SINGLE POT SYNTHESIS OF BIOCOMPATIBLE SILVER NANOCOLLOIDS

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CERTIFICATE

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Dedicated to my Loving Parents

LIST OF FIGURES

ABSTRACT

Over the past few decades, inorganic nanoparticles, whose structures exhibit significantly novel and improved physical, chemical, and biological properties, phenomena, and functionality due to their nanoscale size, have elicited much interest. Nanophasic and nanostructured materials are attracting a great deal of attention because of their potential for achieving specific processes and selectivity, especially in biological and pharmaceutical applications. Silver nanoparticles (AgNPs) are already in use in numerous consumer products including textiles, personal care products, food storage containers, laundry additives, home appliances, paints, and even food supplements. AgNPs are added to all these products because of their bactericidal effects. On the basis of these uses, it is likely that AgNPs will be released to the aquatic environment, be a source of dissolved silver, and possibly exert toxic effects on aquatic organisms. In this article, I describe a simple onepot rapid synthesis route to produce uniform silver nanoparticles by thermal reduction of $AgNO_3$ using oleylamine as reducing and capping agent. To enhance the dispersal ability of as-synthesized hydrophobic silver nanoparticles in water, while maintaining their unique properties, a facile phase transfer mechanism has been developed using biocompatible block copolymer pluronic F-127. Formation of silver nanoparticles is confirmed by X-ray diffraction (XRD), transmission electron microscopy (TEM) and UV– vis spectroscopy.

INDEX

CONTENTS **PAGE NUMBER**

CHAPTER 1 *INTRODUCTION*

1.1 History

Silver is a metallic chemical element with the chemical symbol **Ag** (Latin: *argentum*, from the Indo-Europeanroot **arg*- for "white" or "shining") and atomic number 47. A soft, white, lustrous transition metal, it has the highest electrical and thermal conductivity of any metal. The metal occurs naturally in its pure, free form (native silver), as an alloy with gold and other metals, and in minerals such as argentite and chlorargyrite. Most silver is produced as a by-product of copper, gold, lead, and zinc refining.

Silver has long been valued as a precious metal, and it is used to make ornaments, jewelry, high-value tableware, utensils (hence the term *silverware*), and currency coins. Today, silver metal is also used in electrical contacts and conductors, in mirrors and in catalysis of chemical reactions. Its compounds are used in photographic film and dilute silver nitrate solutions and other silver compounds are used as disinfectants and microbiocides. While many medical antimicrobial uses of silver have been supplanted by antibiotics, further research into clinical potential continues.

Figure 1.1 Electrolytically refined silver

Silver is a very ductile and malleable (slightly harder than gold) monovalent coinage metal with a brilliant white metallic luster that can take a high degree of polish. It has the highest electrical conductivity of all metals, even higher than copper, but its greater cost and

tendency to tarnish have prevented it from being widely used in place of copper for electrical purposes. Despite this 13,540 tons of silver were used in the electromagnets used for enriching uranium during World War II (mainly because of the war time shortage of copper). Another notable exception is in high-end audio cables. Fig 1.1 shows the appearance of refined silver.

Among metals, pure silver has the highest thermal conductivity (the non-metal diamond and super fluid helium II are higher) and one of the highest optical reflectivity. (Aluminium slightly out does silver in parts of the visible spectrum, and silver is a poor reflector of ultraviolet light). Silver also has the lowest contact resistance of any metal. Silver halides are photosensitive and are remarkable for their ability to record a latent image that can later be developed chemically. Silver is stable in pure air and water, buttarnishes when it is exposed to air or water containing ozone or hydrogen sulfide to form a black layer of silver sulfide which can be cleaned off with dilute hydrochloric acid. The most common oxidation state of silver is +1 (for example, silver nitrate: $AgNO_3$); in addition, +2 compounds (for example, silver(II) fluoride: AgF_2) and the less common +3 compounds (for example, potassium tetrafluoroargentate($K[AgF_4]$) are known.

Silver metal dissolves readily in nitric acid (HNO_3) to produce silver nitrate ($AgNO_3$), a transparent crystalline solid that is photosensitive and readily soluble in water. Silver nitrate is used as the starting point for the synthesis of many other silver compounds, as an antiseptic, and as a yellow stain for glass in stained glass. Silver metal does not react with sulfuric acid, which is used in jewellery-making to clean and remove copper oxide fire scale from silver articles after silver soldering or annealing. However, silver reacts readily with sulfur or hydrogen sulfide (H_2S) to produce silver sulfide, a dark-colored compound familiar as the tarnish on silver coins and other objects. Silver sulfide also forms silver whiskers when silver electrical contacts are used in an atmosphere rich in hydrogen sulfide.Figure 1.2 shows a commercial helicopter cessana 210 which is equipped with a silver iodide generator for cloud seeding.

Silver chloride (AgCl) is precipitated from solutions of silver nitrate in the presence of chloride ions, and the other silver halides used in the manufacture of photographic emulsionsare made in the same way using bromide or iodide salts. Silver chloride is used in glass electrodes for pH testing and potentiometric measurement, and as a transparent cement for glass. Silver iodide has been used in attempts to seed clouds to produce rain.Silver

halides are highly insoluble in aqueous solutions and are used in gravimetric analytical methods.

Figure 1.2 Cessna 210 equipped with a silver iodide generator for cloud seeding

Silver oxide (Ag_2O) produced when silver nitrate solutions are treated with a base, is used as a positive electrode (cathode) in watch (batteries) Silver carbonate (Ag_2CO_3) is precipitated when silver nitrate is treated with sodium carbonate (Na_2CO_3) [1]. Silver fulminate (AgONC), a powerful, touch-sensitive explosive used in percussion caps, is made by reaction of silver metal with nitric acid in the presence of ethanol (C_2H_5OH). Another dangerously explosive silver compound is silver azide (AgN_3), formed by reaction of silver nitrate with sodium azide [2].

Latent images formed in silver halide crystals are developed by treatment with alkaline solutions of reducing agents such as hydroquinone, metol (4-(methylamino) phenol sulfate) or ascorbate which reduces the exposed halide to silver metal. Alkaline solutions of silver nitrate can be reduced to silver metal by reducing sugars such as glucose, and this reaction is used to silver glass mirrors and the interior of glass Christmas ornaments. Silver halides are soluble in solutions of sodium thiosulfate($Na_2S_2O_3$) which is used as a photographic fixer, to remove excess silver halide from photographic emulsions after image development [2].

Silver metal is attacked by strong oxidizers such as potassium permanganate ($KMnO_4$) and potassium dichromate ($K_2Cr_2O_7$), and in the presence of potassium bromide (KBr), these compounds are used in photography to bleach silver images, converting them to silver halides that can either be fixed with thiosulfate or re-developed to intensify the original image. Silver forms cyanide complexes (silver cyanide) that are soluble in water in the presence of an excess of cyanide ions. Silver cyanide solutions are used in electroplating of silver.

1.2 Applications

Dentistry

Silver can be alloyed with mercury, tin and other metals at room temperature to make amalgams that are widely used for dental fillings. To make dental amalgam, a mixture of powdered silver and other metals is mixed with mercury to make a stiff paste that can be adaptedto the shape of a cavity. The dental amalgam achieves initial hardness within minutes but sets hard in a few hours.

Photography and electronics

Photography used 30.98% of the silver consumed in 1998 in the form of silver nitrate and silver halides. In 2001, 23.47% was used for photography, while 20.03% was used in jewelry, 38.51% for industrial uses, and only 3.5% for coins and medals. The use of silver in photography has rapidly declined, due to the lower demand for consumer color film from the advent of digital technology, since in 2007 of the 894.5 million ounces of silver in supply, just 128.3 million ounces (14.3%) were consumed by the photographic sector, and the total amount of silver consumed in 2007 by the photographic sector compared to 1998 is just 50%.

Some electrical and electronic products use silver for its superior conductivity, even when tarnished. For example, printed circuits can be made using silver paints, and computer keyboards use silver electrical contacts. Some high-end audio hardware (DACs, preamplifiers, etc.) are fully silver-wired, which is believed to cause the least loss of quality in the signal. Silver cadmium oxide is used in high voltage contacts because it can withstand arcing.During World War II the short supply of copper brought about the government's use of silver from the treasury vaults for conductors at Oak Ridge National Laboratory. (After the war ended the silver was returned to the vaults.)

Small devices such as hearing aids and watches commonly use silver oxide batteries due to their long life and high energy/weight ratio. Another usage is high-capacity silver-zinc and silver-cadmiumbatteries.

Mirrors and optics

Mirrors which need superior reflectivity for visible light are made with silver as the reflecting material in a process called silvering, though common mirrors are backed with aluminum. Using a process called sputtering, silver (and sometimes gold) can be applied to glass at various thicknesses, allowing different amounts of light to penetrate. Silver is usually reserved for coatings of specialized optics, and the silvering most often seen in architectural glass and tinted windows on vehicles is produced by sputtered aluminum, which is cheaper and less susceptible to tarnishing and corrosion. Silver is the reflective coating of choice for solar reflectors.

Other industrial and commercial applications

Silver's catalytic properties make it ideal for use as acatalyst in oxidation reactions, for example, the production of formaldehyde from methanol and air by means of silver screens or crystallites containing a minimum 99.95 weight-percent silver. Silver (upon some suitable support) is probably the only catalyst available today to convertethylene to ethylene oxide (later hydrolyzed to ethylene glycol, used for making polyesters) an important industrial reaction. Because silver readily absorbs freeneutrons, it is commonly used to make control rods that regulate the fission chain reaction in pressurized water nuclear reactors, generally in the form of an alloy containing 80% silver, 15% indium, and 5% cadmium. Silver is used to make solder and brazing alloys, and as a thin layer on bearing surfaces can provide a significant increase in galling resistance and reduce wear under heavy load, particularly against steel.

Medicinal

Silver ions and silver compounds show a toxic effect on some bacteria, viruses, algae and fungi, typical for heavy metals like lead or mercury, but without the high toxicity to humans that are normally associated with these other metals. Its germicidal effects kill many microbial organisms *in vitro*, but testing and standardization of silver products is difficult [3].

Hippocrates, the "father of medicine"[4] wrote that silver had beneficial healing and anti-disease properties, and the Phoenicians used to store water, wine, and vinegar in silver bottles to prevent spoiling. In the early 1900s people would put silver dollars in milk bottles

to prolong the milk's freshness [5]. Its germicidal effects increased its value in utensils and as jewellery. The exact process of silver's germicidal effect is still not entirely understood, although theories exist. One of these is theoligodynamic effect, which explains the effect on microorganisms but would not explain antiviral effects.

Silver is widely used in topical gels and impregnated into bandages because of its wide-spectrum antimicrobial activity. The anti-microbial properties of silver stem from the chemical properties of its ionized form, Ag^{+}. This ion forms strong molecular bonds with other substances used by bacteria torespire, such as molecules containing sulfur, nitrogen, and oxygen [6].When the Ag^{+} ion forms a complex with these molecules, they are rendered unusable by the bacteria, depriving them of necessary compounds and eventually leading to the bacteria's death.

Silver compounds were used to prevent infection in World War I before the advent of antibiotics. Silver nitrate solution use continued, then was largely replaced by silver sulfadiazine cream (SSD Cream) [7] which generally became the "standard of care" for the antibacterial and antibiotic treatment of serious burns until the late 1990s [8]. Now, other options, such as silver-coated dressings (activated silver dressings), are used in addition to SSD cream. However, the evidence for the effectiveness of such silver-treated dressings is mixed.They are marred by the poor quality of the trials used to assess these products.Consequently a systematic review by the Cochrane Collaboration (published in 2008) found insufficient evidence to recommend the use of silver-treated dressings to treat infected wounds [9].

There has been renewed interest in silver as a broad-spectrum antimicrobial agent. One application has silver being used with alginate, a naturally occurring biopolymer derived from seaweed, in a range of products designed to prevent infections as part of wound management procedures, particularly applicable to burn victims [10].The year 2007, saw the first antibacterial glass introduced to fight hospital-caught infection: it is covered with a thin layer of silver. In addition, the U.S. Food and Drug Administration (FDA) has recently approved an end tracheal breathing tube with a fine coat of silver for use in mechanical ventilation, after studies found it reduced the risk of ventilator associated pneumonia.

Another example uses the known enhanced antibacterial action of silver by applying an electric field. It was found recently that the antibacterial action of silver electrodes is greatly improved if the electrodes are covered with silver nano rods [11]. Silver is commonly used in catheters. Silver alloy catheters are more effective than standard catheters for reducing bacteriuria in adults in hospital having short term catheterisation. This meta-analysis clarifies discrepant results among trials of silver-coated urinary catheters by revealing that silver alloy catheters are significantly more effective in preventing urinary tract infections than are silver oxide catheters. Though silver alloy urinary catheters cost about $6 more than standard urinary catheters, they may be worth the extra cost since catheter-related infection is a common cause of nosocomial infection and bacteremia.

Various silver compounds, devices to make homeopathic solutions and colloidal silver suspensions are sold as remedies for numerous conditions. Although most colloidal silver preparations are harmless, there are cases where excessive use led to argyria over a period of months or years. High doses of colloidal silver can result in coma, pleural edema, and hemolysis [12].

Clothing

Silver inhibits the growth of bacteria and fungi. It keeps odor to a minimum and reduces the risk of bacterial and fungal infection. In clothing, the combination of silver and moisture movement (wicking) may help to reduce the harmful effects of prolonged use in active and humid conditions.

Silver is used in clothing in two main forms:

- A form in which silver ions are integrated into the polymer from which yarns are made (a form of nanotechnology)
- A form in which the silver is coated onto the yarns.

In both cases the silver prevents the growth of a broad spectrum of bacteria and fungi.

1.3 METHODS FOR PREPARATION

Silver is a metal. A variety of preparation routes have been reported for the preparation of metallic Nanoparticles These methods are:

(1) Reverse micelles process [13,14]

(2) In situ method [19,21],

(3) Chemical reduction method [24]

(4) Ultrasonic method [25],

(5) Electron irradiation process [28],

(6) Thermal decumposition process [29],

(7) Green synthesis route [30,31]

(1) Reverse micelles process: Yingwei Xie, Ruqiang Ye, Honglai Liu (2005) prepared nano silver by this method.Since reverse micelles system was used to form metal nanoparticles by Boutonnet et al. [13]first, this method have been paid more and more attention [14,15]. However, most surfactants used were toxic and will pollute the environment. Biosurfactant (BS) [16,17] as a natural surfactant, which derived from microbial origin are bulky and have complicated structures, higher biodegradability, lower toxicity, and excellent antiviral activities. So biosurfactant as a"green" stabilizer is one of the best candidates. It is believed that biosurfactant will be increasingly attraction as multifunctional materials for the new century [18].

(2) In Situ method: The in situ nanoparticle synthetic methodology was first reported by Rubner [19]. In brief, by utilizing LBL assembled thin films as nanoreactor, nanometer-sized metal particles have been synthesized in-situ in the films. For instance Rubner utilized PAH/PAA polyelectrolyte multilayer thin film as nano reactor to synthesize in situ nanometer-sized metal Ag NPs in hydrogen atmosphere [20,21]. Moreover, Rubner prepared theantibacterial coatings based on hydrogen-bonded multilayer containingin situ synthesized Ag NPs on planar surfaces and on magneticcolloidal particles [22]. This in situ nanoparticle synthesis in LbL assembled films as nanoreactor afforded facile and precise control of the

concentrations of homogeneously dispersed nanoparticles.However, owing to the electron active polyelectrolyte multilayer films, the process requires the ion exchange and sequential reduction in hydrogen atmosphere. On the other hand, Kim reported that single crystalline silver nanowires were synthesizedinside the pores of self-assembled electrochemically active calyx 4 hydroquinones (CHQs) nanotubes by electro/photochemicalredox reaction [23]. Ag ions were included in the cavity of CHQsthrough cation–p interactions.

(3) Chemical reduction method: Ivan Sondiet al. (2002) used this method for the synthesis of Silver nano particle [24].The precipitation process, described here, yields highly concentrated and stable dispersions of monodispersed silver nanoparticles in a simple and cost-effective manner, by reduction of concentrated aqueous solutions of silver nitrate with ascorbic acid in aqueous medium. Daxad 19 wasselected as the most suitable dispersant for this purpose, based on preliminary evaluations of the protective abilityof several classes of dispersing agents. Obtaining such adesired system is a subject of many limitations, includingthe mentioned choice of the stabilizing agent, and of otherexperimental parameters (i.e., concentration of reactants,pH, and method of mixing).

(4) Ultrasonic method: Amir Reza Abbasi et al.(2009) reported the synthesis of silver nano particle by this method.The effect of ultrasonic irradiationon chemical reactions is to accelerate them and to initiate new reactions that are difficult to carry about under normal conditions[25,26]. The advantage of using ultrasound radiation is that it does not need high temperatures during the reactions, use of surfactantsis not necessary and it yields smaller particles [26]. Also, thereaction rate increased with increasing sonic amplitude [25]. The effects of ultrasound radiation on chemical reactions were reported in the recent works [26,27].Amir Reza Abbasi et al.have developed asimple sonochemical route to prepare nanostructures of AgI and studiedsome parameters, such as effects of stirring, temperature, concentration, sonication time and reaction time on growth and morphologyof the AgI nano-structures. The results show that with change in reaction conditions, nanoparticle structures changes to nanowires.

(5) Electron irradiation process:K A Bogle et al.(2006) developed a new method based on electron irradiationfor the synthesis of nanoparticles.This method is easy in operation, and even a period of about10 min is sufficient to obtain the signature of the nanoparticlesthrough the change in colour of the solution [28]. In this work, silver nanoparticles have been

synthesized by irradiating solutions,prepared by mixing $AgNO_3$ and PVA in different ratios,with 6 MeV electrons at room temperature.

(6) Thermal decmposition process: Don Keun Lee and Young Soo Kangformed silver nanocrystallites by the thermaldecomposition of a Ag^{+1}oleate complex, which wasprepared by a reaction with $AgNO_3$ and sodium oleate in awater solution. The resulting monodispersed silvernanocrystallites were produced by controlling the temperature (290°C) [29]. Transmission electron microscopic(TEM) images of the particles showed a 2-dimensionalassembly of the particles with a diameter of 9.5 ± 0.7 nm,demonstrating the uniformity of these nanocrystallites.Anenergy-dispersive X-ray (EDX) spectrum and X-raydiffraction (XRD) peaks of the nanocrystallites showed thehighly crystalline nature of the silver structure.

(7) Green synthesis route: Virender K. Sharma et al .(2008) developed this method for the synthesis of silver nanoparticle.The green synthesis of Ag nanoparticles involves three main steps, whichmust be evaluated based on green chemistry perspectives, including(1) selection of solvent medium, (2) selection of environmentallybenign reducing agent, and (3) selection of nontoxic substances for the Ag nanoparticle stability [30].In this method, Ag nanoparticle are prepared using water as anenvironmentally benign solvent and polysaccharides as a cappingagent, or in some cases polysaccharides serve as both a reducing and acapping agent. For instance, synthesis of starch-Ag NPs was carriedout with starch as a capping agent and β-D-glucose as a reducing agentin a gently heated system [30]. The starch in the solution mixture avoids use of relatively toxic organic solvents [31]. Additionally, the binding interactions between starch and Ag nanoparticle are weak and can be reversible at higher temperatures, allowing separation of thesynthesized particle.

1.4 Advantage of Silver nanoparticle

Nanotechnology is expected to open some new aspects to fight and prevent diseases using atomic scale tailoring of materials. The ability to uncover the structure and function of biosystems at the nanoscale, stimulates research leading to improvement in biology, biotechnology, medicine and health care. The size of nanomaterials is similar to that of most biological molecules and structures; therefore, nanomaterials can be useful for both in *vivo* and in *vitro* biomedical research and applications. The integration of nanomaterials with biology has led to the development of diagnostic devices, contrast agents, analytical tools,

physical therapy applications, and drug delivery vehicles**.** In all the nanomaterials with antibacterial properties, metallic nanoparticles are the best. Nanoparticles increase chemical activity due to crystallographic surface structure with their large surface to volume ratio.

The development of new resistant strains of bacteria to current antibiotics has become a serious problem in public health; therefore, there is a strong incentive to develop new bactericides [32]. Bacteria have different membrane structures which allow a general classification of them as Gram-negative or Gram positive. The structural differences lie in the organization of a key component of the membrane, peptidoglycan. Gram negative bacteria exhibit only a thin peptidoglycan layer (~2–3nm) between the cytoplasmic membrane and the outer membrane [33];in contrast, Gram-positive bacteria lack the outer membrane but have a peptidoglycan layer of about 30 nm thick .Silver has long been known to exhibit a strong toxicity to a wide range of micro-organisms [34]; for this reason silver-based compounds have been used extensively in many bactericidal applications.Silver compounds have also been used in the medical field to treat burns and a variety of infections. Several salts of silver and their derivatives are commercially employed as antimicrobial agents [35]. Commendable efforts have been made to explore this property using electron microscopy, which has revealed size dependent interaction of silver nanoparticles with bacteria .Nanoparticles of silver have thus been studied as a medium for antibiotic delivery and to synthesize composites for use as disinfecting filters and coating materials. However, the bactericidal property of these nanoparticles depends on their stability in the growth medium, since this imparts greater retention time for bacterium nanoparticle interaction. There lies a strong challenge in preparing nanoparticles of silver stable enough to significantly restrict bacterial growth.

A recent medical study showed that only silver nanoparticles with sizes less than 10nm (1,000 times smaller than the width of a human hair) were able to enter cells and disrupt them. The same study showed that silver nanoparticles are highly toxic to the bacteria that colonize the lungs of cystic fibrosis sufferers often with fatal consequences.

CHAPTER-2 *EXPERIMENTAL TECHINQUES*

2.1 Material

For this synthesis Silver Nitrate (99.8%), hexane (99%),Acetone and diphenyl ether were procured from *s.d fine-chem.Ltd.* Oleylamine and pluronic F-127 obtained from *Sigma-Aldrich.* Absolute ethanol (99.9%) was obtained from Merck. All the chemicals were used as-received without any purification.

2.1.1 Synthesis: Preparation of Silver nano particle

Preparation of uniform silver nano particle was carried out in a simple one-pot experiment,oleyalamine and diphenyl ether(v/v 1:2) were mixed in a 200-ml 3-neck round bottle flask(RBF),equipped with a stirrer,condenser and thermometer. Experimental set up is shown in figure 2.1.

In first condition the mixture of oleyalamine (5 ml) and diphenylether (10 ml) was heated to 180°C at a rate of 5°C /min. When temperature reached to 180°C , 524 mg $AgNO_3$ added to this mixture under continuous stirring and refluxed at 180°C for half an hour. Upon addition of $AgNO_3$,the colour of the mixture immediately turned to blue. Strong surface plasmon resonance(SPR) was observed, indicating the formation of silver nanoparticle.It was agitated and ripens at 150°C for another 2 hours.

Figure 2.1 Experimental Setup of experiment

The product was purified by precipitation-redispersion process. 50 ml absolute ethanol was added to mixture once it was cooled to room temperature .Nanoparticle were isolated from the suspension by centrifugation at 12000 rpm for 10 min. For this process 50 ml ethanol was added to cooled mixture. This ethanol mixed mixture was then centrifuged for 10 minutes at 12000 rpm. This process is repeated for three times to completely remove impurities and excess surfactants. After this 20 ml n-hexane is added to this centrifuged mixture. Now the suspension was again centrifuged for 10 minutes at 12000 rpm. After that 50 ml ethanol was added to it. Again this solution was centrifuged for the same time at same speed as. Finally,undispersed residues were removed and remaining silver nanoparticles were collected.. These particles were mixed with acetone and heated until acetone evaporates. When acetone evaporates completely particles were collected.

In the second condition all the criteria remains same except temperature was raised to 200°C from180°C .In figure 2.2 the blue colour is showing surface Plasmon resonance from Silver nanoparticle.

Figure 2.2 Blue colour showing surface plasmon resonance from Silver nanoparticle

2.1.2 Phase transfer of hydrophobic Silver nanoparticle via ligand exchange:

Chemiadsorption of oleylamine on nanoparticles'surface makes them hydrophobic. Hydrophilic nature of nanoparticles is an essential criterion for their biological applicability; hence, we have developed a facile phase transfer mechanism to produce water dispersible

silver nanoparticles using pluronic F-127.Briefly, 20 mL of 0.2 M aqueous solution of pluronic F-127 was mixed with equal volume of stock solutionof silver nanoparticles in hexane in a 100-mL beaker. It was covered with a perforated aluminum foil to control the evaporation of hexane. The mixture was magnetically stirred until the organic phase evaporated completely. To confirm phase transfer of silver nanoparticles, equal volume of fresh hexane solution was poured into the aqueous solution of silver nanoparticles. On successful phase transfer, both aqueous and organic phases would remain immiscible. The added organic phase was isolated from the aqueous phase by centrifugation.

2.2 Characterization Techniques

The characterization of Silver nanoparticles synthesized by Thermal reductionreaction method was carried out with various characterization methods which are described below:

2.2.1 X-Ray Diffraction Studies (XRD)

X-ray diffraction is the most wide spread technique for determining the phase identification, crystal structure, lattice parameter of the crystalline solids. A typical powder XRD instrumentation consist of four main components such as X-ray source, specimen stage, receiving optics and X-ray detector as shown in fig3.1. The source and detector with its associated optics lie on the circumference of focusing circle and the sample stage at the centre of the circle. The angle between the plane of the specimen and the X-ray source is θ, known as Bragg's angle and the angle between the projection of X-ray and the detector is 2θ. For the XRD analysis, fine powder samples were mounted on the sample holder and the powder was assumed to consist of randomly oriented crystallites. When a beam of X-ray is incident on the sample, X-rays are scattered by each atom in the sample.If the scattered beams are in phase, these interfere constructively and one gets the intensity maximum at that particular angle. The atomic planes from where the X-rays are scattered are referred to as 'reflecting planes'The Bragg's law relates the wavelength (λ) of the X-ray reflected the spacing between the atomic planes (d) and the angle of diffraction (θ) as follows:

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

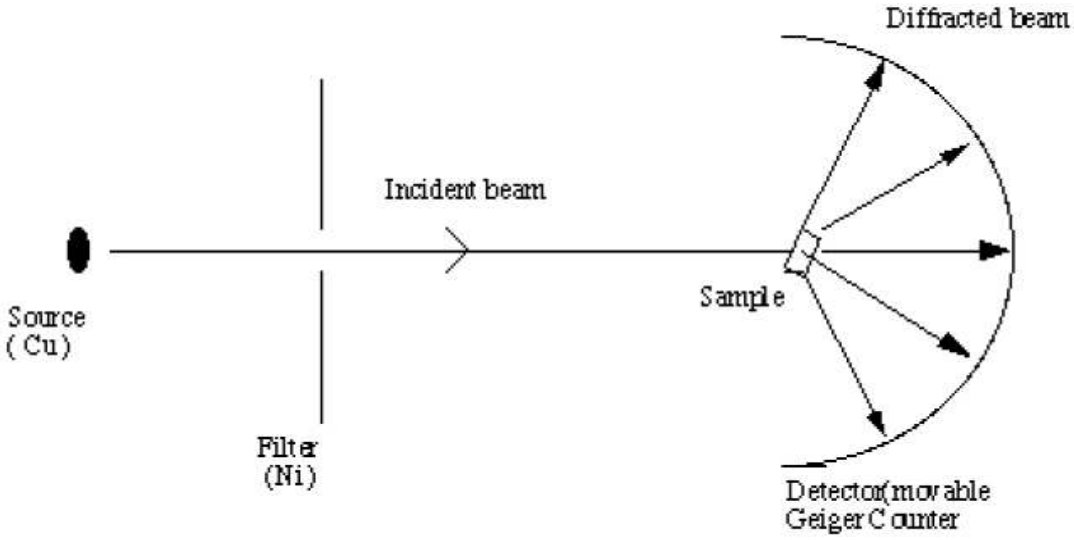


Figure 2.3 X-ray Scattering

For the first order diffraction, n=1, and knowing θ and λ, one can calculate the interplanar spacing d–value for a particular plane. After recording the X-ray diffraction pattern, first step involves the indexing of XRD peaks. The indexing means assigning the correct Miller indices to each peak of the diffraction pattern. The correct indexing is done only when all the peaks in the diffraction pattern are accounted for the process. There are three main methods for indexing a diffraction pattern,

(i) Comparing the measured XRD pattern with the standard data base (JCPDS cards)

(ii) Analytical methods

(iii) Graphical methods.

In case of fine particles, with reduction in the size of the particles, the XRD lines get broadened, which indicates clearly that particle size has been reduced. Information of the particle size is obtained from the full width at half maximum (FWHMs) of the diffraction peaks. The FWHMs (β) can be expressed as a linear combination of the contributions from the strain (ε) and particle size (L) through the following relation:

$$\mathbf{\cos \theta/\lambda \ \ 1/L + \varepsilon \sin \theta/\lambda}$$

2.2.2 UV-visible spectroscopy

Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis) refers to absorption spectroscopy in the ultraviolet-visiblespectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared (NIR)) ranges. The absorption in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, moleculesundergo electronic transitions. This technique is complementary to fluorescence spectroscopy, in thatfluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state.

Figure 2.4 DU640 UV/Vis spectrophotometer.

The instrument used in ultraviolet-visible spectroscopy is called a UV/Vis **spectrophotometer**. It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (I_o). The ratio I / I_o is called the transmittance, and is usually expressed as a percentage (%T). The absorbance, A, is based on the transmittance:

$$A = -\log(\%T / 100)$$

The basic parts of a spectrophotometer are a light source, a holder for the sample, a diffraction gratingor monochromator to separate the different wavelengths of light, and a detector. The radiation source is often a Tungsten filament (300-2500 nm), a deuterium arc lamp, which is continuous over the ultraviolet region (190-400 nm) or more recently, light emitting diodes (LED) and Xenon arc lamps for the visible wavelengths. The detector is typically a photodiode or a CCD. Photodiodes are used with monochromators, which filter

the light so that only light of a single wavelength reaches the detector. Diffraction gratings are used with CCDs, which collects light of different wavelengths on different pixels.

A spectrophotometer can be either single beam or double beam. In a single beam instrument all of the light passes through the sample cell. $I_o$must be measured by removing the sample. This was the earliest design, but is still in common use in both teaching and industrial labs.In a double-beam instrument, the light is split into two beams before it reaches the sample. One beam is used as the reference; the other beam passes through the sample.The reference beam intensity is taken as 100% Transmission (or 0 Absorbance), and the measurement displayed is the ratio of the two beam intensities.

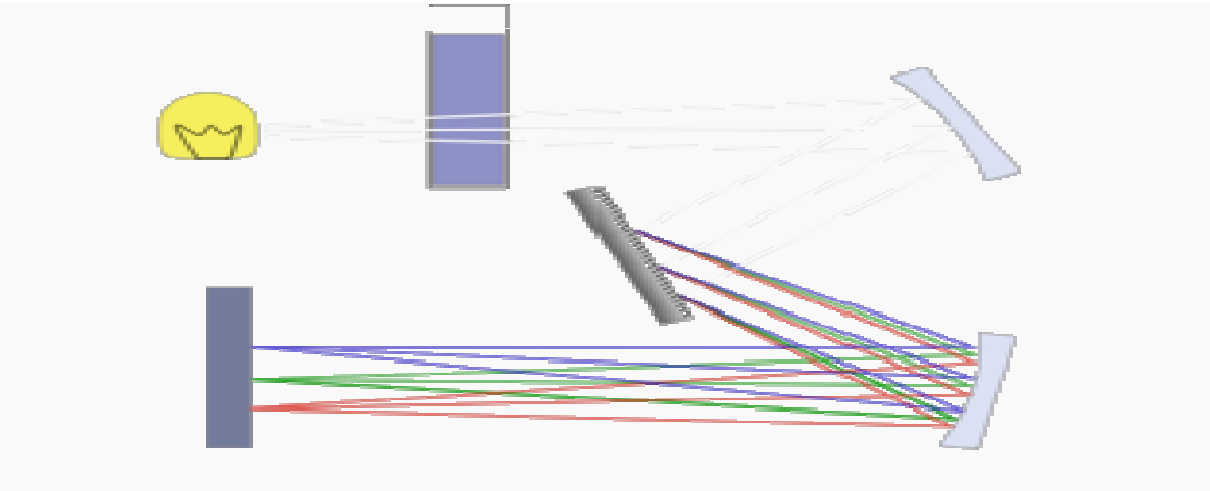


Figure 2.5 Diagram of a single-beam UV/Vis spectrophotometer

Some double-beam instruments have two detectors (photodiodes), and the sample and reference beam are measured at the same time. In other instruments, the two beams pass through a beam chopper, which blocks one beam at a time. The detector alternates between measuring the sample beam and the reference beam in synchronism with the chopper. There may also be one or more dark intervals in the chopper cycle. In this case the measured beam intensities may be corrected by subtracting the intensity measured in the dark interval before the ratio is taken.

Samples for UV/Vis spectrophotometry are most often liquids, although the absorbance of gases and even of solids can also be measured. Samples are typically placed in a transparent cell, known as acuvette. Cuvettes are typically rectangular in shape, commonly with an internal width of 1 cm. (This width becomes the path length, L, in the Beer-Lambert

law.) Test tubes can also be used as cuvettes in some instruments. The type of sample container used must allow radiation to pass over the spectral region of interest. The most widely applicable cuvettes are made of high quality fused silica or quartz glass because these are transparent throughout the UV, visible and near infrared regions. Glass and plastic cuvettes are also common, although glass and most plastics absorb in the UV, which limits their usefulness to visible wavelengths.

A complete spectrum of the absorption at all wavelengths of interest can often be produced directly by a more sophisticated spectrophotometer. In simpler instruments the absorption is determined one wavelength at a time and then compiled into a spectrum by the operator. A standardized spectrum is formed by removing the concentration dependence and determining the extinction coefficient (ε) as a function of wavelength.

Applications

UV/Vis spectroscopy is routinely used in thequantitative determination of solutions oftransition metal ions and highly conjugatedorganic compounds.

The Beer-Lambert law states that the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length. Thus, for a fixed path length, UV/Vis spectroscopy can be used to determine the concentration of the absorber in a solution. It is necessary to know how quickly the absorbance changes with concentration. This can be taken from references (tables of molar extinction coefficients), or more accurately, determined from acalibration curve.

A UV/Vis spectrophotometer may be used as a detector for HPLC. The presence of an analyte gives a response assumed to be proportional to the concentration. For accurate results, the instrument's response to the analyte in the unknown should be compared with the response to a standard; this is very similar to the use of calibration curves. The response (e.g., peak height) for a particular concentration is known as the response factor.

The wavelengths of absorption peaks can be correlated with the types of bonds in a given molecule and are valuable in determining the functional groups within a molecule. The Woodward-Fieser rules, for instance, are a set of empirical observations used to predict λ_{max}, the wavelength of the most intense UV/Vis absorption, for conjugated organic

compounds such as dienes and ketones. The spectrum alone is not, however, a specific test for any given sample. The nature of the solvent, the pH of the solution, temperature, high electrolyte concentrations, and the presence of interfering substances can influence the absorption spectrum. Experimental variations such as the slit width (effective bandwidth) of the spectrophotometer will also alter the spectrum. To apply UV/Vis spectroscopy to analysis, these variables must be controlled or accounted for in order to identify the substances present.

Spectral bandwidth

A given spectrometer has a spectral bandwidth that characterizes how monochromatic the light is. If this bandwidth is comparable to the width of the absorption features, then the measured extinction coefficient will be altered. In most reference measurements, the instrument bandwidth is kept below the width of the spectral lines. When a new material is being measured, it may be necessary to test and verify if the bandwidth is sufficiently narrow. Reducing the spectral bandwidth will reduce the energy passed to the detector and will, therefore, require a longer measurement time to achieve the same signal to noise ratio.

Wavelength error

In liquids, the extinction coefficient usually changes slowly with wavelength. A peak of the absorbance curve (a wavelength where the absorbance reaches a maximum) is where the rate of change in absorbance with wavelength is smallest. Measurements are usually made at a peak to minimize errors produced by errors in wavelength in the instrument that is errors due to having a different extinction coefficient than assumed.

2.2.3 Fourier Transform Infrared Spectroscopy

FTIR (Fourier Transform Infrared) Spectroscopy, or simply FTIR Analysis, is a failure analysis technique that provides information about the chemical bonding or molecular structure of materials, whether organic or inorganic. It is used in failure analysis to identify unknown materials present in a specimen, and is usually conducted to complement EDX analysis.

The technique works on the fact that bonds and groups of bonds vibrate at characteristic frequencies. A molecule that is exposed to infrared rays

absorbs infrared energy at frequencies which are characteristic to that molecule. During FTIR analysis, a spot on the specimen is subjected to a modulated IR beam. The specimen's transmittance and reflectanceof the infrared rays at different frequencies are translated into an IR absorption plot consisting of reverse peaks. The resulting FTIR spectral pattern is then analyzed and matched with known signatures of identified materials in the FTIR library.

Unlike SEM inspection or EDX analysis, FTIR spectroscopy does not require a vacuum, since neither oxygen nor nitrogen absorbs infrared rays. FTIR analysis can be applied to minute quantities of materials, whether solid, liquid, or gaseous. When the library of FTIR spectral patterns does not provide an acceptable match, individual peaks in the FTIR plot may be used to yield partial information about the specimen.

One of the most basic tasks in spectroscopy is to characterize the spectrum of a light source: How much light is emitted at each different wavelength. The most straightforward way to measure a spectrum is to pass the light through a monochromator, an instrument that blocks all of the light except the light at a certain wavelength (the un-blocked wavelength is set by a knob on the monochromator). Then the intensity of this remaining (single-wavelength) light is measured. The measured intensity directly indicates how much light is emitted at that wavelength. By varying the monochromator's wavelength setting, the full spectrum can be measured. This simple scheme in fact describes how some spectrometers work.

Fourier transform spectroscopy is a less intuitive way to get the same information. Rather than allowing only one wavelength at a time to pass through to the detector, this technique lets through a beam containing many different wavelengths of light at once, and measures the total beam intensity. Next, the beam is modified to contain a different combination of wavelengths, giving a second data point. This process is repeated many times. Afterwards, a computer takes all this data and works backwards to infer how much light there is at each wavelength.To be more specific, between the light source and the detector, there is a certain configuration of mirrors that allows some wavelengths to pass throughbut blocks others (due to wave interference). The beam is modified for each new data point by moving one of the mirrors;this changes the set of wavelengths that can pass through.As mentioned, computer processing is required to turn the raw data (light intensity for each mirror position) into the desired result (light intensity for each wavelength). The

processing required turns out to be a common algorithm called the Fourier transform (hence the name, "Fourier transform spectroscopy"). The raw data is sometimes called an "interferogram".

The method of Fourier transform spectroscopy can also be used for absorption spectroscopy. The primary example is "FTIR Spectroscopy", a common technique in chemistry.In general, the goal of absorption spectroscopy is to measure how well a sample absorbs or transmits light at each different wavelength. Although absorption spectroscopy and emission spectroscopy are different in principle, they are closely related in practice; any technique for emission spectroscopy can also be used for absorption spectroscopy. First, the emission spectrum of a broadband lamp is measured (this is called the "background spectrum"). Second, the emission spectrum of the same lamp shining through the sample is measured (this is called the “sample spectrum”. The sample will absorb some of the light, causing the spectra to be different. The ratio of the "sample spectrum" to the "background spectrum" is directly related to the sample's absorption spectrum.

Accordingly, the technique of "Fourier transform spectroscopy" can be used both for measuring emission spectra (for example, the emission spectrum of a star), and absorption spectra (for example, the absorption spectrum of a glass of liquid).Single fibers or particles are sufficient enough for material identification through FTIR analysis. Organic contaminants in solvents may also be analyzed by first separating the mixture into its components by gas chromatography, and then analyzing each component by FTIR.

2.2.4 Thermogravimitric Analysis

Thermogravimetric Analysis (TGA) measures weight changes in a material as a function of temperature or time under a controlled atmosphere. Its principal uses include measurement of a material's thermal stability and composition. Thermogravimetric analysis instruments are routinely used in all phases of research, quality control and production operations. Thermal Gravimetric Analysis (TGA)is a simple analytical technique that measures the weight loss (or weight gain) of a material as a function of temperature. As materials are heated, they can loose weight from a simple process such as drying, or from chemical reactions that liberate gasses. Some materials can gain weight by reacting with the atmosphere in the testing environment. Since weight loss and gain are disruptive processes to the sample material or

batch, knowledge of the magnitude and temperature range of those reactions are necessary in order to design adequate thermal ramps and holds during those critical reaction periods.

It is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can be used to tell the point at which weight loss is most apparent. Again, interpretation is limited without further modifications and deconvolution of the overlapping peaks may be required. TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures,absorbed moisture content of materials, the level of inorganic and decomposition points of explosives andsolvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation.

Simultaneous TGA-DTA/DSC measures both heat flow and weight changes (TGA) in a material as a function of temperature or time in a controlled atmosphere. Simultaneous measurement of these two material properties not only improves productivity but also simplifies interpretation of the results. The complementary information obtained allows differentiation between endothermic and exothermic events which have no associated weight loss (e.g., melting and crystallization) and those which involve a weight loss (e.g., degradation).

TGA - Principle of Operation

A sample of the test material is placed into a high alumina cup that is supported on, or suspended from an analytical balance located outside the furnace chamber. The balance is zeroed, and the sample cup is heated according to a predetermined thermal cycle. The balance sends the weight signal to the computer for storage, along with the sample temperature and the elapsed time. The TGA curve plots the TGA signal, converted to percent weight change on the Y-axis against the reference material temperature on the X-axis.

Figure 2.6 Diamond Pyris TGA/DTA thermal analyzer

.**Application:**

- TGA is a useful technique for assessing the effectiveness of oven drying solution polymerized polymer samples. The volatilization of residual solvent is typically associated with the initial weight loss process in a TGA heating run. In some cases, absorbed moisture may be liberated over this same temperature range, though. After the initial solvent (or moisture) weight loss process, TGA profiles will typically plateau to some constant weight level until the polymer degradation temperature range is reached. The weight fraction of residual solvent (or moisture) and the onset and maximum rate weight loss degradation temperatures are readily determined by TGA.
- The glass fiber content of composite samples is also readily analyzed by TGA. The polymer resin is degraded and burned off in heating these types of composite specimens to high temperatures in an air atmosphere. The noncombustible glass fiber is left behind as a residue. The weight fraction of glass fiber in the composite is determined using the TGA residue analysis.

2.6 Transmission electron microscope

Transmission electron microscopy (TEM) is used to obtain information from samples that are thin enough to transmit electron. In TEM, the whole area of observation is illuminated

using an electron source of adequate intensity. The transmitted electrons are generally used to form either an image or a diffraction pattern of the specimen .The formation of image and electron diffraction in TEM can be understood from schematic ray diagram as shown in fig.2.7 When a crystal of lattice spacing 'd' is illuminated with electrons of wavelength 'λ', the diffracted waves will be produced at specific angles 2θ for n =1, satisfying the Bragg's condition $2d \sin\theta = n\lambda$. The diffracted waves form diffraction spots on the back focal plane. In an electron microscope, the use of electron lenses allows the regular arrangement of diffraction spots to be projected on a screen and the electron diffraction pattern can be observed. If the transmitted and the diffracted beam interfere on the image plane, a magnified image can be observed. The space where the diffraction pattern forms is called the reciprocal space, while the space at the image plane or at a specimen is called the real space.

In TEM, by adjusting the electron lenses, both the microscope images and diffraction patterns can be observed. Thus in the analysis of microstructures of materials, both observation modes can be successfully combined. In an investigation of electron diffraction pattern, the electron microscope images of the nano phosphor is first observed of the whole area and then by inserting an aperture in a specific area and adjusting the electron lenses a diffraction pattern of the area is obtained.

The latter observation mode is called selected area electron diffraction (SAED). Because a selected area diffraction pattern can be obtained from each grain, the crystal structure and mutual crystal orientation relationship between adjacent grains can easily be clarified. The observational dimension selected from the object is usually limited to about 0.1 micrometer in diameter. However, in micro diffraction method, the diffraction pattern can be obtained from an area correspondingly to only a few nanometers in diameter. Then, by passing the transmitted beam or one of the diffracted beams through an aperture and changing to the imaging mode, the image with enhanced contrast can be observed. The observation mode using the transmittedbeam is called the bright field method, and the image observed is a bright field image.

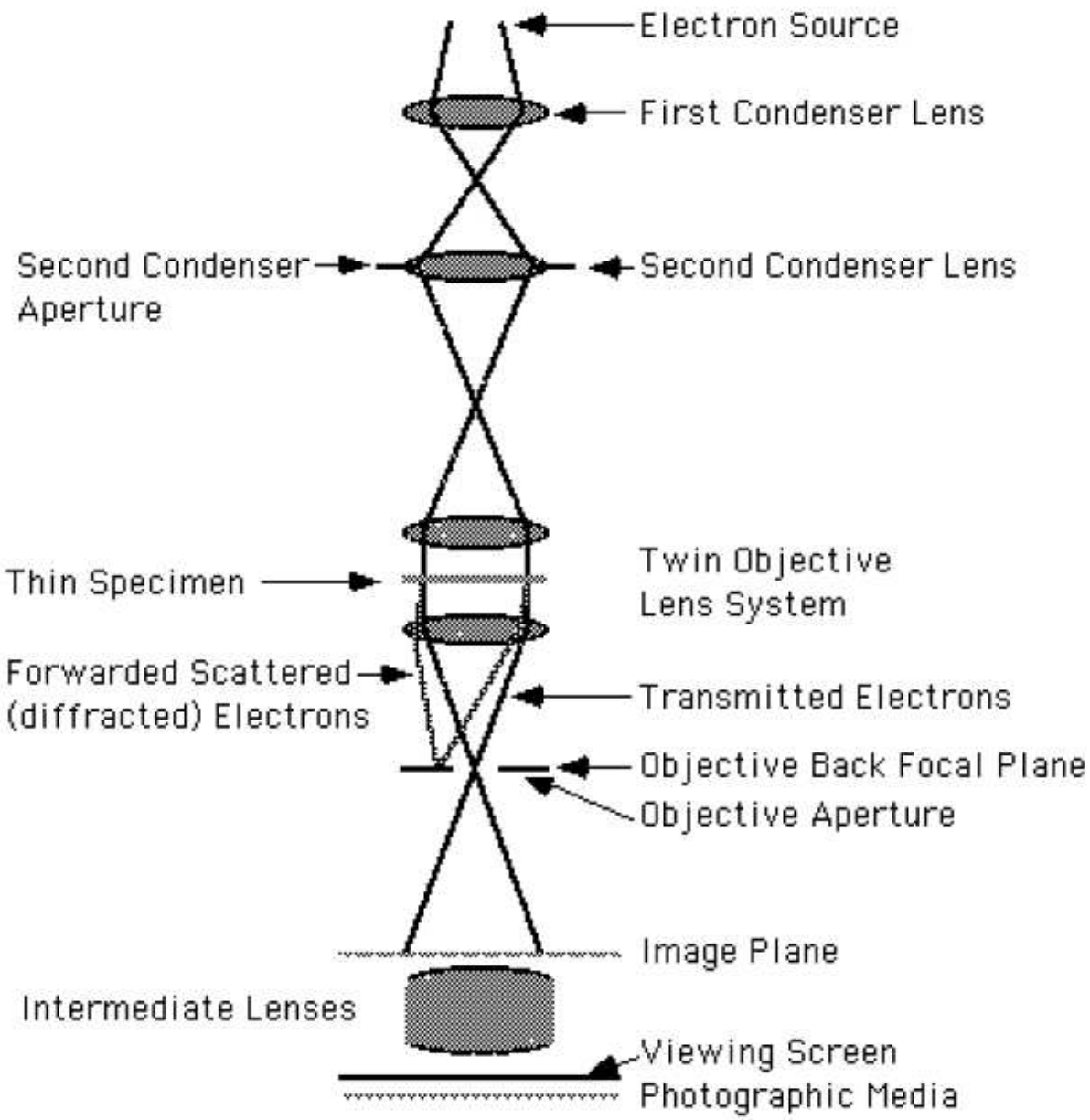


Figure 2.7 Schematic ray diagram of TEM

CHAPTER 3 *RESULTS AND DISCUSSIONS*

3.1 Preparation of Silver nanoparticles:

Recently, Hiramatsu and Osterloh (2004) and Chenet al. (2007) [36] have developed a versatile technique to produce highly monodispersed silver nanoparticles by using toluene/hexane or liquid paraffin as a solvent. Here, we have used diphenyl ether as the single solvent for synthesis of silver nanoparticles. For homogeneous nucleation of silver Nanoparticles from $AgNO_3$ by oleylamine, it is necessary to have nucleation temperature greater than 150 °C [36]. Therefore, to achieve fast and homogenous nucleation, we have inserted $AgNO_3$ into the solution of oleylamine–dipehnylether, preheated at 180 °C.It is reported earlier that Oswald ripening is very crucial to produce narrowly dispersed nanoparticlesof silver [37]. Therefore, in the second stage of preparation, we have lowered the reaction temperature to 150°C, as it is known that ripening at lower temperature will have a better control on the growth rate of individual crystallites [37]. Therefore, when the system temperature is lowered and the system is allowed to ripen, larger size nuclei will grow further in size at the cost of smaller one, i.e. smaller size nuclei will dissolve in the medium, which will provide favorable conditions for homogeneous growth. The entire process took only 2.5 h compared to the other methods wheretime period is nearly 6–8 h[37]. In second condition when we increase temperature 180 °C to 200 °C, total yield of silver nanoparticle we obtained is more then earlier one.

3.2 Phase transfer of hydrophobic silver Nanoparticles via ligand exchange:

Thermal reduction of $AgNO_3$ by oleylamine produces silver nanoparticles with hydrophobic surfaces. Oleylamine is chemically bound on the surface of silver due to the formation of Ag–N bond [38], which keeps them hydrophobic and dispersible in hexane. In this work, we have utilized block co-polymer pluronic F-127 to transfer hydrophobic silver nanoparticles into aqueous medium. Pluronic F-127 is made up of two hydrophilic A chains of poly ethylene oxide (PEO) and one hydrophobic B chain of poly propylene oxide (PPO) in an ABA configuration. At first, pluronic replaces the original oleylamine ligands on the surface of Nanoparticles and become the new ligand due to the complexation interaction between pluronic and oleylamine [38]. PPO segment of pluronic is adsorbed on silver nanoparticles as their surfaces are hydrophobic. Hydrophilic nature of PEO segments of pluronic-capped

nanoparticles transferred them into the aqueous medium and keeps them dispersible in water. By exchanging the original ligands (oleylamine) with block-co-polymer pluronic F-127, the transferred nanoparticles exhibited good stability in water, even after being washed with hexane.

Figure 3.1 Nanoparticles of silver dispersed in two media

Figure 3.1 shows the image of the original and transferred nanoparticles dispersed in two media.The upper medium is hexane and the lower one is water. Original silver nanoparticles were easily dispersed in hexane.

3.3 Characterization of Silver nanoparticle:

Here we discuss results obtained from the X-ray diffraction, transmission electron microscopy (TEM), FTIR, TGA and UV spectroscopy. The results are mainly divided in two parts (i) Structural and morphological analysis and (ii) chemical analysis. Further we have also calculated particle size of the synthesized samples from X-ray analysis.

Structural and Morphological Analysis:

3.3.1 X-RD Analysis: The XRD pattern of as-synthesized (in 200 °C) silver nanoparticles (Fig4.2) matches the face-centered cubic (fcc) structure (space group Fm 3 m) of the bulk silver with the broad peaks at 38.2°, 43.6°, 64.2° and 77.1°.

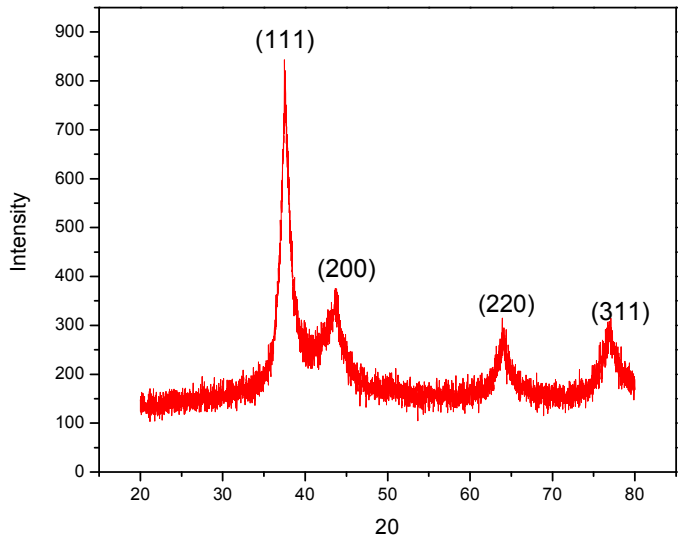


Figure 3.2: XRD spectrum of as-synthesized silver nanoparticles

These are corresponding to (111), (200), (220) and (311) planes ,respectively. The line broadening of X-ray diffraction peaks is primarily due to the small particle size. The average crystallite size obtained by classical Scherer equation with a geometric factor of 0.9 over (111) reflection is 6.5 nm. The calculated value of lattice parameter is 4.09 °A , which is consistent with the standard powder diffraction file for silver.

3.3.2 TEM Analysis: TEM analysis of Silver nanoparticles is done with H7750-itachi Model. From the figure we can see that particles size are spherical and average size is ~5 nm. All nanoparticles are monodispersed and equally distributed.

3.3.3 Thermo gravimetrical analysis:

In fig 3.4(a) from the graph ,upto 220 °C there is no major weight loss. A sharp weight loss of 12% was observed in figure 3.4(a) in the temperature range of 220-400 °C. This might be due to the decomposition of physiadsorbed oleylamine. In figure 3.4(b) similar weight loss (≈

12%) is observed in two steps. In the first step 9 % weight loss is observed upto 340 °C. which again correspond to the dissociation of physiadsorbrd oleylamine. Further 3 % weight loss is observed from 340- 650 °C, which correspond to the decomposition of chemiadsorbed oleylamine. Hence, from the TGA analysis, it is concluded that when Ag NPs are prepared at 180°C,oleylamine is completely adsorbed on the surface of nano particles by physical interaction, while in case of NPs prepared at 200 °C oleylamine is partially adsorbed by physical and partially by chemical means. In either of the cases 12 % oleylamine is decorated on the surface of nanoparticles, which corresponds to the monolayer coating.

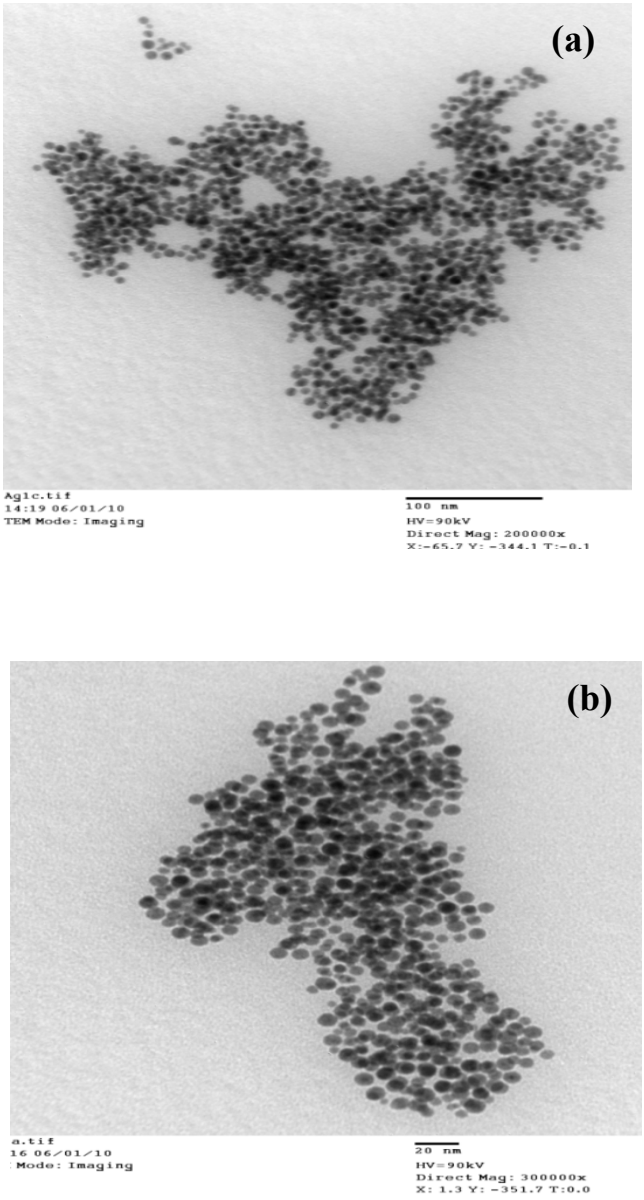


Fig 3.3 TEM image of Ag Nps at magnification (a) 200000X ,(b) 300000X,

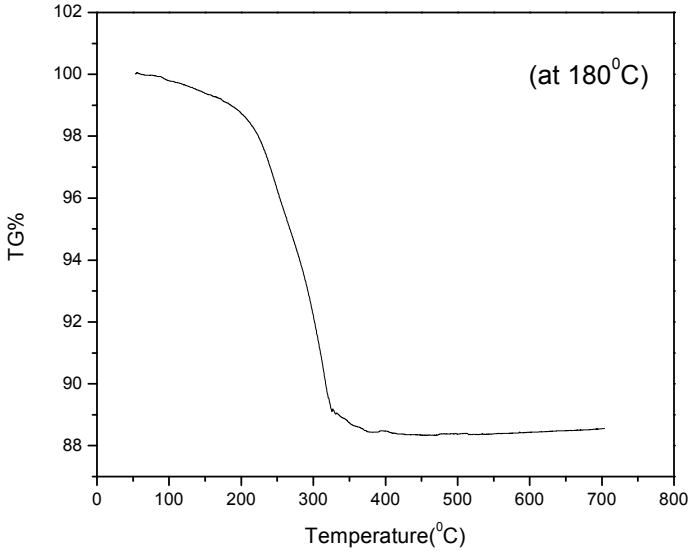


Fig3.4(a) TGA thermogram of silver nanoparticles prepared at 180 °C

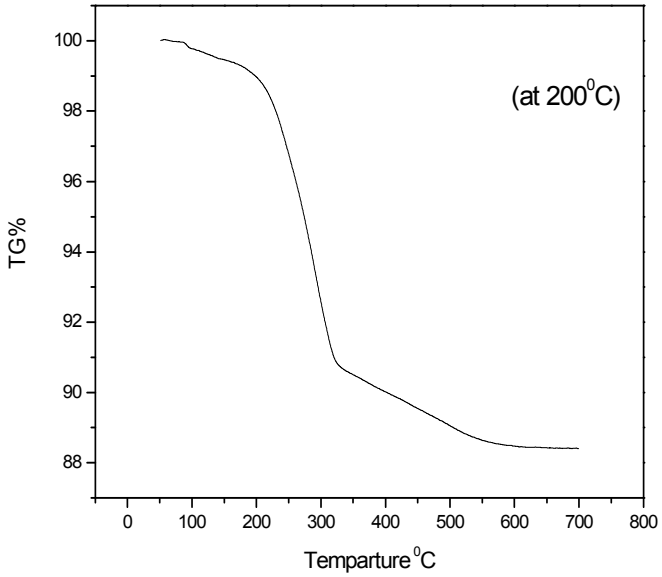


Fig3.4 (b):TGA thermogram of silver nanoparticles prepared at 200 °C

3.4 Spectroscopic analysis

3.4.1 UV Spectroscopy:

The UV–vis extinction spectra, such as the shifting, intensity and full width at half maximum (FWHM) of absorption peaks, have proven to be quite sensitive to the shape, size and size distribution of silver nanoparticles [39]. In the spectrum of silver nanoparticles (Fig 3.5c), a single surface plasmon resonance band (SPR) is observed. From the careful analysis of the spectrums, it is found that the SPR band is centered at 404 nm before phase transfer. In both synthesization condition (a) temperature 180°C (b) temperature 200 ºC, SPR peak is observed in 404 nm. While it is red shifted to 405.6 nm after phase transfer. The little red shift in the phase transferred nanoparticles is due to the difference in the surface absorbed species and dielectric medium [40]. According to the Mie's theory [41] only a single SPR band is expected in the absorption spectra of spherical metal nanoparticles,whereas anisotropic particles could give rise to two or more SPR bands depending on the shape of the particles. In our case, a single SPR band is observed, which predicts that our particles are spherical in shape. Further, phase transfer does not alter the shape of the SPR band, which excludes the possibility of formation of agglomerates during the phase transfer. The reduction in the intensity of SPR band for the phase transferred nanostructures is due to its lower concentration.

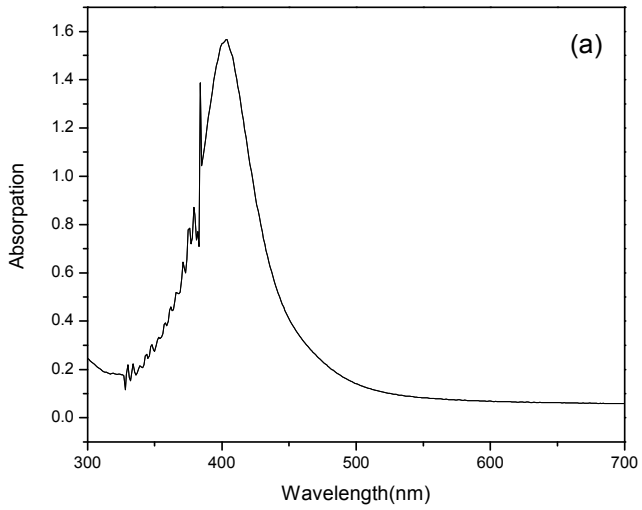


Figure 3.5: UV-vis spectra of Silver nanoparticle at prepared at 180 °C before phase transfer

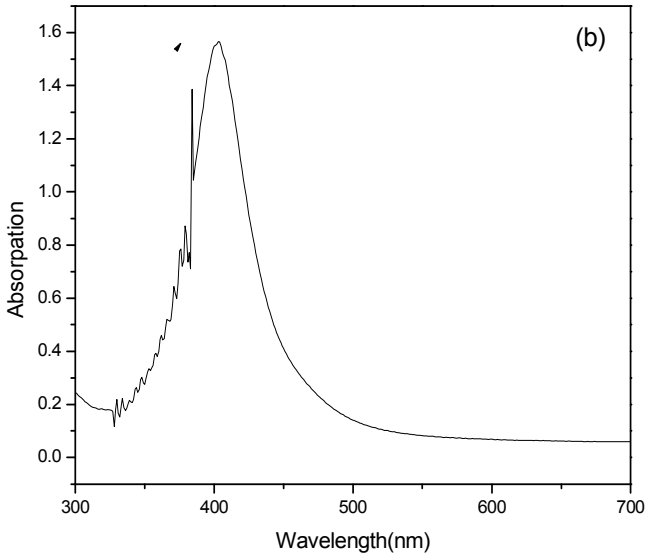


Figure 3.5: UV-vis spectra of Silver nanoparticle prepared at 200 °C before phase transfer

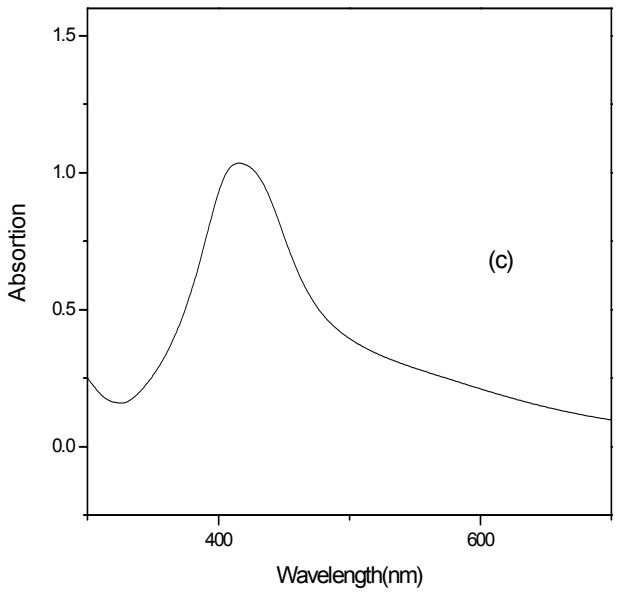
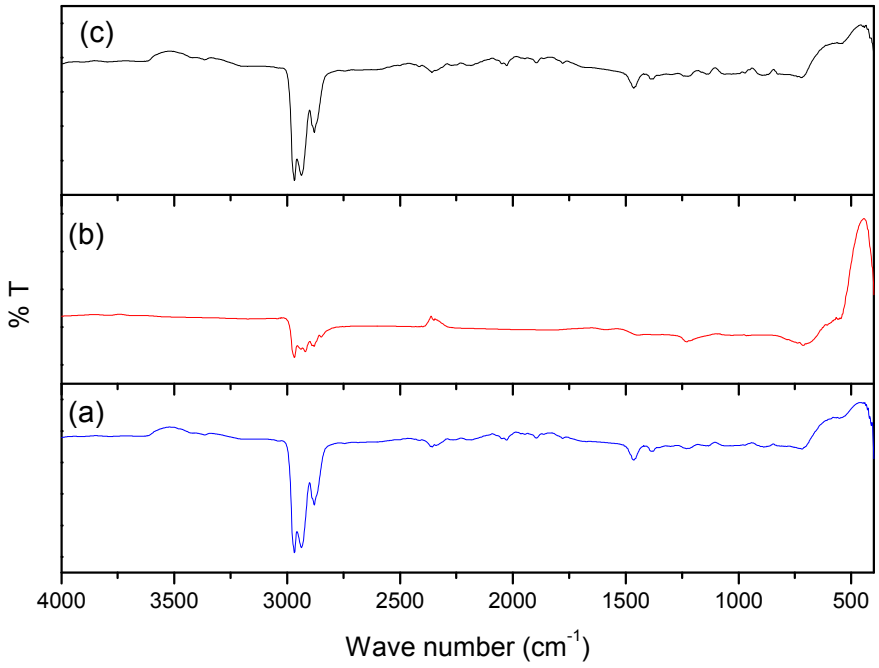


Figure 3.5 (c) UV-vis spectra of Silver nanoparticle after phase transfer.

3.4.2 FTIR Analysis: In order to fully understand the formation mechanism of silver nanoparticles, FTIR spectroscopy was used to probe the chemical composition of the surface of the silver nanoparticles. Aliphatic amines here were choosen as both reducing and capping agent. Organoamines can passivate the surface of silver nanoparticles. Here carbon double bond in oleylamine does not affect the reduction process, and oleylamine may undergo metal-ion-induced oxidation to nitriles. Actually, a number of metal compounds, such as nickel peroxide, cuprous chloride, osmium oxide, and argentic oxide, have been used as catalysts to the oxidative transformation of primary amines to nitriles.

Curves a, b and c in figure 3.6 show the FTIR spectra of hexane, oleylamine, and as obtained silver nanoparticles (AgNPs), respectively. Because both hexane and oleylamine are aliphatic compounds, their FTIR spectra are similar. However, there are three peaks existing only in curves b and c of figure 3.6. The bands slightly greater than 3000°C cm^{-1} for the =C-H stretching vibration, the absorption band around 1620 cm^{-1} assigned to the combined motion of NH_2 scissoring and N-H bending, and the bands at 966 cm^{-1} and 1070 cm^{-1} attributed to the =C-H out-of-plane and in plane bending respectively. Thus it is reasonable to consider that Ag nanoparticle are capped by oleylamine or compounds with structure similar to that of oleylamine.



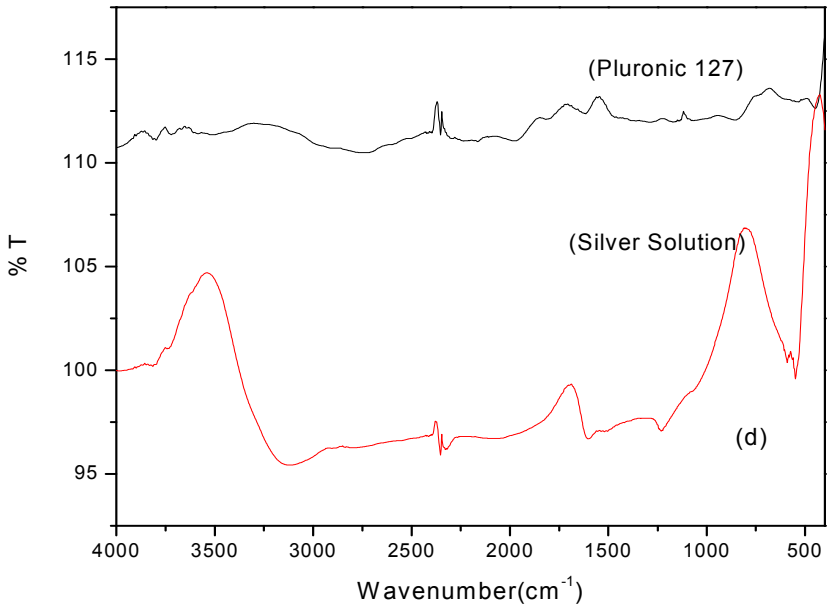


Figure3.6: FTIR spectra of (a) commercial hexane (b) oleylamine and (c) as-synthesized silver nanoparticle prepared at 200 °C (d) phase transfer silver NPs and pluronic F-127

3.5 Conclusions

Uniform hydrophobic silver nanoparticle is prepared by slow and controlled reduction of $AgNO_3$by oleylamine.Stable aqueous colloidal suspension of silver nanoparticle has been prepared using pluronic F-127. X-ray diffraction studies indicate that single phase silver nanoparticles are produced with size 6.5 nm. The pattern matches with fcc and lattice parameter is found to be 4.09 A°. Tem analysis indicates that particles are monodispersed having average size 5 nm. There is no marked difference in the UV-visible spectra of Ag NPs before and after the phase transfer, which indicates that phasile phase transfer mechanism developed in the present study do not alter the properties at core nanoparticles. TGA analysis reveals that Ag NPs are decorated with 12 % oleylamine, which correspond to the monolayer coating. FTIR study confirms functionalization of Ag NPs with oleylamine,

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