Islamabad

For the award of the degree of MS physics

Signature: ______________________________

(Acting Chairperson, Department of Physics)

Dr. Shamaila Sajjad
Chairperson
Department of Physics (FC, FBAS)
International Islamic University
Islamabad

M. Arshad

Signature: ______________________________

(Dean FBAS, IIUI, Islamabad)

This thesis is submitted to the Faculty of Basic and Applied Sciences (FBAS),

International Islamic University Islamabad (IIUI) in partial fulfillment of the

requirement for the degree of MS Physics

بسم الله الرحمن الرحيم

Declaration of Originality

I hereby declare that the work contained in this thesis and the intellectual content of this thesis are the product of our own work. This thesis has not been previously published in any form nor does it contain any material of the published resources which could be treated as infringement of the international copyright law.

I also declare that I do understand the terms of copyright and plagiarism and that in case of any copyright violation or plagiarism found in this work, I will be beld fully responsible of the consequences of any such violation.

Ambreen Akram

320-FBAS/MSPHY/F-14

Certificate

This is to certify that the work contained in this thesis entitled: "Synthesis and characterization of gold-silver nanostructure with controlled optical properties" has been carried out by Ambreen Akram, Registration No. 320-FBAS/MSPHY/F-14 in Pakistan Institute of Nuclear Science and Technology (PINSTECH) under the supervision of Dr. Shaista Shahzada and Dr. Amjad Nisar. In my opinion, this is fully adequate in scope and quality for the degree of MS Physics.

Supervisor ____________________
Dr. Shaista Shahzada
Assistant professor,
Department of Physics
International Islamic university, Islamabad.

Co-Supervisor ____________________
Dr. Amjad Nisar
Principal Scientist,
Nanomaterials Research Group
Physics Division (PINSTECH), Islamabad.

Department of Physics

Dated: 19-04-2017

Certificate of Approval

It is certified that the work presented in this thesis entitled "**Synthesis and characterization of gold-silver nanostructure with controlled optical properties**" by **Ambreen Akram**, Registration No. **320-FBAS/MSPHY/F-14** is of sufficient standard in scope and quality for the award of degree of MS Physics from International Islamic University, Islamabad.

Committee

External Examiner:

Dr. Iftikhar Hussain Gul
Associate professor
SCME, NUST, Islamabad.

Internal Examiner

Dr. Waqar Hussain Shah

Assistant Professor, Department of Physics.

International Islamic University, Islamabad.

Supervisor

Dr. Shaista Shahzada,

Assistant Professor, Department of Physics.

International Islamic University, Islamabad.

Co-Supervisor

Dr. Amjad Nisar, Principal Scientist

Pakistan Institute of Nuclear Science and Tech.

PINSTECH, Islamabad.

Acknowledgment

Praise is to the One, the Almighty, the merciful and the beneficent Allah, who is the source of all knowledge and wisdom, taught us what we knew not. I offer my humblest thank to the Holy Prophet (Peace be upon him) who is forever a model of guidance and knowledge for humanity.

I also acknowledge my supervisor Dr. Shaista Shahzada and my Co-Supervisor Dr. Amjad Nisar for their inspiring guidance, remarkable suggestions, constant encouragement and co-operation during my project work. Without their support and guidance, this project could not have been possible. I gratefully acknowledge for their technical support during my thesis.

I am highly thankful to Dr. Shafqat Karim who permitted me to continue my research work in NRG lab and I greatly acknowledge Dr. Mashkoor Ahmad and Dr. Ghaffar for solving queries and helped me by sharing their inspirational knowledge. I admire the behavior of Mr. Afzal, Mr. Shakeel and Mr. Tahir in our lab during my research work.

I am very grateful to my friends Saba Noreen, Ayesha Bashir, Sadia Tabassum, Anum Zafar, Ammara, Atiqa, and class fellows for giving me encouragement, appreciation and helped in completing this project.

Ambreen Akram

Dedication

This thesis is dedicated to my beloved parents

My adorable brothers Altamash Imran, Danish Imran

And

My husband Saif-ur-Rehman

Table of Contents

List of Figures

List of Tables

Abstract

Gold and silver are the noble metals tuning the unique optical properties due to the solid absorption spectrum in the visible area with the wide range of applications in the biomedical and material sciences. The nanoparticles of gold and gold-silver with changing amount of silver have been successfully synthesized by co-precipitation method. Silver shells of different thickness have been prepared by decreasing amount of Ag^+ over the gold sol with ascorbic acid as a reducing agent. A hydrothermal process was used to produce the Au/SiO_2 and $Au\text{-}Ag/SiO_2$ nanoparticles. These nanoparticles were characterized by scanning electron microscopy (SEM), energy disperse X-ray spectroscopy (EDS), dynamic light scattering (DLS) and Ultraviolet-visible spectroscopy .Scanning electron microscopy results show that the synthesized material are like Nano clusters having a size in nm range. Energy disperse X-ray spectroscopy studies confirms that Au-Ag nanoparticles are formed. Dynamics light scattering was used to measure the particle size Au and Au-Ag nanoparticles. Au seed having particle size 36nm .when gold seed coated with silver shell, particle size increased with increasing silver concentration from 44 to 96 nm. UV/Vis spectra studies revealed that absorption spectrum appears at 532 and 415 nm of gold and silver are due to surface Plasmon resonance band, respectively. The blue shift was observed due to the coherent oscillations of all free electrons in the conduction band induced by the interacting electromagnetic field with increasing the concentration of silver. Au/SiO_2 and $Au\text{-}Ag/SiO_2$ nanoparticles have been also used as a photo catalyst in the Photo catalytic experiment under UV light for the degradation of methylene blue (MB) dye at two different pH (pH-5 and pH-9). No significant degradation was attained at ph-5. Degradation efficiency increases from 50% in 50min to 95% in 16min via increasing pH value of methylene blue dye from pH-5 to pH-9.The photo catalytic activity of $Au\text{-}Ag/SiO_2$ slightly higher than Au/SiO_2 which means photo catalytic activity was also enhanced by Ag coating

Chapter. 1

Introduction

In the past years Nanotechnology is one of the growing field in the scientific world particularly in material and biomedical sciences which deals with the manipulation and characterization of matter at nanoscale [1].

The influence of nanotechnology expands from its therapeutic, moralistic, psychological and ecological application. Most important advantages of nanotechnology in daily life comprise cleaning up existing pollution, water distillation system, low cost electricity production systems, physical development, nanomedicine, improved food production systems, and nanoelectronics [2].

1.1 Noble Metals

Metals that oppose oxidation and rust in moist air are called noble metals. These elemental metals are also called precious metals because it is uncommon, valued and have high economic value. The following noble metals are listed below in order of decreasing atomic number [3].

- Gold
- Platinum
- Iridium
- Osmium
- Silver
- Palladium
- Rhodium
- Ruthenium

1.1.1 Physics Definition of Noble Metal

In physics the description of noble metal is further redistricted than chemistry because it involves that the d-bands of electronic configuration he occupied. Silver, gold and copper are considered as a noble metals ,as all d-like bands are occupied and do not exceed the Fermi levels[3].

1.1.2 Uses of Noble Metals

Noble metals are used are for

- Making jewelry
- Coinage
- Electrical applications
- Productive coating
- As a catalyst[4]
- Automotive industry
- Pen nibs
- Thermal insulation
- Medical applications

1.2 Optical Properties

Properties of materials at nanoscale can be adjusted through controlling the dimension, structure, or extend of clusters. For instance, the optical properties (absorption bands) of metal nanoparticles can be adjusted through controlling particle dimension and shape. The control of size of the material has influenced on the optical properties. The dimension dependency can be usually distinguished into two groups. First is quantum size effect (as the system becomes more restricted as the spacing between energy levels increased), and the second is associated to surface Plasmon resonance [5].

1.2.1 Surface Plasmon Resonance

Surface Plasmon resonance is the coherent oscillations of all the free conduction electron, leading to an in-phase excitations [6]. When the dimension and structure of a metal nanocrystal is lesser than the wavelength of incoming light, a surface Plasmon resonance is produced [7].

Dipolar oscillations of the particle among negatively charged free electron and its positively charged lattice is called surface Plasmon resonance. The energy of the surface Plasmon resonance be influenced by number of free electrons and dielectric medium around the nanoparticles.

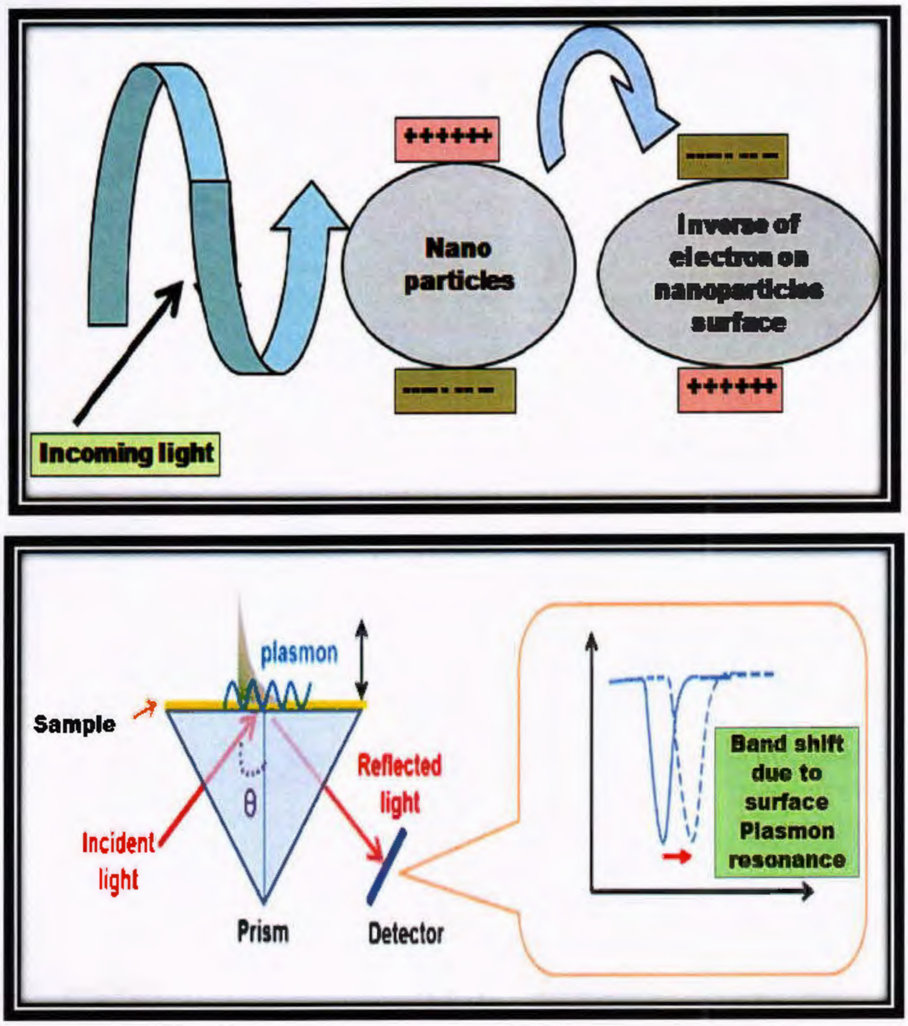

Figure 1: Origin of surface Plasmon resonance due to the collective excitations of electron in the conduction band by the interaction of electromagnetic field.

Figure demonstrates schematically how a surface Plasmon oscillations of metallic particles is generated in an uncomplicated behavior. The electric field of an incident radiations brings a polarization of free electrons comparative to the ationic lattice.

1.2.2 Quantum Size Effect

Distinctive optical property of material at nanoscale may also occur from quantum size effect. When the dimension of a nanocrystal (i.e. single crystal nanoparticles) is lesser than the value de Broglie wavelength, electrons and holes are spatially restricted and electric dipoles are produced, and specific electronic energy level would be created in all materials. Similar to a particle in a box, the spacing between energy levels increases with decreasing dimension [5]. The energy shift is derived by formula shown in figure:

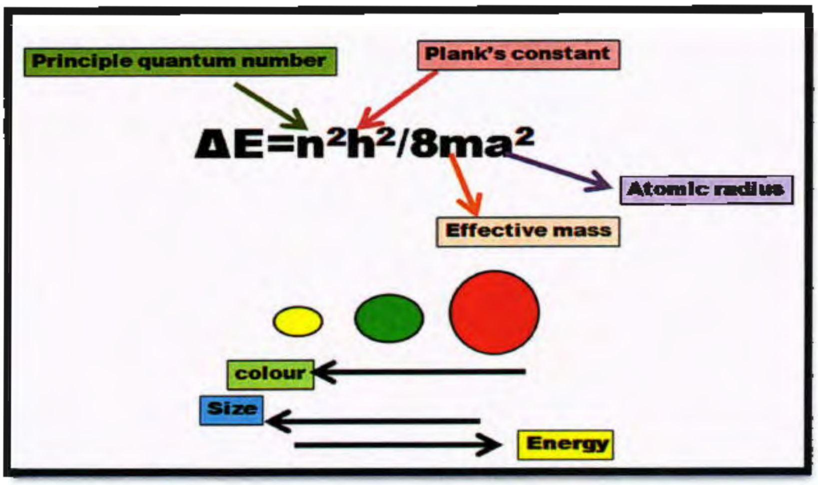

Figure 2: Quantum size effect

1.3 Basic Mechanism of Photo Catalysis

Photo catalysis is a procedure in which reaction take places when a photo catalyst interact with a incident light of appropriate energy to generate reactive oxidizing species which can lead to the Photo catalytic conversion of a pollutant. In this process energy of light is greater than the band gap of photo catalyst excites an electron from valence band to conduction band produce a positive hole in the valence band.

$$\text{Photo catalyst} + h\upsilon \rightarrow h_{VB}^{+} + h_{CB}^{-}$$

$$(\text{Hole})^{+}_{VB} + \text{dye} \rightarrow \text{dye}^{\cdot +} \text{ (oxidation of dye)}$$

$$(\text{Hole})^{+}_{VB} + \text{OH} \rightarrow \text{OH}^{\cdot}$$

$$\text{OH} + \text{dye} \rightarrow \text{degradation of the dye}$$

Electron hole pair is produced due to which redox reaction takes place. The electrons in the conduction band show oxidation when interact with atmospheric oxygen and produce a superoxide radical anion while holes in valence band show reduction leads to the production of hydroxyl radical. Both radicals are very volatile for the degradation of organic compounds such as Methylene blue. The mechanism of photo catalysis also shown in figure below [8].

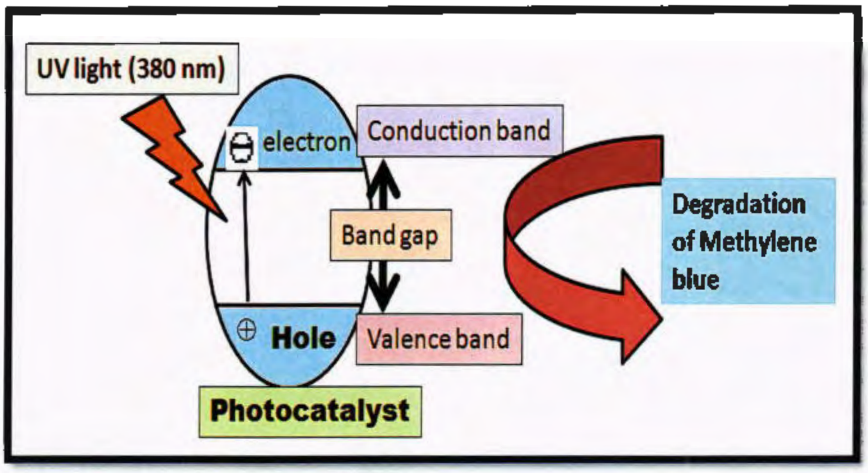

Figure 3: Schematic diagram of photo catalysis process.

1.3.1 Application of Photo Catalysis

Photo catalysis has following applications are as fellow:

- Self-cleaning surfaces
- Air purification
- Water treatment

1.4 Literature Review

In 2008 Yong Yang et al observed the surface enhanced Raman scattering-active properties using Au@Ag and Ag @Au nanocomposites which was prepared by seeding growth technique for logical applications [9].

In 2002 Lehui Lu et al have been synthesized the nanocomposites using gold and silver by seeding growth. By controlling shape, size and structure of gold-silver nanocomposites enhanced the monodispersity and used for the application of Raman spectroscopy as a substrate [10].

In 2006 Ken-Tye Yong et al prepared an Au and Ag shell by simple method on the surface of polystyrene spheres having a diameters 188 and 543 nm, respectively .Size, thickness, shape and optical properties were controlled by changing the concentration of gold and silver. These nanostructures were characterized by the various techniques such as SEM, TEM and UV-visible spectroscopy [11].

In 2014 Harihar Nath Verma et al prepared a gold nanoparticle by citrate reduction method. The structure, dimension, and composition of prepared gold nanoparticles were determined via different techniques like TEM and spectrophotometry [12].

In 2011 paper Hai-Long Jiang, Tomoki Akita et al provided sequential deposition reduction method for preparing bimetallic gold/silver nanoparticles. The composition, morphology and absorption bands were examined by EDS, TEM and UV spectroscopy. Then these nanoparticles were used as catalyst for heterogeneous catalysis activity at room temperature. [13].

In 2005 Zhihui Ban et al have been prepared Fe@Au nanoparticles by partial replacement reaction .The morphology, composition, structure and magnetic properties were examined by various techniques such as TEM, XRD, EDS, TDAG and UV spectroscopy. These nanoparticles also display absorption bands from 520 to 680 nm [14].

In 2005 Andr5ew Burrows and Bineto et al have been synthesized Au Ag nanoparticles via successive reduction of metal salt on pre-made seed in the presence of surfactant and study the optical properties using Mie theory [15].

In 2013 Na zhou et al have been synthesized TiO_2 coated gold-silver core- shell nanoparticles and their photo catalytic activities using visible light irradiation were calculated by photo-degradation of toxic dyes .[16].

1.5 Motivation of Research

The aim of our research is to control the size and optical properties of the gold and gold-silver nanoparticles by using the co-precipitation method because it is inexpensive method, simple process, easily performed in short time and good product performance.

Gold and silver are noble metals nanoparticles we can tune optical properties easily because they have strong absorption band in the visible region of electromagnetic spectrum, easy to prepare, quite stable and show intense colors due to coherent excitation of the free electrons in conduction band induced by the interacting electromagnetic spectrum. These nanoparticles are the good for Plasmon enhancement of photo catalytic activity due to the tunable surface Plasmon band in visible region by controlling their size.

Gold and gold-silver nanoparticles having a extensive variety of applications such as in catalysis, bio sensing, diagnostic imaging, drug delivery vehicles, cancer diagnosis, and therapy.

Chapter. 2

Methods and Materials

Literatures assessment indicates that several researchers have been developed various processes of nano materials synthesis to control their dimension, morphology, structure and chemical composition [17].

Methodologies for synthesis of nano materials can be divided into two categories

- ✓ Chemical technique e.g. via aqueous method
- ✓ Physical technique e.g. via vapour deposition method[18,19]

2.1 Physical Technique

Physical technique is a process in which precursor is physically carried out from source and move towards the substrate. In physical processes, nano-scale objects are made by processing larger objects in size. Integrated circuit fabrication is an example for top down nanotechnology. Now it has been grown to the level of fabricating nano electromechanical systems (NEMS) where tiny mechanical components such as levers, springs and fluid channels along with electronic circuits are embedded to a tiny chip. The starting materials in these fabrications are relatively large structures such as silicon crystals. Lithography is the technology which has enabled making such tiny chips and there are many types of them such as photo, electron beam and ion beam lithography. In some applications larger scale materials are grinded to the nanometer scale to increase the surface area to volume aspect ratio for more reactivity. Nano gold, nano silver and nano titanium dioxide are such nano materials used in different applications.

2.2 Chemical Technique

Chemical technique is basically the chemical reaction among source gases; the product of which condenses through the production of a solid material inside the reaction vessel. These methods are used to produce nanoparticles from atoms are chemical processes based on transformations in solution e.g. sol-gel processing, chemical vapour deposition (CVD), plasma or flame spraying synthesis, hydrothermal method, co-precipitation atomic or molecular condensation. These chemical processes rely on the availability of appropriate "metal-organic" molecules as precursors. [20].

Basically we use chemical techniques for the preparation of nanostructured materials because it is low-cost and without difficulty performed in our labs .This technique produce nanostructures of high yield and uniformity. Nanostructured material syntheses which are mostly we used in our lab are discussed below.

- ✓ Hydrothermal
- ✓ Co-precipitation synthesis

2.3 Hydrothermal Synthesis

In hydrothermal synthesis precursors are mixed in the aqueous solution. Water is used as a solvent which rises the dissolving influence, energy to dispersion and mass transport of the liquid by increasing its internal friction. It is performed in steel pressure vessels called autoclaves with or without Teflon liners under controlled temperature and pressure. The temperature can be high than the boiling point of water, attaining the pressure of the vapour saturation. The internal pressure can be determine by the temperature and concentration of the solution added to the autoclave. It is low-cost method, used for the formation of small particles in ceramics industry and created high quality, single crystal with unvarying shapes and sizes nanostructures [21].

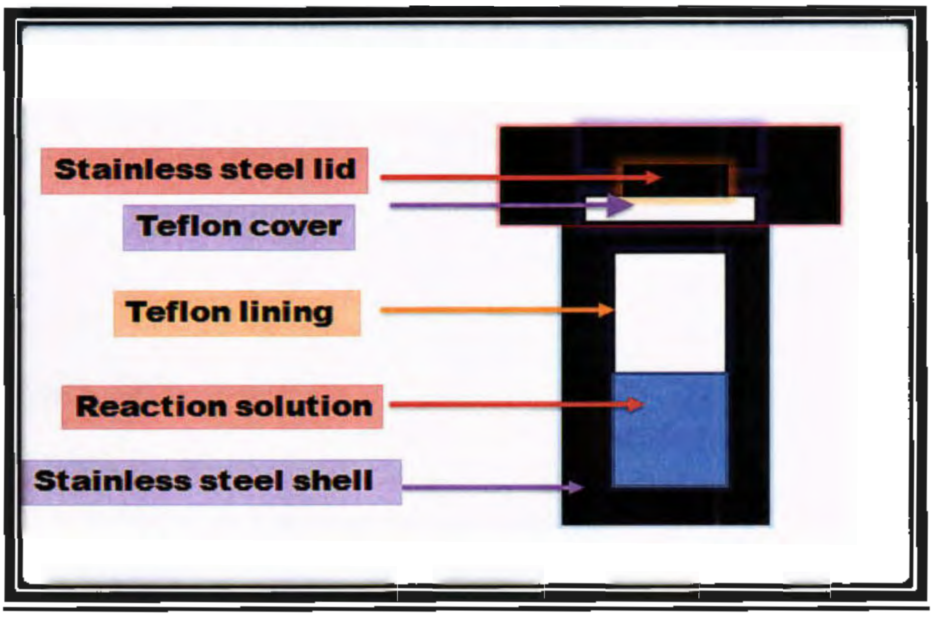

Figure 4: Teflon lined stainless steel autoclave by hydrothermal method

2.4 Co-Precipitation Synthesis

Another process to produce nanoparticles is the precipitation method. In this process precursors are dissolved in water. The nanoparticles will nucleate and grow in the solution when added different dissolving precursors during stirring. During the nucleation and growth process water is used as a solvent .After some time when the particles become stable allogmeration occur and precipitates form in water. The resulting solution are then filtered to obtain the nanoparticles and is calcined after filtration [22]. It is low cost-method and fast process. The disadvantage of this method is complexity to control the particle size and also difficult to protect the particles from impurities.

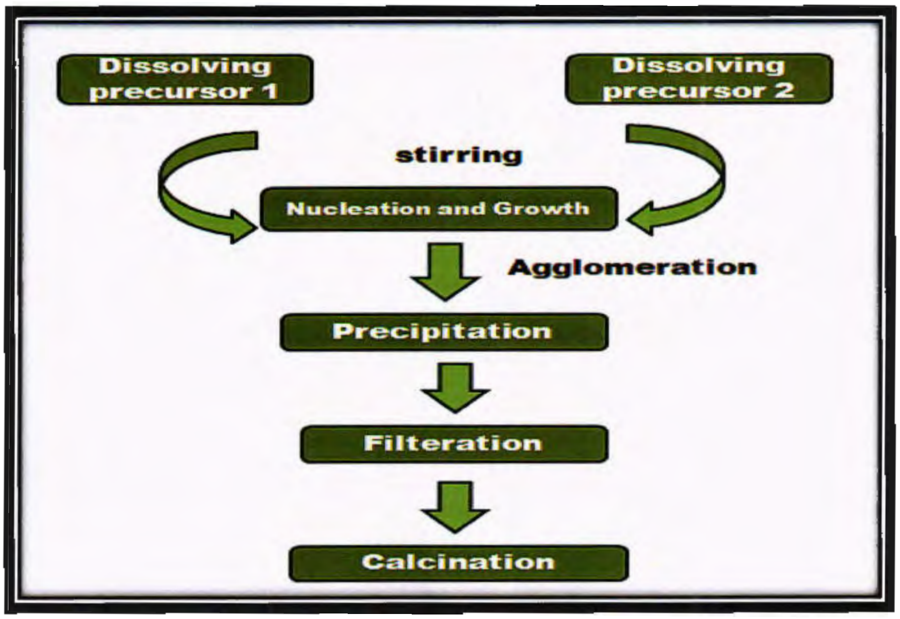

Figure 5: Flow diagram of Co-precipitation method

2.5 Experimental Section

2.5.1 Material Used

Each chemicals utilized in our experimental research work were of analytical grade and used as received without purification. Silver nitrate ($AgNO_3$,>99.9%),$HAuCl_4.2H_2O$ were bought from RFCL, India. Sodium brohydride ($NaBH_4$,>99%) was provided from S.D.Fine-Chemicals. Sodium hydroxide (NaOH,>97%), Ascorbic acid ($C_6H_8O_6$,>99%) and hydrochloric acid (HCl,>36.5%) were purchased from Merck chemicals. Poly (ethylene glycol)-block-poly (propylene glycol)-

block-poly (ethylene glycol) $(EO)_{20}$-$(PO)_{70}$-$(EO)_{20}$,Tetraethyl orthosilicate, (TEOS ,>99%), Cetyltrimethyl ammonium bromide (CTAB ,>99%), Ethanol (C_2H_5OH) were purchased from Sigma-Aldrich, Germany. Methylene blue (MB) dye was provided from Alfa Aesa .Deionized water was used for all experiments.

2.5.2 Preparation of Gold Hydrosol

First a gold seed was made by adding 2.5mL aqueous, 5×10^{-4} M Gold (III) chloride (22μL) solution and 2.5mL aqueous, 0.2M CTAB (0.1822g) solution with gentle stirring for 10 minutes in a beaker. Next 0.3mL of 0.1M $NaBH_4$ was mixed to the above mixture by stirring for 15 minutes. The color of the solution changed into pink slowly which showing the formation of gold hydrosol.

2.5.3 Preparation of Spherical-shaped Gold Nanoparticles

Secondly a spherical gold nanoparticles was made by adding aqueous 5mL, 0.2M CTAB (0.36445g) solution and 5mL aqueous, 1mM Gold (III) chloride (90μL) solution with stirring in a small beaker at room temperature .The color of the solution changed into deep yellow because of the complexion of CTAB and gold solution. Next aqueous 0.07mL, 0.01M ascorbic acid was added as a reducing agent in the above yellow solution and solution became colorless due to the reduction of Au^{3+} to Au. Then 0.05mL of previous gold hydrosol was mixed to the above colorless solution. Color of the solution changed into red slowly at room temperature which showing the spherical-shaped gold nanoparticles was formed [23].

2.5.4 Preparation of Gold-silver Nanoparticles

Gold-silver nanoparticles were prepared by aqueous 0.8mL of gold hydrosol diluted with 4mL deionized water in a beaker. This diluted hydrosol solution was mixed to different concentrations (0.1, 0.25, 0.5, 0.75 mL) of 1mM $AgNO_3$ with constant stirring. Next 0.1 mL of 0.1M NaOH was mixed to above four solutions to sustain the basicity and then 0.1ml of 0.1M ascorbic acid was added to reduce Ag^+ to Ag. Color of the hydrosol turned from pink to orange to yellow with increasing amount of $AgNO_3$.

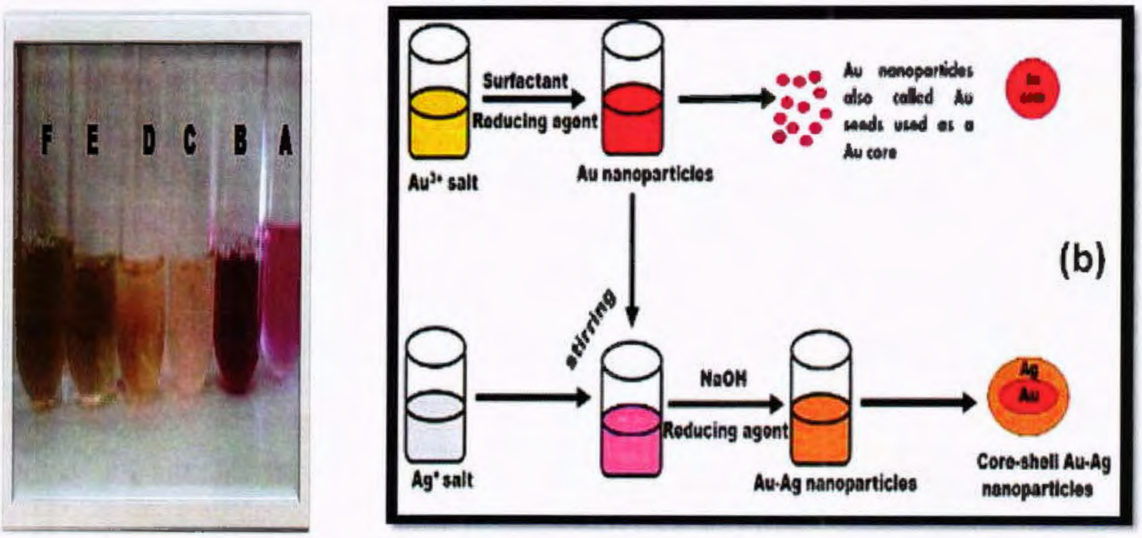

Figure 6: A is gold hydrosol, B is spherical gold nanoparticles and C to E showing color changes of gold-silver nanoparticles with increasing amount of silver. (b) Schematic diagram of synthesis procedure of gold-silver nanoparticles.

2.5.5 Preparation of Silver Nanoparticles

Silver nanoparticles were prepared by aqueous 0.8mL of0.03M CTAB diluted with 4mL deionized water in a beaker. Then diluted solution was mixed 0.5mL of 1mM $AgNO_3$ with constant stirring. Next 0.1 mL of 0.1M NaOH was mixed to above four solutions to sustain the basicity and then 0.1ml of 0.1M ascorbic acid was added to reduce Ag^+ to Ag.

2.5.6 Preparation of Au/SiO_2 and Au-Ag/SiO_2 Nanoparticles

Take 2g of triblock copolymer (p123) and add 2-4 molar HCl and keep under stirring. After 45 min stirring, add drop wise 4 ml TEOS (tetra ethyl orthosilicate) under high stirring. Keep stirring rate high for ~ 2-3 min and then slow down. After another 30 min, add drop wise Au-Ag nanoparticles in the form of solution. Keep this mixture under stirring for ~24 hr for aging. After 24 hr, transfer this mixture into Teflon lined autoclave and keep in oven at ~80-100 °C for 6-12 hr. After heat treatment, wash 2-3 times with distilled water and ethanol and finally collect the Au-Ag/SiO_2 by centrifuge. Dry the Au-Ag/SiO_2 at ~60 °C.Same procedure was followed for the preparation of Au/SiO_2 nanoparticles.

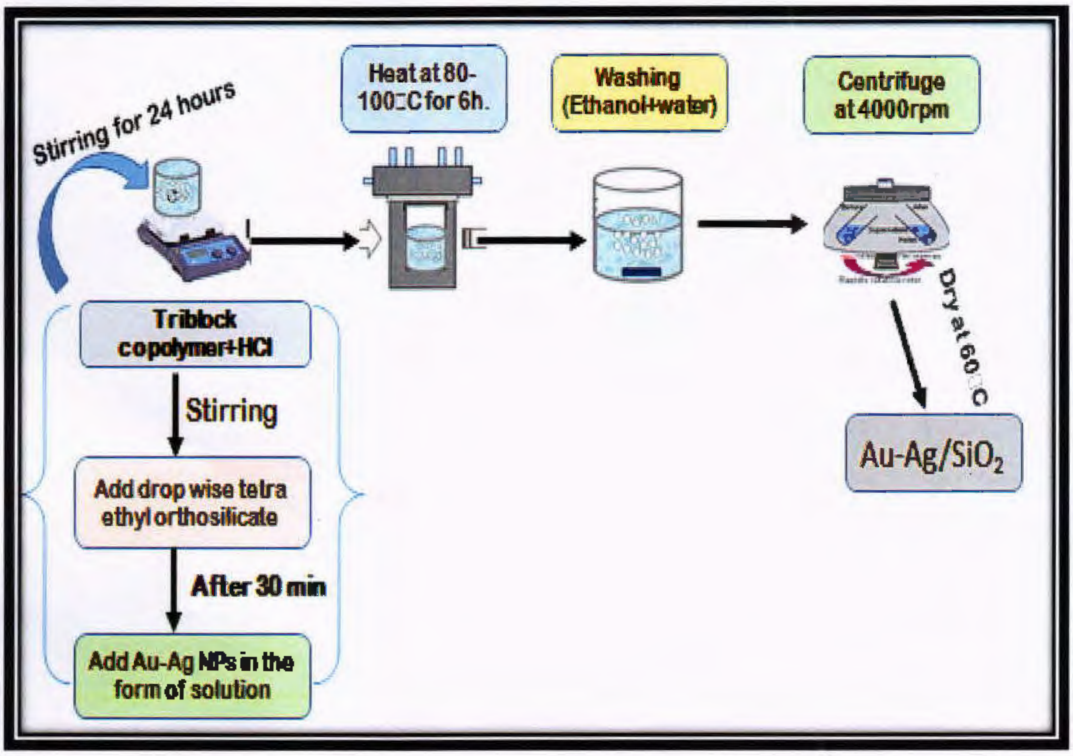

Figure 7: Schematic diagram of Au-Ag/SiO_2 nanoparticles preparation.

2.5.7 Dye Solution

Methylene blue dye is used to calculate the photo catalytic efficiency of the prepared nanostructures at pH-9 and standard pH. The pH of the solution was maintained by 1M of NaOH and HCl solutions. While the concentrations of the photo catalyst and MB dye were 3mg and 30ml (10ppm), respectively. The solution was then placed on stirrer for 30min in the dark and 3ml sample was stored as a reference. After 30 minutes the UV light is switch on and sample was placed under the UV light with constant stirring till the maximum degradation was attained.

Chapter. 3

Characterization Techniques

Characterization techniques are used to study for the different analysis and measurements of nanostructured materials.

- ✓ Structure analysis
- ✓ Property measurements

Different techniques that are used in this project are explained below.

3.1 Scanning Electron Microscopy

Scanning electron microscopy is the most common instrument in the field of nanotechnology used to study the topography, composition and surface morphology of the tested sample. The main components of SEM are shown in below figure.

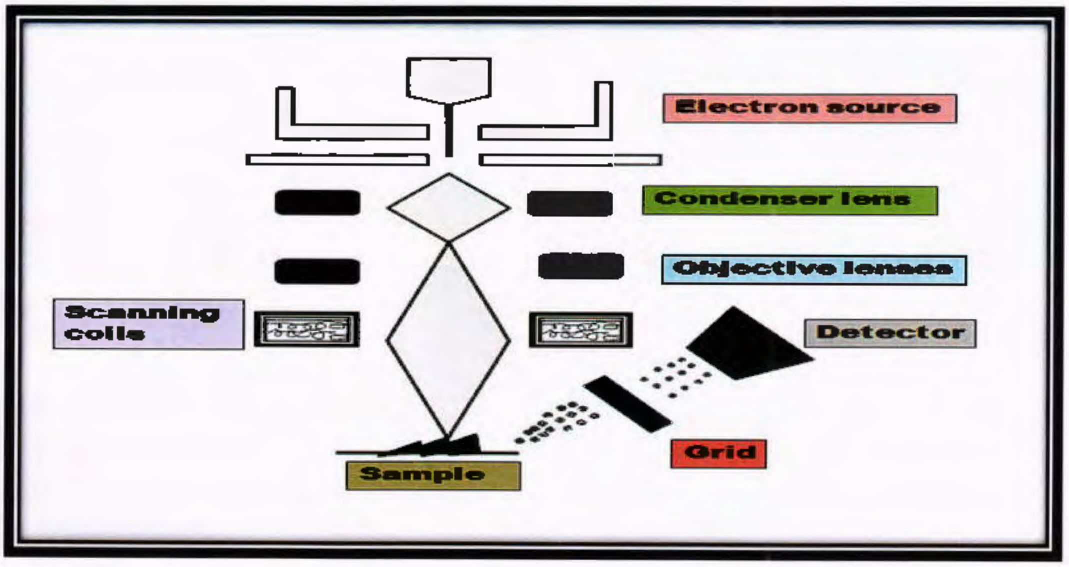

Figure 8: Schematic set-up of scanning electron microscope.

In a SEM when an electron beam hits the surface an excess signals are produced through the surface in the form of photons. These signals are released from the sample and composed by detectors to make an image [20].

There are three types of images are produced in SEM.

- Secondary electron images
- Backscattered electron images
- Elemental X-ray image

Figure 9: FEI Nova Nano SEM 450

The normal resolution power of SEM varies from 50nm to 100nm and it has magnification power from 20X to 50000X.

3.2 Energy Dispersive X-ray Spectroscopy

EDX is a tool which is used to identify the different elemental composition of the sample in detail .This built-in spectrometer connected with SEM. A beam of electron incident on the sample produces secondary electrons and creates many holes in the electron shells. Electrons from outer shell will move into the inner shell and release some energy in the form of X-rays. The elemental composition and energy of X-ray emitted from the sample can be identified by energy dispersive X-ray [24].EDX is tremendously helpful for metallographic, biomaterial studies and quantitative analysis.

3.3 Dynamic Light Scattering

Dynamic light scattering is mainly flexible and helpful technique used to measure the size of the particle in the sub-micron region. The schematic working setup of DLS are shown in figure.

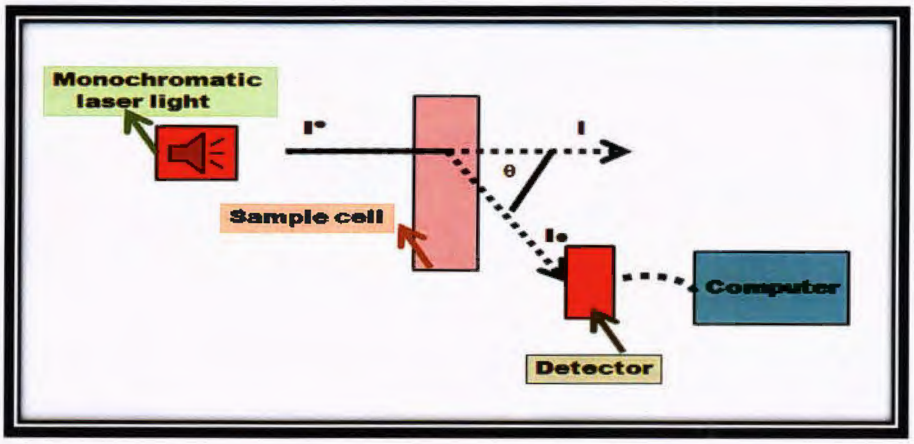

Figure 10: Schematic working setup of DLS

DLS works on the principle of Brownian motion. The random motion of the particles in a liquid is called Brownian motion. DLS is determined by collisions with the solvent particles there, which are in stable because of their thermal energy.

Particle size is given in terms of hydrodynamic radius. Hydrodynamic radius is the diameter of the sphere that has the same translational diffusion coefficient as the particle which can be measured from Stokes-Einstein equation as given below [25].

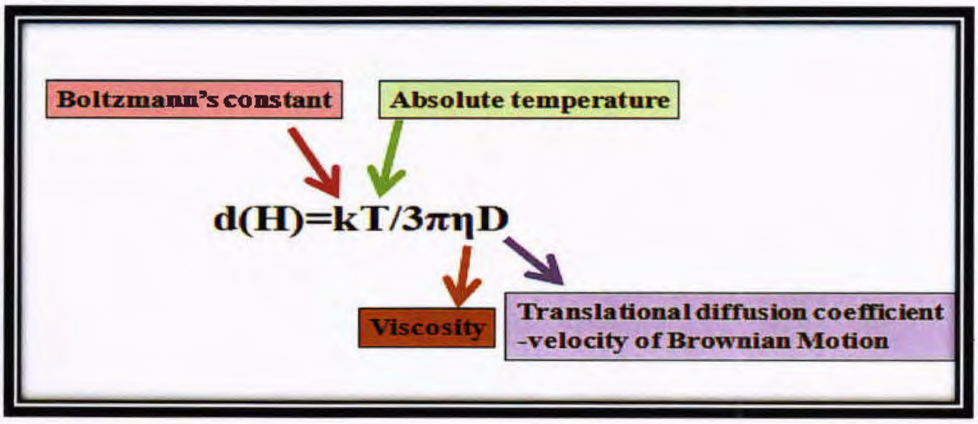

Figure 11: Stokes-Einstein equation

The above relationship shows particle size can be measured by diffusion speed if the temperature and viscosity of the sample are known.

It calculates difference in scattered intensity with time at fixed scattering angle. Particles hanged in liquid go through Brownian motion. If the particle size will be larger than the Brownian motion will be slow. It also measures the zeta potential of particles and molecular weight of the organic compounds. We use dynamic light scattering having a model (telasizer ZS90) as shown in figure.

Figure 12: Dynamic light scattering (telasizer ZS90)

It is time consuming technique especially for slow dynamics. It only measures the particle size of transparent sample. It is sensitive instrument for mechanical disturbances.DLS operator can get complete data about without requiring to have significant knowledge. It is basically very high-quality for calculating particle size in the range 0.1nm to 10μm.

3.6 Ultraviolet-visible Spectroscopy

Ultraviolet-visible spectroscopy is the best technique for the characterization of nanostructured materials which absorb radiation in the visible region like gold and silver [7].The device used in the ultraviolet visible spectroscopy is called spectrometer.

Molecules having non-bonding electrons be able to absorb energy in ultraviolet or visible region to move these electrons to higher antibonding-electrons.Energy of the radiation can be calculated by formula: $E=hf$ [26,27].If the electron absorb a light of longer wavelength then it can more easily be excited. Beer Lambert law is used to determine the concentration of absorbing sample which is given below in the figure.

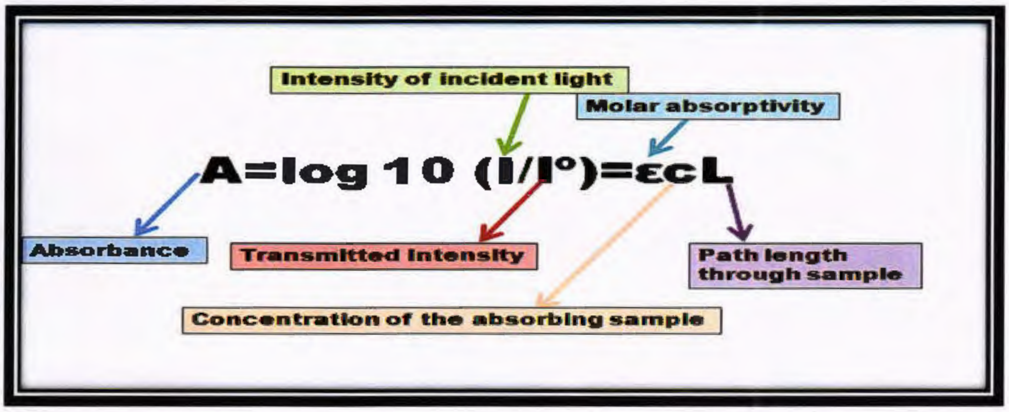

Figure 13: Beer Lambert law

UV-visible spectroscopy instrument works on the principle of spectrophotometer. The basic parts of the spectrophotometer are given below:

- ✓ Monochromator: to split the different wavelength of light.
- ✓ Detector: to detect the light.
- ✓ Tungsten filament/Xenon arc lamp: to produce light in ultraviolet and visible region.
- ✓ Charged coupled device: to see the output data.
- ✓ Two cuvettes: to put the sample and reference [28].

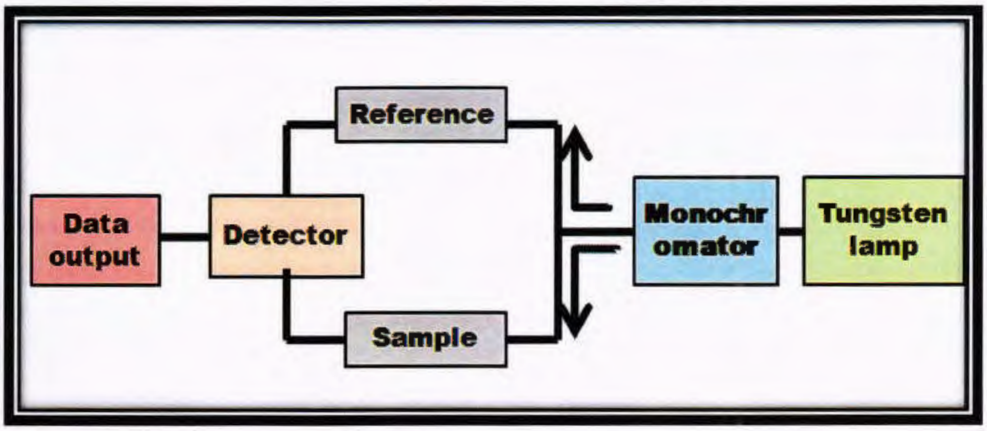

Figure 14: Simplified schematic of a double beam UV-Visible spectrophotometer

It is used in the semiconductor industry to measure the thickness and optical properties of the material. It is also used to measure the reflectance of light. It may be used as a detector for high- performance liquid chromatography. We use Ultra Violet Visible (UV-Vis) spectra-SPECORD 205 UV-Vis-spectrophotometer for measurements is shown in figure.

Figure 15: SPECORD 205 UV-Vis spectrophotometer

3.6 UV Light

We use UV light source (Xenon light (PLS-SXE 300 UV). PLS-SXE300 UV lamp is the most superior Photo catalytic light source in CHINA, which can be utilized in the fields of water splitting to generate hydrogen, degradation of pollutants, speeding up the experiment by simulating visible light and Ultraviolet light of the sunlight. PLS-SXE 300UV lamp have been utilized in more than 100 labs at home and in a foreign country, especially in the most strongest Photo catalytic researching center, so the light source have been the Standard light source and necessary equipment for photo catalytic research. The spectrum of UV light is shown in figure [29].

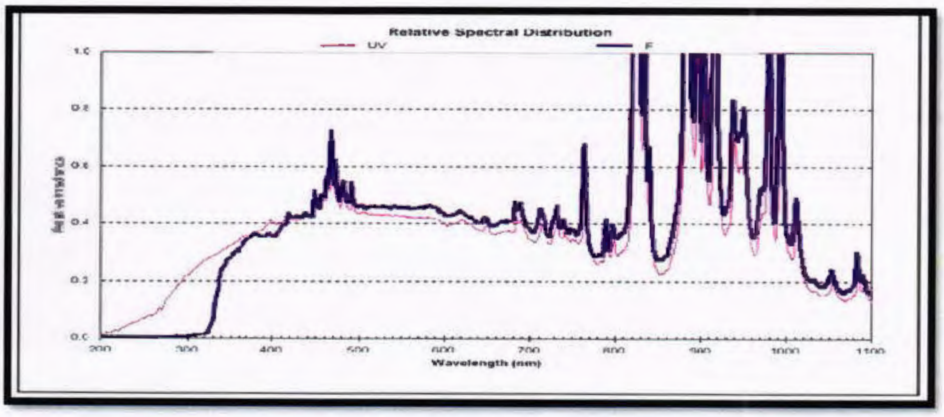

Figure 16: PLS-SXE300UV (the pink line) lamp in photo catalysis processes [30]

Chapter No. 4

Results and Discussion

4.1 Development of Gold-Silver Based Nanoparticles

We use co-precipitation method to prepare gold-silver based nanostructures. First produce a gold hydrosol and then this gold hydrosol coated with silver .We vary the amount of silver to investigate the effect of amount on morphology and optical properties of nanostructure material as explained in the previous chapter. The detailed explanation on the structure, morphology, chemical composition and absorption bands in the visible region of electromagnetic spectrum. Moreover, it describes the analysis of absorption spectrums of degradation of MB, efficiency of photo catalyst and kinetic curves.

4.2 Fundamental Characterizations

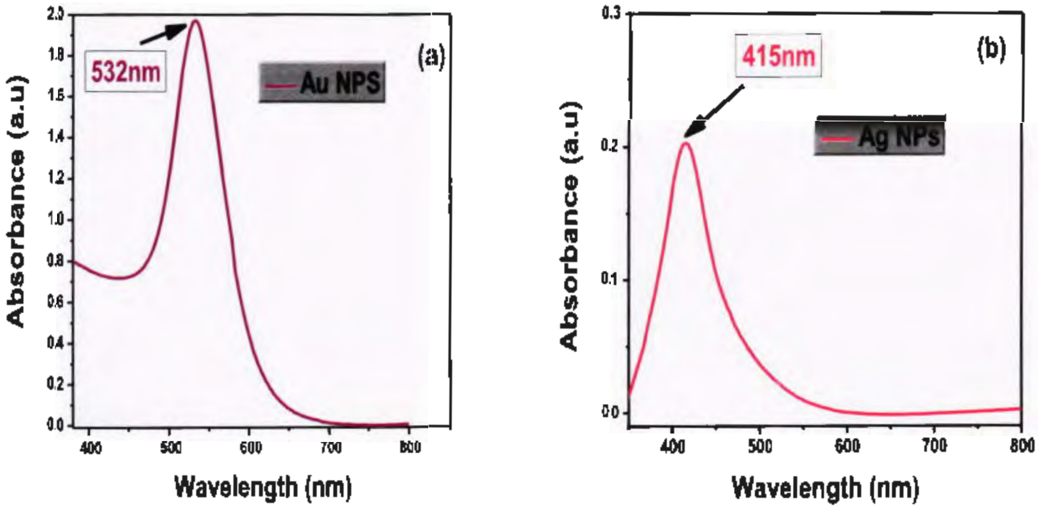

Figure17: UV/Vis spectra of Au and Ag nanoparticles

Figure 16 shows the UV/Vis spectra of Au and Ag nanoparticles having an absorption bands with peaks at 532 and 415 nm are due to surface Plasmon resonance band, respectively.

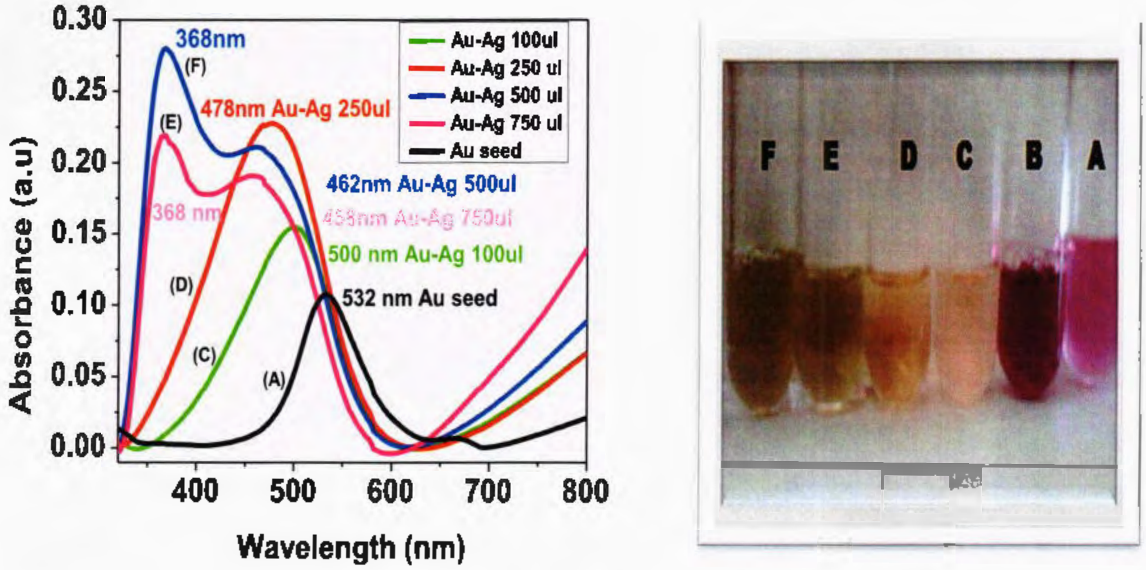

Figure 18: UV/Vis spectra of Au seed (A) and Au-Ag nanoparticles with increasing concentration (C to F) of Ag (Inset shows the color changes of the particles)

Figure 17 shows the UV/Vis spectra of Au seed and Au-Ag nanoparticles with changing concentration of silver. When the gold seed were coated with silver shell disappearance of surface Plasmon resonance peak of gold was observed due to the formation of silver layer on the Au seed. As with increasing the concentration of silver slightly blue shift was observed. The gold seed exhibit the absorption band at 532 nm and also shows the small hump around 690 nm which indicates that some particles having rod like shape. Spectrums (C) and (D) shows single maximum absorption bands at 500 and 478 nm indicates formation of homogeneous shell layer on Au seed [31]. The appearance of two absorption bands in the spectrums (E) and (F) at 462,458 and 368 nm shows the partial coverage of gold by silver particles or the creation of independent particles [32]. It has been also observed that color of Au-Ag nanoparticles varying with the increasing concentration of silver salt along with ascorbic acid. In this study with increasing silver thickness the color of the solutions changing are preserved as seen in fig 17.

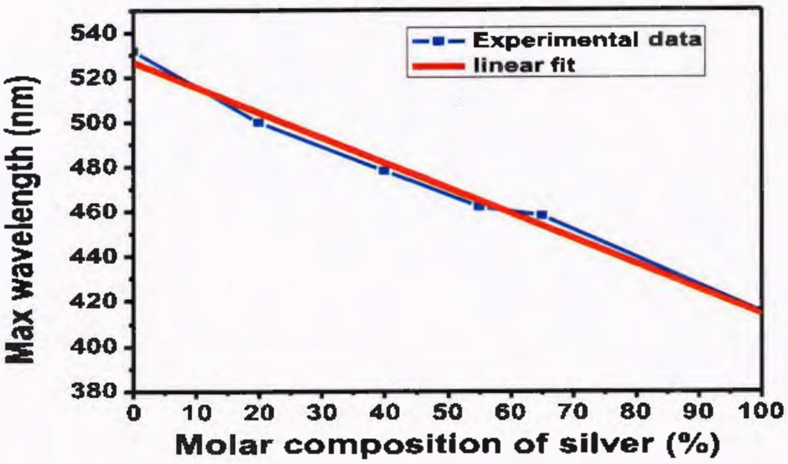

Figure 19: Variation of Absorption maxima of experimental curve with increasing mole fraction of silver

Figure 18 shows the plot of the SPR band with rising mole fraction of silver and it shows nonlinear behavior as that of our experimental plot which indicates that our synthesized particles are core shell nanoparticles rather than alloy. For alloy nanoparticles it shows a linear behavior for the same plot [33].

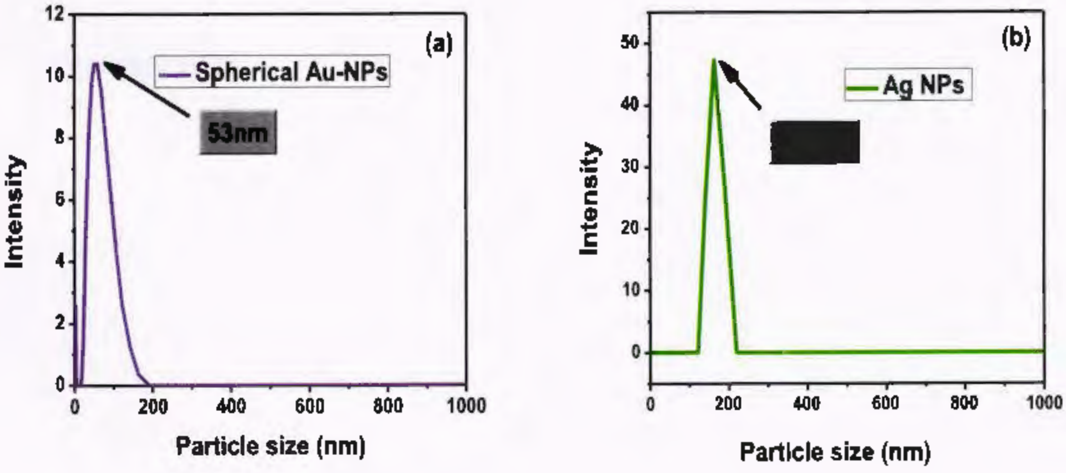

Figure 20: Dynamic light scattering measurement of spherical Au and Ag nanoparticles

Dynamics light scattering is a technique to measure the particle size. Fig 19 gives information about the particle size of spherical Au and Ag nanoparticles. The size of gold and silver nanoparticles is 53 and 162 nm respectively.

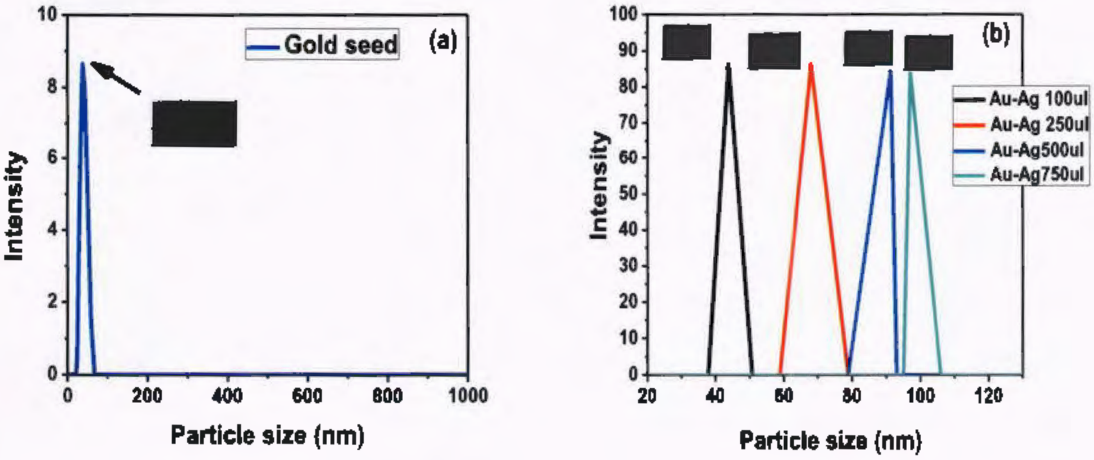

Figure 21: Dynamic light scattering measurements of Au core and Au-Ag nanoparticles with increasing concentration of Ag.

Fig 20 shows particle size of Au seed and Au-Ag nanoparticles with increasing concentration of silver. (a) Shows Au seed having particle size 36nm and (b) shows when gold seed coated with silver shell, particle size increased with increasing silver concentration.

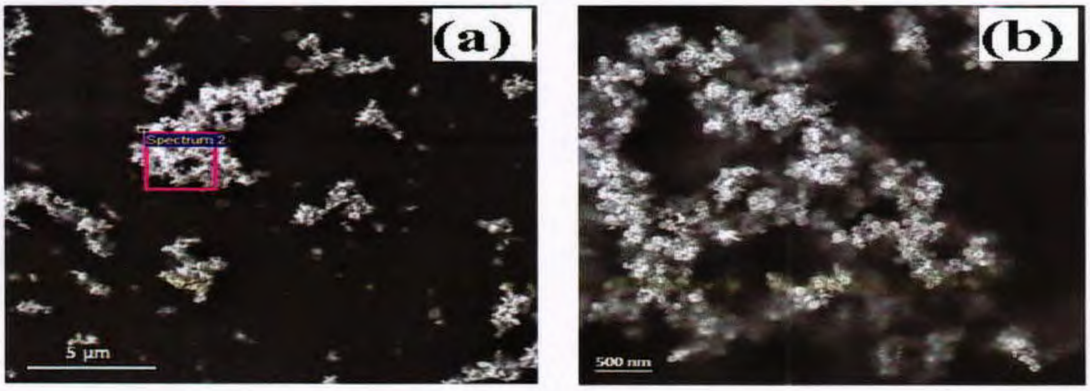

Figure 22: SEM image of Au-Ag nanoparticles with silver concentration 750µL **(a)** at low resolution **(b)** at high resolution.

In SEM analysis we obtain information about the morphology and size of the synthesized sample. Figure 21 (a and b) shows the image of Au-Ag nanoparticles with the silver amount of 750µL at high resolution and low resolution, respectively. These images show that the shape nanoparticles are like a nano clusters. The size of the nanoparticles is approximately 100nm.

Energy dispersive x-ray gives information about the elemental composition. Figure 22 tells about the elemental composition of Au-Ag nanoparticles with silver concentration 750µL. The O peak comes from atmosphere and the Si peak exists due to the silicon wafer. The weight percentages are shown of following elements are shown in figure.

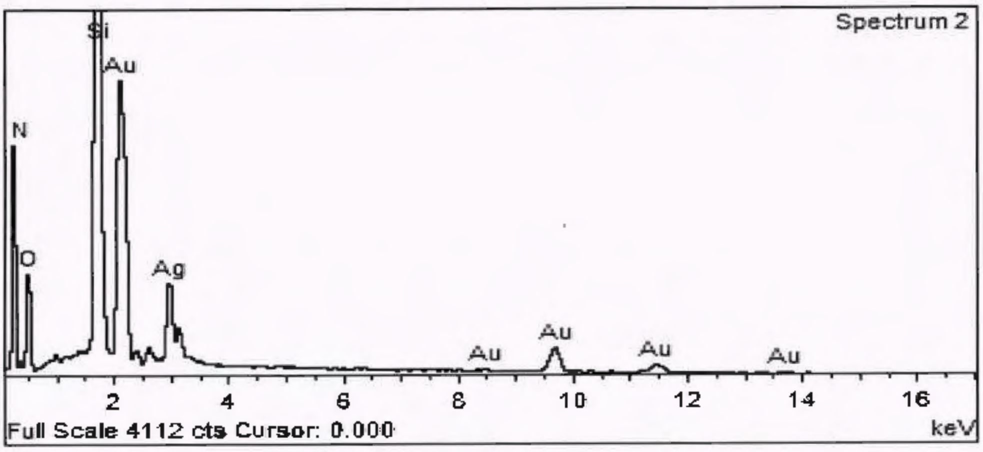

Figure 23: EDX results of Au NPs and Au-Ag NPs.

Table 1: EDX atomic/weight percentage of elements present in the sample

Element	Weight %
N k	6.26
O k	14.25
Si k	31.56
Ag L	9.84
Au M	35.09

4.2 Photo Catalytic Measurements

The Photo catalytic activities of Au/SiO_2 and Au-Ag/SiO_2 nanoparticles were evaluated by the degradation of methylene blue (MB) under UV light (380nm) irradiation. The prepared solution contains 30μM methylene blue in the presence of 3mg Au/SiO_2 and Au-Ag/SiO_2 as a catalyst. In above figures 23 (a) shows UV-Vis spectra 0f direct photolysis of MB without any photo catalyst for comparison in which no obvious degradation occurred. Only 33% of MB degraded in 75 minutes. The wavelength of MB was observed at 650 nm.

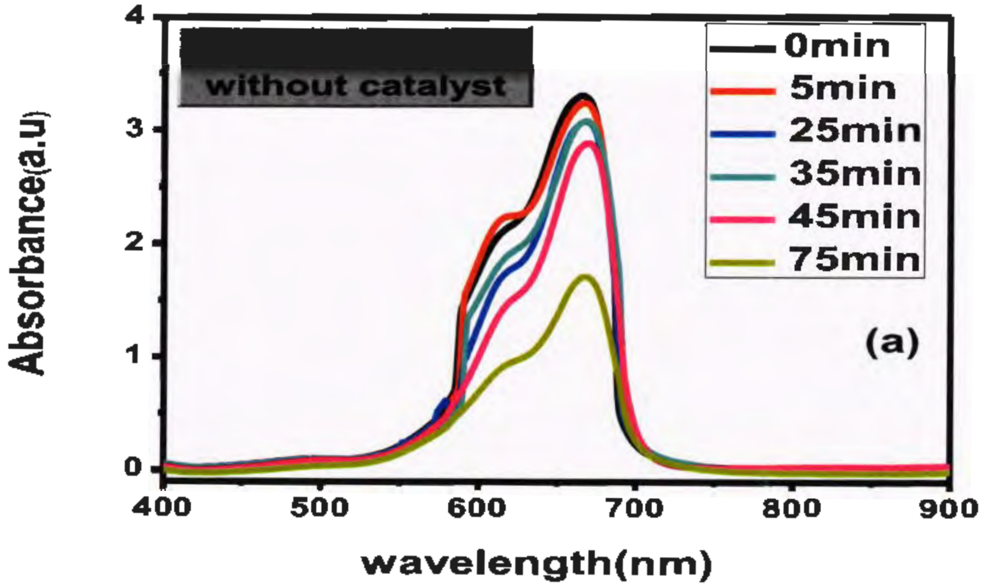

Figure 24: (a) Absorption spectra of MB in the absence of Catalyst Au/SiO_2 at standard pH-5.

Fig 24(b) shows UV-Vis spectra of MB in the presence of Au/SiO_2 as a photo catalyst at pH-5.MB was found to be gradually degrade under UV light irradiation.50% of MB degraded after irradiating the sample for 50 minutes. Fig 24 (c) shows UV-Vis spectra of MB in the presence of Au/SiO_2 as a photo catalyst at pH-9. MB was found to be degraded in a short time under UV light irradiation.85% of MB degraded after irradiating the sample for 16 minutes.

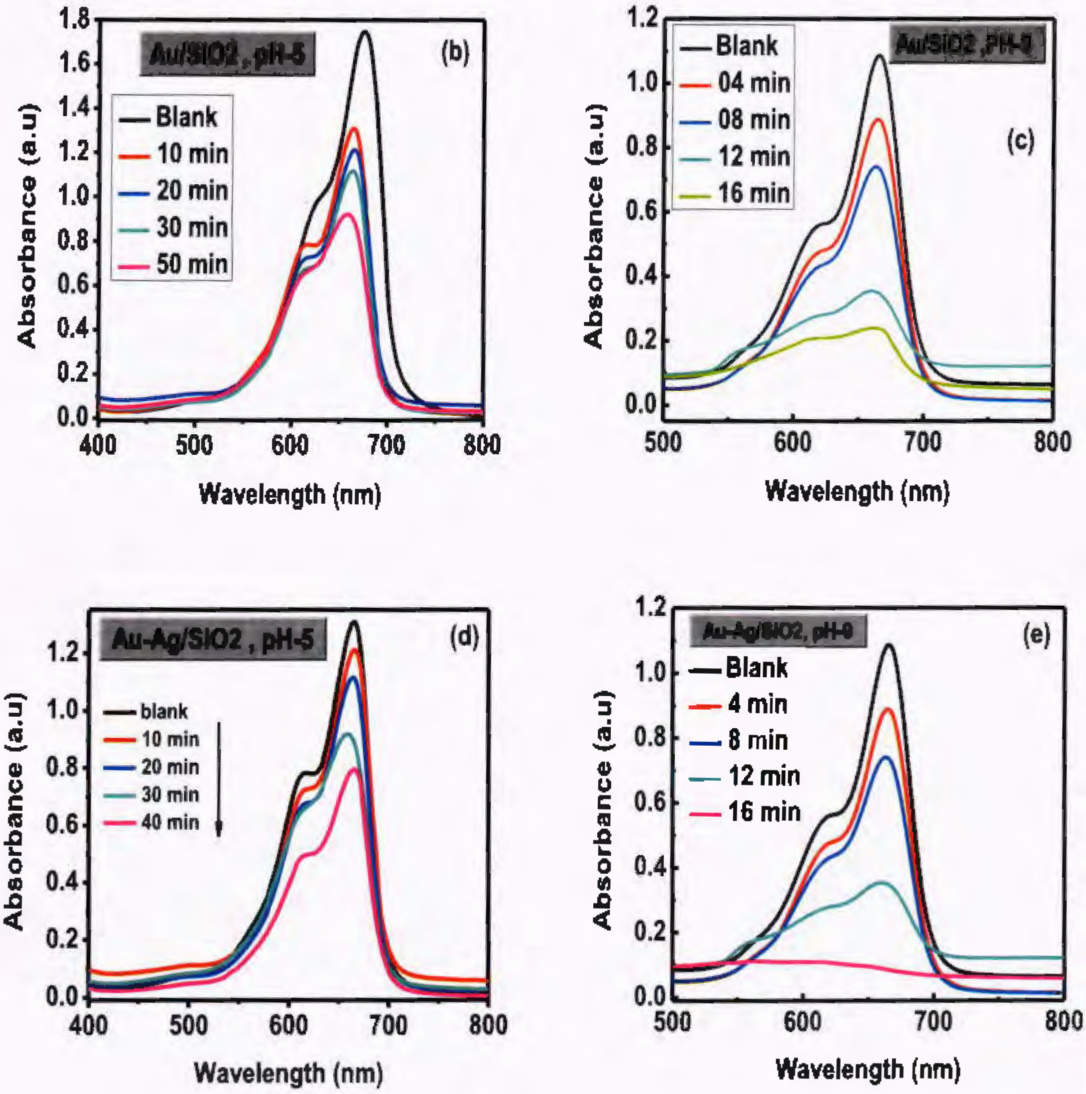

Figure 25: (b) Absorption spectra of MB in the presence of catalyst Au/SiO$_2$ at standard pH-5, (c) Absorption spectra of MB in the presence of catalyst Au/SiO$_2$ at pH-9,(d) Absorption spectra of MB in the presence of catalyst Au-Ag/SiO$_2$ at standard pH-5 ,(e)Absorption spectra of MB in the presence of catalyst Au-Ag/SiO$_2$ at pH-9

Fig 24(d) shows UV-Vis spectra of MB in the presence of Au-Ag/SiO$_2$ as a photo catalyst at pH-5. MB was found to be gradually degraded under UV light irradiation.50% of MB degraded after irradiating the sample for 40 minutes. Fig 24 (e) shows UV-Vis spectra of MB in the presence of

Au-Ag/SiO$_2$ as a photo catalyst at pH-9. MB was found to be degraded efficiently under UV light irradiation.98% of MB degraded after irradiating the sample for 16 minutes. Results shows that pH and photo catalyst both play plays an important role in the Photo catalytic activity of MB .It was observed that by increasing the ph photo degradation irradiation time of MB decreased and prepared Au/SiO2 and Au-Ag/SiO$_2$ nanoparticles become more efficient due to electrostatic interaction between negative photo catalyst surface and the methylene blue cation . The pH value of solution was controlled before starting the reaction which enhance the surface charge properties of Au/SiO$_2$ and Au-Ag/SiO$_2$. During the process of photo catalysis when electron jump from valence band to conduction band electron hole pair generate on the surface of the SiO$_2$ in the presence of catalyst of gold and gold coated silver under UV light due to which redox reaction occur and hydroxyl ion and radical were produced which degraded the MB dye.

4.2.1 Degradation Efficiency Methylene Blue

Fig 25 shows percentage efficiency of degradation ($A_t/A_•$) versus the irradiation time at different pH in which A_t is the absorbance of MB solution at each time interval of irradiation and $A_•$ is the initial absorbance. The results indicates that Au/SiO$_2$ and Au-Ag/SiO$_2$ nanoparticles displayed higher Photo catalytic efficiency at pH-9 than at pH-5.The photo catalytic activity of Au-Ag/SiO$_2$ slightly higher than Au/SiO$_2$ .It means Photo catalytic activity was also enhanced by Ag coating.

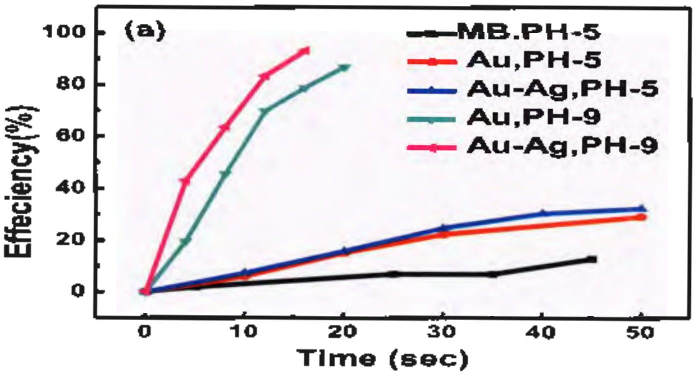

Figure 26: Photo degradation efficiency of MB under UV light irradiation in the absence and presence of photo catalysts (Au/SiO$_2$ and Au-Ag/SiO$_2$ nanoparticles) at pH-5 and pH-9

4.2.1 Kinetic Curve of Methylene Blue

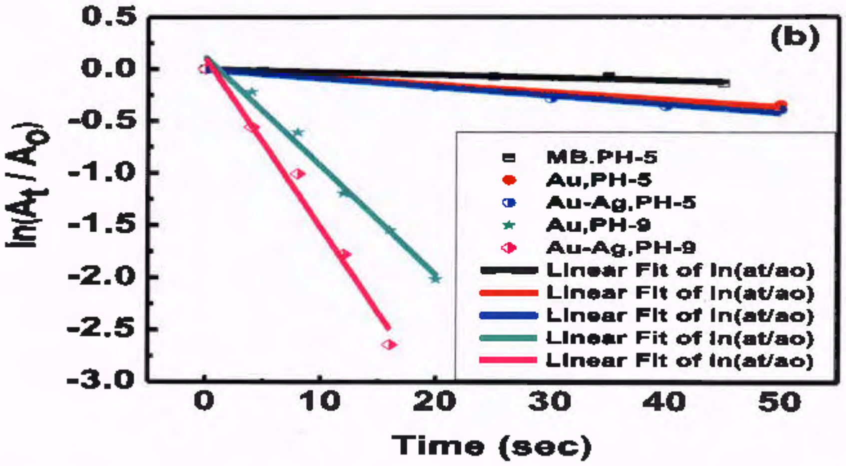

Figure 27: Kinetics curves of Photo degradation of MB under UV light irradiation in the absence and presence of photo catalysts (Au/SiO_2 and $Au\text{-}Ag/SiO_2$ nanoparticles) at pH-5 and pH-9.

Fig 26 shows the kinetics curve of photo degradation of MB dye at different pH which gives information about photo degradation rate (K) and correlation co-efficient (R^2) .The degradation of dye can be considered as a pseudo- first order reaction. When A_0 is small: $\ln (A_t/A_{\bullet}) = kt$, where k is the apparent first order rate constant which was calculated in the absence and presence of photo catalyst at pH-5 and pH-9 as shown in the table.

Table 2: Rate constant of MB dye at pH-9 and pH-5

Dye	Catalyst	pH	K(min^{-1})	Correlation Co-efficient (R^2)
MB	Au-Ag/ SiO_2	9	0.1045	0.9846
	Au/ SiO_2	9	0.1027	0.9777
	Au-Ag/SiO_2	5	0.0083	0.9745
	Au/SiO_2	5	0.0071	0.9679
	Without catalyst	5	0.0026	0.9036

Chapter. 5

Conclusion and Future Recommendations

5.1 Conclusion

In this research work Au and Au-Ag nanoparticles have been synthesized using co-precipitation method. SiO_2 shell on these nanoparticles has been successfully synthesized by hydrothermal method. The optical properties of particles controlled with varying concentration of silver on Au seed. The nanoparticles are highly stable and exhibit tune surface Plasmon resonance. The blue shift was observed because of the coherent excitations of free electrons in the conduction band induced by the interacting electromagnetic field with increasing the concentration of silver. Au/SiO_2 and $Au\text{-}Ag/SiO_2$ nanoparticles have been successfully used as a photo catalyst in the Photo catalytic activity under UV light for the degradation of MB dye at two different ph. It was observed that $Au\text{-}Ag/SiO_2$ nanoparticles is more efficient photo catalyst than Au/SiO_2 nanoparticles.

5.2 Future recommendation

Au and Ag nanoparticles can be synthesized with the combination of different materials to improve more the catalytic activity. As optical measurements are also shape dependent consequently Au and Ag nanostructures of different shapes can be made to observe it's another outcome on the catalytic measurements. Catalytic properties can be studied in further catalysis applications like water purification, Air purification and self-cleaning surfaces. These nanoparticles can also be useful in medical field for sensing of biomolecules such as in biosensor like glucose, enzymes etc. diagnostic imaging, drug delivery vehicles, Cancer, diagnosis and therapy.

References

[1] M. Naziruddinkhan and M.Ahoshan, "Nanostructured Materials :Classification,Properties and Fabrication", Nova science publishers ,New York,(2010),27.

[2] B. Bhushan, "Handbook of Nanotechnology", Springer, Berlin, (2004).

[3] A. Holleman, N. Wiberg, "Inorganic Chemistry", Academic Press, (2001).

[4] I.Thornton and Z.Makuch, "Handbook for Sustainable Heavy Metals Policy and Regulation,Series" , Springer-Verlag, (2002) .

[5] G. Cao, "Nanostructures and nanomaterials Synthesis, Properties and Application", Imperial College Press, Shelton Street Covent Garden London, **57**, (2004).

[6] C.F. Bohren and D.R. Huffman , "Adsorption and Scattering of Light by Small Particles", Wiley, New York, (1983).

[7] U. Kreibeg and M. Vollmer, "Optical Properties of Metal Clusters", Springer-Verlag , Berlin, **25**,(1995).

[8] M.Pelaeza, T. Nolanb, C. Pillai ,K. Seeryc, P.Falarasd, G. Kontosd, S.M. Dunlope, W.J. Hamiltone, J.Anthony Byrnee and D. Dionysioua, "A review on the visible light active titanium dioxide photocatalyt for environmental applications", journal of science direct,**125**, (2012),349.

[9] Y. yang,J. shi,G. Kawamura and M. Nogami, "Microwave assisted synthesis of sensitive silver substrate for surface-enhanced Raman scattering spectroscopy", journal of scripta materialia,58, (2008),862.

[10] L. Lu and H.Wang , "Seed mediated growth of large,monodispersecore-shell gold-silver with silver like optical properties", journal of chem. comm, (2002), 144.

[11] B.Zhihui and A. Barnakov, "The synthesis of core-shell iron@gold nanoparticles and their characterization" , journal of material chemistry, **15**,(2005), 4660

[12] Harihar and N. Verma, "Gold nanoparticle: synthesis and characterization", Veterinary World,7, (2014), 2231.

[13] L. Jiang, T.Akita, T.Ishida and M.Haruta, "Synergistic Catalysis of Au@Ag Core-Shell Nanoparticles Stabilized on Metal-Organic Framework",journal of American chemical society,**133,**(2011),1304.

[14] V.Kumar,S. Yadav, "Plant-mediated synthesis of silver and goldnanoparticles and their applications", journal of Chem Technol Biotechnol ,**84**, (2009),157.

[15] B. Rodriguez-Gonzalez,A. Burrows,M.Watanabe and j.Kiely, " Fabrication of Bimetallic Core-Shell and Alloy Ag-Au Nanoparticles on a DNA Template", journal of master chemistry ,**15**,(2005),1755.

[16] L. Polavarapu, Nengyue Gao, Yanlin Pan and Qing-Hua Xu,"Preparation of TiO2 coated Au/Ag core/shell nanorods for Plasmonic enhancement of visible light photocatalytic activity" Nanoscale, **5**,(2013), 4236 .

[17] A.T.Bell, "The impact of Nanoscienceon Hetrogeneous Catalysis.Science",**299**, (2003), ,1688.

[18] Grunes,J.,Zhu, G.A Somorjai, "catalysis and Nanoscience",Chem comm., (2003), 2257.

[19] K.J.Klabunde, Nanoscale materials in Chemistry.New york,Wiley-Interscience, 2001.

[20] M.Naziruddin ,M.Ahoshan and M.S. Alsalhi, "Nanostructured Materials:Classification,Properties and Fabrication", Nova science publishers, New York,(2010),26.

[21] L.Fang, G.Pelcckis and I.Wang, "Microstructured and magnetic properties in $Sn_{1-x} Fe_xO_2$ (x=0.01,0.05,0.10) nanoparticles synthesized by hydrothermal method",journal of Alloys and Compounds ,**491**,(2010),679.

[22] A.Rouanet, G. Pinchelin, C.Roucau, E.Snoeck and C.Monty, "NanophaseMaterials", Kluwer Academic Publishers, the Netherlands, Dordrecht, (1994).

[23] S.Pyne, P.Sarkar, S.basu, G. Prasad Sahoo and D. Kumar Bhui, "Synthesis and photophysical properties Au@Ag(core@shell) nanoparticles disperse in poly vinnl alcohol matrix" ,journal of nanopart research,**13**,(2011),1759-1767.

[24] C. Richard Brundle, Charles A. Evans Jr, Shaun Wilson, "Encyclopedia of materials characterization", Butterworth-Heinemann, (1992).

[25] R.Pecora, "Dynamic light scattering measurement of nanometer particles in liquid",journal of nanoparticle research,**3**,(2000),123-131.

[26] Douglas A.skoog, Donald M. West ,F.James Holler ,Analytical Chemistry: An Introduction ,Saunders Snburst serie,1999,7.

[27] A. Skoog, M .West and F.james Holler , "Fundamentals of Analytical Chemistry" ,Stanley R. Crouch,7,(2003).

[28] Skoog, douglas , F. James, and R.Stanley , "Principles of Instrumental Analysis, Thomson Brooks, Belmont" ,**6**,(2007),169.

References

[29] http://ccne.mofcom.gov.cn/1293013

[30] Lun Pan, T. Zhang, Songbo Wang, Zhe Li and Xiangwen Zhang , "Cu_2O film via hydrothermal redox approach: morphology and photocatalytic performance", journal of American chemical society ,**5**,(2011), 3736.

[31] M.Kahraman, O.Aydun and M.Culha , "Oligonucleotide Mediated Ag- Au Core-Shell Nanoparticles",Journal of springer science,**4**, (2009),293.

[32] S.Pande, S.K.Ghosh, S.Panigrahi and S.Basu, "Synthesis and size-selective catalysis by supported gold nanoparticles: study on heterogeneous and homogeneous catalytic process", journal of physical chemistry, **111**,(2007),10806.

[33] S.Pyne, P.Sarkar, S.basu, G. Prasad Sahoo and D. Kumar Bhui, "Synthesis and photophysical properties Au@Ag(core@shell) nanoparticles disperse in poly vinnl alcohol matrix" ,journal of nanopart research,**13**,(2011),1759-1767.