Development of novel synthesis method of silver nanoparticles using benzene thiol and disulfide derivatives bearing triazine group and their catalyst application

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Chapter 1

General Introduction

1.1. Background

Coinage metals, such as Au, Ag, and Cu have historically been very significant materials. They were famous primarily in ancient civilization for their capability to reflect light. As our understanding about these precious metals and control of the atomic world increased, their applications become more powerful and sophisticated. 1-5 Now a days the majority of these metals have been successfully used in electronics, catalysis and as structural materials, as the size of the transient metal particles decreases down to the nanometer scale, they exhibit many unique optical, electrical, and chemical properties that cannot be observed in the their bulk materials. 6-10 Nanometer-size metallic particles show unique and greatly changed physical, chemical, optical and biological properties compared to their macro scaled counterparts, due to their high surface-to-volume ratio.11-15 The scientific and engineering communities have been witnessing extraordinary progress in the field of nano science and nanotechnology. Nano science can be defined as a whole knowledge on fundamental properties of nano-size objects. It is widely agreed that nanoparticles are clusters of atoms in the size range of 1–100 nm. The prefix ‘nano’ indicates one billionth or 10^{-9} m.16-18 After the development of microscopes, capable of displaying particles as small as atoms has allowed scientists to see what they are working with. U. S. Department of Energy provides a comparison of various objects to imagine exactly how small a nanometer is. The (Figure 1) chart starts with objects that can be seen by the naked eye, such as an ant, at the top of the chart, and progresses to things about a nanometer or less in size, such as the ATP molecule used in humans to store energy from food. 19
Figure 1. “The Scale of Things”, created by the U. S. Department of Energy, provides a comparison of various objects.

Moreover, nanoparticles are roughly the distance off five silicon or ten hydrogen atoms aligned in a line. For comparison, the hydrogen atom is ~0.1 nanometers, a virus is ~100 nanometers, a red blood cell is approximately 7,000 nanometers in diameter and an average human hair is 10,000 nanometers wide. The current outstanding performance of nano science is realized in nanotechnology as new materials and functional facilities. Currently, nano chemistry with its prominent role is the fastest developing field of nano science. Nano science offers the electrifying opportunity to study a state of matter that is intermediate between bulk and isolated atoms or molecules, as well as the effect of spatial confinement on electron behavior. It also
provides an opportunity to probe the issues associated to surfaces or interfaces because of their interfacial nature. In other words, nano science and nanotechnology are fields that focus on: (i) the development of synthetic methods and surface analytical tools for building structures and materials, (ii) the changes in chemical and physical properties due to miniaturization, and (iii) the use of such properties in the development of novel and functional materials and devices. Metallic nanoparticles exhibit a wide range of size and shape dependent properties and have found application in myriad fields, including catalysis, sensing, photovoltaics, nanophotonics, optoelectronics, bio sensing, molecular diagnostics, antibacterial activity and data storage. For example, the antibacterial activity of various metal nanoparticles such as silver nanoparticles is mainly related to their size; that is, the smaller the silver nuclei, the higher and its antibacterial activity. In addition, the catalytic activity of these nanoparticles is also dependent on their shape, size distribution, and chemical-physical environment. Thus, strong control over the size and size distribution is a crucial task. Generally, unique control of shape, size, and size distribution is usually achieved by changing the synthesis strategies, reducing agents and stabilizers.

The nano revolution conceptually started decades ago, with gradual advancements such as the invention of techniques like Transmission electron microscopy (TEM), Atomic force microscopy (AFM), Scanning electron microscope (SEM), Dynamic Light Scattering (DLS) and others, nanotechnology today has reached a stage where, it is considered as the future to all technologies. There are a wide variety of techniques that are capable of creating new nanostructures with various degrees of quality, speed and cost. Scientists taking proactive approach to advancing from the current discovery phase in the creation of nano materials into a
production phase that is efficient and reduces waste while maintaining green chemistry parameters.

1.2. Historical Overview of Nano Silver

Nanoparticles have a long and fascinating history. Their preparation is neither an unique result of modern research nor confined to man-made materials. Ancient Civilizations used colloidal metal nanoparticles for their dazzling colors, and they can be found in the stained glass windows of the middle Ages, and yet, they continue to attract considerable attention today. The preparation of these nanoparticles has a long and storied history dating back to millennia. Noble metal such as gold and silver nanoparticles, have found their way into glasses for over 2000 years.\textsuperscript{41-42} They have mostly been used as colorants, particularly for church windows. The color appeared as a result of the nucleation and growth of small metallic nanoparticles, whose maximum size yielding a strong color.\textsuperscript{43} In 15\textsuperscript{th} century brightly colored porcelain was prepared, containing silver and silver-copper alloy nanoparticles (Figure. 2).\textsuperscript{44} The technique was tremendously developed in the Islamic world during the 9\textsuperscript{th} century and appeared in Mesopotamia. These decorations showed stunning optical properties due to the presence of distinct silver and / or copper nanoparticles dispersed in the outermost layers of the glaze. They exploited the reducing atmosphere obtained by heating dried genista up to 600\textdegree{} C to obtain nanoparticles by reducing metal salts or their oxides previously deposed on the ceramic piece from a vinegar solution. Figure 3 (a), demonstrated iridescence under striking reflection with shiny blue and green colors.\textsuperscript{45} Transmission electron microscopy (TEM) analysis reported a double layer of silver nanoparticles with smaller sizes (5–10 nm) in the outer layer and larger ones (5–20 nm) in the inner layer (Figure 3 (b)). The distance between the two layers is constant at about 430 nm, resulted into interference effects (Figure. 3(c)). The light scattered by the
second layer has a phase shift with respect to the one scattered by the first layer, and due to the phase shift depends on the wavelength of the incoming light, each wavelength is scattered differently.

![Figure 2. Glazes containing copper and silver nanoparticle](image)

15th and 16th centuries (Renaissance): Pottery of Deruta (Umbria, Italy)
Figure 3. Photograph of a medieval piece of a glazed ceramic observed by scattered light and specular reflection (a). TEM image of the double layer of silver nanoparticles (b). Schematic representation of interference phenomena due to the double layer (c). With permission of Trans Tech Publications and Dr. Philippe Sciau.
The stained glass of a beautiful rose can be seen at the world heritage Cathédrale Notre-Dame de Chartres in France. The stained glass made in medieval times is displayed in (Figure (4)). After decades of scientific research, chemistry clarified the reasons behind the generation of the sharp colors. These striking colors were controlled by the size and the shape of gold and silver nanoparticles.

The first formal scientific analysis of nanoparticles took place in 1831, when Michael Faraday investigated the ruby-red colored colloids of gold and publish the finding that the color was due to the small size of the metal particles. In 1889 more than 120 years ago, M. C. Lea reported the synthesis of a citrate stabilized silver colloid with average diameter size of 7-9 nm. Their stabilization by citrate and average size in the nanoscale are identical to recent research related to nanosilver formation using silver nitrate and citrate. Nanosilver stabilized by proteins has been reported as early as 1902. Since 1897, nanosilver under the name “Collargol” has been manufactured commercially and used in medical applications. Tremendous amount of nanosilver preparations were also invented in the next decades, for example the gelatin stabilized silver nanoparticles patented by Moudry in 1953 with 2-20 nm diameter and silver nanoparticle impregnated carbon with a diameter of silver particles below 25 nm. It is noteworthy, that the innovators of nanosilver formulations understood decades ago that the fastest growth of the emerging technology required nanoscale silver, as the following statement from a patent: “for proper efficiency, the silver must be dispersed as particles of colloidal size less than 250 Å [less than 25 nm] in crystallite size” This long history of pragmatic production and use of colloidal nanosilver has resulted in an extensive research and knowledge about these nanoparticles over the last 100 years, even if this research is not reported under “nano” terminology. The earlier half of 20th century filled with huge commercial sale of medicinal
nanoscale silver colloids, known under different trade names began and during the half past century their use became widespread. These nanosilver products were sold as over-the-counter medications and also used by doctors to treat various diseases.\textsuperscript{53-55}

Figure 4. Rosace nord stained glass in the Cathédrale Notre-Dame de Chartres (France), color changes depend on the size and shape of gold and silver nanoparticle.
1.3. Preparation of Silver nanoparticles by chemical reduction

Innumerable techniques are available including chemical and physical routes to prepare silver nanoparticles (AgNps). Laser ablation, evaporation condensation are the most important physical approaches to prepare AgNps. Physical synthesis methods, due to the absence of solvent contamination in the prepared thin films and the homogeneity of nanoparticles distribution are the advantages of physical fabrication methods in comparison to chemical processes. High temperature (> 1000 C), vacuum and expensive instruments are requirements of physical methods for the synthesis of AgNps. In comparison, chemical routes to synthesize AgNps involves reducing agents are easier and convenient methods, using dilute aqueous solution and few simple equipment. In general, chemical reduction routes involve reducing agents that are reacted with a salt of the metal according to the following chemical equation

\[ \text{mM}^{n+} + \text{Red} = \text{mM}^{0} + \text{Red}^{mn+} \]

The most common approach for synthesis of AgNps is chemical reduction by organic and inorganic reducing agents. In general, different reducing agents such as sodium citrate, ascorbate, sodium borohydride (NaBH₄), elemental hydrogen, polyol process, Tollens reagent, N, N-dimethylformamide (DMF), and poly (ethylene glycol) block copolymers are used for reduction of silver ions (Ag⁺) in aqueous or non-aqueous solutions. These reducing agents reduce Ag⁺ and lead to the formation of metallic silver (Ag⁰), which is followed by agglomeration into oligomeric clusters. These clusters eventually lead to the formation of metallic colloidal silver particles. It is important to use protective agents to stabilize dispersive AgNps during the course of metal nanoparticle preparation, and protect the AgNps that can be absorbed on or bind onto nanoparticle surfaces, avoiding their agglomeration.
1.4. Stabilization of Silver nanoparticles

Nanoparticle surface atoms are very important when studying the stability and reactivity of nanoparticles. In fact, when the percentage of atoms on the surface of the nanoparticle increases, they become more reactive yet less stable. Nano clusters are only kinetically stable, which means they must be stabilized against aggregation. otherwise, they will aggregate into large particles and, eventually, they will become bulk material so as to reach their thermodynamic point of minimal energy. 76

In order to avoid the aggregation process, stabilization must be achieved. This can be done in two different ways: - Electrostatic stabilization: 77 it occurs by the adsorption of ions on the nanoparticle surface. This adsorption generates an electrical double layer resulting in a Columbic repulsion force between individual particles. Steric stabilization: 78 it occurs when nanoparticle surfaces are surrounded by layers of sterically bulky materials, which form a steric barrier and prevent close contact between individual particles. Those two processes, which are shown in (Figure 5), are not only necessary when working with metal nanoparticles but also when synthesizing almost any kind of nanoparticles in solution.

Figure 5. Graphic examples of steric stabilization (A) and electrostatic Stabilization (B)
There are many examples AgNps synthesized in some different media and stabilized via one of the two mentioned methods. When trying to achieve electrostatic stabilization, it is common to use a kind of reductant salt, whose ions surround the formed nanoparticles and form the double layer. On the other hand, when stabilizing nanoparticles via sterically bulky materials, some kind of surfactants can be used. Depending on the potential use of the resulting nanoparticles, they can be surrounded by thiols, dendrimers, polymers, and biomolecules such as DNA or proteins or organic ligands. The presence of surfactants comprising functionalities (e.g., thiols, amines, acids, and alcohols) for interactions with particle surfaces can stabilize particle growth, and protect particles from sedimentation, agglomeration, or losing their surface properties. Polymeric compounds such as poly (vinyl alcohol), poly (vinylpyrrolidone), poly (ethylene glycol), poly (methacrylic acid), and polymethylmethacrylate have been reported to be the effective protective agents to stabilize AgNps. In one study, Oliveira and coworkers prepared dodecanethiol capped AgNPs, according to Brust procedure based on a phase transfer of an Au\(^{3+}\) complex from aqueous to organic phase in a two-phase liquid-liquid system, which was followed by a reduction with sodium borohydride in the presence of dodecanethiol as stabilizing agent, binding onto the NPs surfaces, avoiding their aggregation and making them soluble in certain solvents. They reported that small changes in synthetic factors lead to dramatic modifications in nanoparticle structure, average size, size distribution width, stability and self-assembly patterns. Kim and colleagues reported the synthesis of spherical AgNps with a controllable size and high mono dispersity using the polyol process and a modified precursor injection technique. In the precursor injection method, the injection rate and reaction temperature were important factors for producing uniform-sized AgNps with a reduced size. Zhang and coworker used a hyper branched (methylene
bisacrylamide minoethyl piperazine) with terminal dimethyl amine groups (HPAMAM-N (CH₃)₂) to produce colloids of silver. The amide moieties, piperazine rings, tertiary amine groups and the hyper-branched structure in HPAMAM- N (CH₃)₂ are important to its effective stabilizing and reducing abilities. Chen and colleagues⁹¹ have shown the formation of mono dispersed silver NPs using simple oleylamine-liquid paraffin system. It was reported that the formation process of these NPs could be divided into three stages: growth, incubation and Oatwald ripening stages. The higher boiling point of 300 °C of paraffin affords a broader range of reaction temperature and makes it possible to effectively control the size of silver NPs by varying the heating temperature alone without changing the solvent. Moreover, the size of the colloidal AgNps could be regulated not only by changing the heating temperature, or the ripening time, but also by adjusting the ratio of oleylamine to the silver precursor. AgNps can be prepared at room temperature, by simple mixing of the corresponding metal ions with reduced polyoxometalates which serves as reducing and stabilizing agents. The dispersion and capping of AgNps by using different cationic and anionic surfactants also enhanced stabilization. In case of anionic surfactant such as SDS (sodium dodecyl sulfate) is based on an electrostatic repulsion. The surface charge of the disperse phase can be enhanced by the ionic surfactant addition providing the electrostatic protection of the AgNps to adhere to one another. Sodium dodecyl sulfate (SDS),⁹² as representatives of the anionic surfactant group, and cetyltrimethylammonium chloride or bromide (CTAC, CTAB),⁹³ as the cationic surfactants, have been employed in several studies and are considered stabilizing agents of immense importance.
1.5. Stabilization of Silver nanoparticles by surfactant

The word surfactant is an abbreviation for surface active agent. A surfactant is characterized by its tendency to adsorb at surfaces and interfaces. Examples of interfaces involving a liquid phase include suspension (solid-liquid), emulsion (liquid-liquid) and foam (liquid-vapour). In many formulated products several types of interfaces are present at the same time. Another general and fundamental property of surface active agents is that monomers in solutions tend to form aggregates, called micelles. Micelles form already at very low surfactant concentrations in water. The concentration at which micelles start to form is called critical micelle concentration (CMC). Micelle formation, or micellization, can be viewed as an alternative mechanism to adsorption at the interfaces for removing hydrophobic groups from contact with the water, thereby reducing the free energy of the system. It is an important phenomenon since surfactant molecules behave very differently depending on whether they are present in micelles or as free monomers. The micelles behave as large molecules and influence the solubility of organic hydrocarbons and oils in aqueous solution and also influence the viscosity. The size of the micelle is measured by the aggregation number which is the number of surfactant molecules associated with a micelle. Only surfactant monomers contribute to surface and interfacial tension lowering. Wetting and foaming are governed by the concentration of free monomers in solution. The micelles can be seen as a reservoir for surfactant monomers. At higher concentrations of the surfactant other aggregates are formed. Different phase structures give very different physicochemical properties. Surfactant adsorption to solid-liquid interfaces occurs by transferring surfactant molecules from bulk solution phase to the solid-liquid interface. This phenomenon happens if the interface is energetically favored by the surfactant in comparison to the bulk solution. Adsorbed surfactant monomers begin to aggregate and form micelle-like
structures at higher surfactant concentration. These structures are called hemimicelles and have one or two surfactant layers. Once these structures form on a solid surface, adsorption of additional surfactant may rapidly increase until a complete bilayers of surfactant covers the solid surface. So following the trend of variations in some terms like surfactant adsorption on carbonate rock or interfacial tension can result important understanding about the surfactant-solid interactions. The adsorption of surfactant at the solid–liquid interface plays an important role in many technological and industrial applications. The behavior of surfactants at the interface is determined by number of forces, including electrostatic attraction, covalent bonding, hydrogen bonding, hydrophobic bonding and solvation of various species. For ionic surfactants, electrostatic interactions are almost the governing factors. If the surfactant and the adsorbent are oppositely charged, the adsorption process is fast. For the case of similarly charged surfactant and adsorbent the process is slow. Nanoparticles are employed like surfactants, and often in association with them, as stabilizing additives of such disperse systems, in different fields of practical interest. Nanoparticles affect the interfacial behavior and the adsorption processes. The interaction between nanoparticles and surfactants plays a major role in the extensive use of nano fluids in industrial and technical applications like colloidal stability and detergency. Usually, many surfactants can be used to form microemulsion, including cationic surfactants such as cetyltrimethylammonium bromide (CTAB), anionic surfactants such as bis(2-ethylhexyl)sulfosuccinate (AOT), sodium dodecyl benzene sulfonate (SDBS) and lauryl sodium sulfate (SDS), and nonionic surfactants such as Triton X-100, 99-101 etc. Correspondingly, the micro emulsion can be divided into three types, namely, cationic micro emulsion, nonionic micro emulsion and anionic micro emulsion. The choice of surfactants should base on the demands of the experiment and reaction conditions. Different surfactant, that is, different micro emulsion
system employed in the fabrication process, AgNps with different diameters or morphologies will be obtained. Water/oil micro emulsion is generally transparent, isotropic liquid media with nano sized water droplets dispersed in the continuous oil phase and stabilized by surfactant molecules at water/oil interface. The micro droplet size can be modified by varying concerned parameters, e.g., The water droplets covered by surfactant molecules, which act as micro reactors for processing reactions, offer a unique microenvironment for the formation of nanoparticles. When the particle size approaches that of the water pool, the surfactant molecules will be adsorbed on the particle surface to inhibit the particles from sticking. In other words, the diameter and morphology of nanoparticles obtained in such a medium can be controlled by the micro reactors based on the micro emulsion droplets, which are very important to fabricate smaller particles in controlled synthesis. As a result, the resultant particles have good monodisperse and high stabilization.  

The preparation procedure of silver nanoparticles in micro emulsion commonly consists in mixing of two micro emulsions carrying silver salt and reducing agent, respectively. After mixing of two micro emulsions, the interchange between reactants takes place during the collisions of water droplets. The exchange process of solubilizates and subsequent reaction can be thought of as consisting of the following five main steps (1) Brownian diffusion of reverse micelles leading to collisions; (2) surfactant layer opening through effective collisions and a coalescence of the micelles happening; (3) diffusion of solubilizate molecules resulting in exchange of materials between micelles; (4) reaction between solubilizates resulting in formation of silver nuclei; (5) the aggregates splitting to return as reverse micelles. The above steps take place time and again until the nuclei grow to attain the size of water-pool. One can be seen that the nucleation reaction and particle growth take place within the micelles and the size and morphology of as-synthesized nanoparticles depend on the size and shape of the micro droplets. In addition, the surfactant molecules are attached on the
surface of particles to stabilize and protect them against further growth. Compared to the particles produced with cationic or nonionic micro emulsions, the resultant particles have a smaller average size and narrower size distribution. Furthermore, the silver colloidal solution has high stabilization and thus can be preserved for a long time without precipitation. At different concentrations, the surfactant molecules can form various molecule aggregations, e.g., micelle, liquid crystal and vesicle which are used as perfect templates to prepare nanostructure materials. May and Ben Shaul found that the change of micelle structures had an energetic barrier. That is, at a low surfactant concentration only spherical micelles appear in solution. When the surfactant concentration in the solution reaches a well-defined saturation value, i.e., second critical micelle concentration (second CMC), the energetic barrier will be overcome and the micelle structure will change from a spherical micelle to other special structure, and then the micelle will be steady again at a new concentration range. For example, if the concentration of surfactant attains to 40–50%, the spherical micelle turns into rod-shaped or column-shaped micelle. Furthermore, the micelle is also able to self-assemble into layer or liquid crystal structure. The special micelles can be usually used as effective structure-directing agents to prepare nanoparticles with desired morphologies. CTAB and CTAC are an important cationic surfactant to synthesize nanoparticles due to its excellent capability to serve as a steric stabilizer and shape controller for nanoparticles. Xiuvan, Li et al. reported the influence of surfactant CTAB (cetyl trimethyl ammonium chloride) on AgNps. They prepared AgNps with narrow size distribution were prepared via a CTAB-induced silver mirror reaction process. This method realized a high Ag concentration of 0.05 mol/l and an ideal stability of the silver colloid over 45 days. CTAB plays as both the dispersant and the complexant in the synthesis process. The formation of CTA–
Br\textsuperscript{−}Ag\textsuperscript{+} complex compound can progress the reductive reaction. CTAB’s chloride counterpart (CTAC) has also been used in the synthesis of anisotropic particles, however with more regular shapes, such as concave cubes, trisoctahedra or rhombic dodecahedra. The reason for such different morphologies obtained with CTAB and CTAC has been attributed to the different ability of bromide and chloride ions to bind on Ag surfaces\textsuperscript{106}

Zhenquan et al.\textsuperscript{107} reported a chemical approach for synthesizing shape-controlled Ag nanoparticles by using the surfactant SDS as a soft template. The experimental approach includes a two-step reaction: the first step is quickly generating Ag seed clusters by a chemical reaction using sodium borohydride as a reducing reagent; the second is the slow growth of controllable Ag nanoparticles by a mild chemical reaction using hydroxylamine hydrochloride as a reducing reagent. Spherical, polyhedral, and fibrous Ag nanoparticles are synthesized successfully in aqueous solution having various SDS concentrations.

Nabel et.al.\textsuperscript{108} successfully prepared silver nanoparticles loaded by three Gemini cationic surfactants having different spacer chain lengths. TEM analysis showed the homogeneity and stability of the formed silver nanoparticles in the presence of the Gemini surfactants. The results showed increased activity of the silver nanoparticles in the presence of the Gemini cationic surfactants. Antimicrobial results of inhibition zone diameter and minimum inhibitory concentration were correlated to Gemini surfactants and their nanoparticles including surface activity and tendency toward adsorption at interfaces.
1.6. Stabilization of Silver nanoparticles by organo sulfur group

Surface modification is an important aspect in developing a “toolbox” for exploring unique applications enabled by nanomaterials. Surface modification is often required for many functional and monodisperse nanoparticles including silver, iron platinum, gold and other materials. To this end, the creation of robust surface chemistry for different nanoparticle systems has been widely studied in recent years. During last two decades organo sulfur compounds playing wonders in the “nano” chemistry world, by chemically modifying the nanoparticle surfaces, having tremendous applications in catalysis, photovoltaics, sensors and others. In organic chemistry, a thiol is an organosulfur compound that contains a carbon-bonded sulfhydryl (–C–SH or R–SH) group (where R represents an alkane, alkene, aromatic or other carbon-containing group of atoms). Thiols are the sulfur analogue of alcohols (that is, sulfur takes the place of oxygen in the hydroxyl group of an alcohol), and the word is a portmanteau of "thion" + "alcohol", with the first word deriving from Greek ("thion") = "sulfur". The SH functional group itself is referred to as either a thiol group or a sulfhydryl group. Their chemical structure is close to alcohols except that sulfur is substituted for the oxygen in the hydroxyl group. Thiols are also known by the term “mercaptan”. Many thiols have strong odors resembling that of garlic.

Chemical derivatisation of solid nanoparticle surfaces by thiol or disulfide has long featured as a means of manipulating interfacial properties in relation to processes such as wetting, adhesion, lubrication, corrosion and electro catalysis, Factors that rule the formation of stable modifying / derivatising layers is therefore of both fundamental and technological importance. The use of organo sulfur groups, thiols or disulfide compounds for modifying noble metal nanoparticles is one of the most developed methods, because organo sulfur groups
strongly coordinate to various metals, such as Ag, Cu, Pt,Hg, Fe, or Au. Sulfur possesses a huge affinity for metal surfaces, and organo sulfur compounds thus will adsorb spontaneously. The metal-sulfur interaction is strong enough to immobilize the thiol groups on the surface of metal nanoparticles. For example, the chemisorption energy between silver and sulfur is estimated at 217 kJ \(^{-1}\) mol. Thiol- or disulfide-capped nanoparticles can be prepared by two methods. First, the sulfur compounds can be grafted on the surface of pre-synthesized nanoparticles covered by solvent molecules which are thus replaced by the sulfur-containing ligands. The second approach is to synthesize an organo sulfur-capped nanoparticle in a one-step process, where the metal precursor and the protective ligand are reacted simultaneously.\(^{113}\) In this case; two processes compete with each other. The first is the growth of the particles leading to a reduction of the total surface. At some point, coordination of the ligands to the surface atoms of the clusters becomes more favorable and stops further growth. The choice of the organo sulfur ligand and the variation of its concentration lead to a control of the particle size. For example, a good AgNps size control between 2 and 5 nm was achieved by varying the dodecanethiol concentration.\(^{114}\) It was shown that varying the reaction conditions, notably the alkanethiol:Ag ratio from 1:1 to 1:12 yields alkanethiolate-protected AgNps for example AgNps particles covered by a hexadecanethiolate monolayer, with core sizes ranging from 0.7 to 5.2 nm. When the same reduction method, using aqueous sodium borohydride, was used to synthesize AgNps covered by mercapto succinic acid, particles in the range 1.4–5.7 nm were obtained. Reduction of AgNO\(_3\) by sodium borohydride in the presence of mercaptopropionic acid lead to particles with diameters ranging from 1.0 to 3.4 nm when the ligand:Ag ratio was varied from 2.5:1 to 0.5:1.\(^{115}\) It is well known that the optical and electrical properties of metal nanoparticles are size-dependent. Since the size of the nanoparticles can be controlled by varying the ligand concentration, an important influence of the
nature and concentration of the ligand on the nanoparticle properties exists. To this end chemisorption of alkyl derivatives on a variety of substrates, in particular n- alkanethiols on Ag surfaces, have received much attention in recent years and in-depth understanding of such systems has emerged. In contrast, characterization of chemisorption consisting of unsaturated systems is in its infancy. In the special case of unsaturated system such as aromatic thiols it was shown that the thiol head group can occupy various adsorption sites on the metal surface, with very small energy differences. The difference consists in the additional electrostatic interaction between the aromatic ring and the surface, depending on the ring orientation relative to the AgNp surface. Aromatic thiol functionalized nanoparticles represent an interesting system owing to the presence of delocalized π-electrons in the aromatic phenyl ring, which results in increased electrical conductivity and the rigidity of aromatic phenyl ring, which reduces the molecular flexibility. Aromatic thiols have promising features in the preparation of thiol capped nanoparticles due to several reasons. First, aromatic thiols are highly anisotropic and the intermolecular interactions are stronger than those between the n-alkanethiols, which may lead to different molecular packing structures. Second, electrons are more delocalized in the aromatic rings than in the alkane chains, as a result the electrical conductance through aromatic thiols is higher.

In the case of short aromatic thiols, other interactions, e.g. between the benzene ring and surface, between functional groups, and the intermolecular π – π interaction can drive the packing structure, which capped nanoparticles. Such strong intermolecular interactions in aromatic thiol, compared with the vander Waals lateral intermolecular interactions that drive n- alkanethiol molecules to assemble in well-defined monolayer structures, can drive the short aromatic thiols to form multilayers network, strongly stabilized the nanoparticles. Aromatic
thiols have the required rigidity. Aromatic molecular short backbone chain also play crucial role in stabilization of AgNps. Aromatic thiols exhibited superior physical and chemical properties compared with saturated alkane systems. In aromatic thiols (SH) both sulfur and benzene moieties were involved to the surface adsorption, changing the R-group imparts different functionality to the particles that can be manipulated according to the intended applications. In short chain aromatic thiol due to the presence of short methylene chains and symmetrical distances, electrons moves faster through delocalized system than saturated system and conjugated molecules are rigid compared with saturated flexible molecules. These unique properties of aromatic thiol attributed to relative ease of ligands (SH) bounded with the nanoparticles surface within short span of time and with superior stability by compact and rigid network. Increasing aromaticity in the backbone chain will enhance stabilization of nanoparticles.

Thiols can interact with metal nanoparticles in two different ways. The first possibility is the adsorption of the intact RSH molecule on the surface. The second possibility is chemisorption of thiols or disulfides on metal surfaces which generates SR groups. Chemisorption of thiols on the metal surface occurs with concomitant cleavage of the S–H bond, binding could occur by the formation of a truly covalent bond between the thiol sulfur and the surface (homolysis of the S - H bond), or chemisorption by donation of electron density from the thiolate group into the metal particle (heterolysis). Versatile reactivity of thiols originates primarily from their specific structure, namely from the presence of a highly reactive center, sulfur atom that can change its valence state, and high liability of the S–H bond which after undergoing heterolytic or homolytic dissociation to give such reactive intermediates as
sulfanyl radicals and \( S \)-centered cations or anions, depending on the conditions. Therefore, thiols have found wide applications in many fields. \(^{120}\)

1.7. Plasmon resonance in noble metal nanoparticles

The interesting optical attributes of metal nanoparticles, as reflected in their bright intense colors, are due to their unique interaction with light. In the presence of the oscillating electromagnetic field of the light, the free electrons of the metal nanoparticle undergo a collective coherent oscillation with respect to the positive metallic lattice. This process is resonant at a particular frequency of the light and is termed the localized surface plasmon resonance (LSPR) oscillation (Figure 9). This electronic oscillation can be simply visualized as a photon confined to the small size of the nanostructure, constituting an intense electric field around the particle. The surface plasmon oscillation\(^ {121}\) decays by radiating its energy resulting in light scattering or decays non radiatively as a result of conversion of absorbed light to heat. The electric field intensity and the scattering and absorption cross-sections are all strongly enhanced at the LSPR frequency, which for gold, silver, and copper lies in the visible region. Since copper is easily oxidized, gold and silver nanostructures are most attractive for optical applications.

![Figure 9. Localized surface plasmon resonance](image)
As the shape or size of the nanoparticle changes, the surface geometry changes, causing a shift in the electric field density on the surface. This causes a change in the oscillation frequency of the electrons, generating different cross-sections for the optical properties including absorption and scattering. The interaction of the metal nanoparticles can be described by Maxwell’s equations and was solved for the case of spherical nanoparticles by Mie. The total extinction and scattering efficiency\(^ {124-125} \) \( Q_{ext} \) and \( Q_{sca} \) for a homogenous sphere are expressed in the following infinite series:

\[
Q_{ext} = \frac{2}{\chi^2} \sum_{n=1}^{\infty} (2\varepsilon + 1) \text{Re} \left[ a_n + b_n \right]
\]  

\[
Q_{sca} = \frac{2}{\chi^2} \sum_{n=1}^{\infty} (2\varepsilon + 1) \left[ a_n^2 + b_n^2 \right]
\]  

\[
Q_{abs} = Q_{ext} - Q_{sca}
\]

\[
a_n = \frac{m \psi_n(mx) \psi_n'(x) - \psi_n(x) \psi_n'(mx)}{m \psi_n(mx) \xi_n'(x) - m \xi_n(x) \psi_n'(mx)}
\]

\[
b_n = \frac{\psi_n(mx) \psi_n'(x) - m \psi_n(x) \psi_n'(mx)}{\psi_n(mx) \xi_n'(x) - m \xi_n(x) \psi_n'(mx)}
\]

Where \( \varepsilon \) is the refractive index of the metal, \( \varepsilon_m \) is the refractive index of the surrounding medium, \( m \) is the ratio of the refractive index of the sphere and the surrounding medium \( (m = \varepsilon / \varepsilon_m) \), \( R \) is the radius of the sphere, \( \lambda \) is the wavelength of light, \( x \) is the size parameter \( (x = 2\pi n m R / \lambda) \), \( \psi_n \) and \( \xi_n \) are the Riccati-Bessel functions and the prime represents
first differentiation with respect to the argument in parentheses. These expressions have been solved in the dipole approximation for spherical nanoparticles much smaller than the wavelength of light (<20nm) where only the dipole contributes to the absorption by the nanoparticle.

\[
Q_{abs} = \frac{18\pi V \varepsilon_m^{3/2}}{\lambda} \times \frac{\varepsilon_2(\lambda)}{[\varepsilon_1(\lambda) + 2\varepsilon_m]^2 + \varepsilon_2(\lambda)^2}
\]  

(1.6)

where \( V \) is the volume of the nanoparticle, \( \varepsilon_m \) is the dielectric constant of the surrounding medium, \( \lambda \) is the wavelength of light, and the dielectric constant of the metal is expressed in the complex form as a function of the wavelength of light, where \( \varepsilon(\lambda) = \varepsilon_1(\lambda) + i\varepsilon_2(\lambda) \).

This allows the calculation of the expected absorption and scattering spectra of small spherical metal nanoparticles.

Changing the dielectric constant of the surrounding material has an effect on the oscillation frequency due to the varying ability of the surface to accommodate electron charge density from the nanoparticles. The expected shift in the absorption spectrum with changing medium dielectric constant (\( \varepsilon_m \)) can be calculated using equation 6. Changing the solvent changes the dielectric constant, but the capping material is most important in determining the shift of the plasmon resonance due to the localized nature of its effect on the surface of the nanoparticles. Chemically bonded molecules can be detected by the observed change they induce in the electron density on the surface, which results in a shift in the surface plasmon absorption maximum. This is the basis for the use of noble metal nanoparticles as sensitive sensors.

Mie originally calculated the surface plasmon resonance by solving Maxwell’s
equations for small spheres interacting with an electromagnetic field. The Mie light scattering model provides a mathematical solution that predicts the solution color of spherical particles with respect to their size. When nanoparticles are not spherical, the observed spectrum will be a result of a combination of the in-plane diameter, out-of-plane height size and shape parameters. The Mie theory, however, cannot be used to directly calculate the surface plasmon resonance bands (SPR) positions of arbitrary anisotropic shapes. Approaches such as discrete dipole approximations (DDA)\textsuperscript{126} have been successfully used to predict the optical properties of prism-shaped AgNPs, where multiple plasmon peaks are predicted for prism-shaped nanoparticles. Jin et al.\textsuperscript{127} reported that a fourth SPRB (out-of-plane dipole) is convoluted within the SPR located between the in-plane quadruple and out-of-plane quadrupole. Additionally, they report that tip corner sharpness of the prism-shaped AgNP greatly affects the position of the in-plane SPR. Schatz et al.\textsuperscript{128} confirmed this observation by DDA modelling of various particle shapes and determined that the amount of red-shifting was roughly determined by the sharpness of the features on the particles.
1.8. Application of Silver nanoparticles as catalyst

The recent scientific advancement in nano science from the last decade, establishing a major research direction of our modern society. This results in miniaturization at the nano scale processes that currently use microsystems. In nano world, bottom-up approach should now replace the classic top-down one, a strategic move that is common to several areas of nano sciences including optoelectronics, sensing, medicine and catalysis. During last decade, chemists have made considerable achievements in application of nanoparticles as heterogeneous catalysis. Homogenous catalysis progressed after the second world war (hydroformylation) and especially since the early 1970s (hydrogenation). Heterogeneous catalysts have many advantages including easy removal of catalyst material after use, work well at high temperature but since long time it suffered due to lack of selectivity and understanding of the mechanistic of the reactions that are indispensable for parameter improvements. Green catalysis aspects now obviously require that environmentally friendly (for instance phosphine-free) catalysts be designed for easy removal from the reaction media and recycling many times with very high efficiency. These demanding conditions bring a new research impetus for catalyst development at the interface between homogeneous and heterogeneous catalysis, gathering the sophisticated fulfilment of all the constraints that were far from being fully taken into account by the pioneers and even the specialists in each catalytic discipline in the former decades. The use of transition-metal nanoparticles (NPs) in catalysis is crucial as they mimic metal surface activation and catalysis at the nanoscale and thereby bring selectivity and efficiency to heterogeneous catalysis. Transition-metal NPs are clusters containing from a few tens to several thousand metal atoms, stabilized by ligands, surfactants, polymers or dendrimers protecting their surfaces. Their sizes vary between the order of one nanometer to several tens or hundreds of nanometers, but the most
active in catalysis are only one or a few nanometers in diameter, i.e. they contain a few tens to a few hundred atoms only. The applicability of Ag NPs as catalysts \(^\text{130}\) depends in general on their size and stability. Smaller nanoparticles exhibit larger surface area for the same volume of material. That means larger active area of the catalyst. Among transition metal nanoparticle, catalysis of silver nanoparticles, has been of great interest in organic synthesis and has expanded rapidly in the past ten years because of nano silver catalysts' unique reactivity and selectivity, stability, as well as recyclability in catalytic reactions. Application of AgNps as an efficient catalyst \(^\text{131}\) requires a model reaction. The reaction must be appealing, reliable and should have a universal attraction so that the reaction can be studied with certainty using a simple experimental set up. At present, only one reaction stands out and has been qualified to study AgNp catalyzed reaction, that is an aqueous phase reduction reaction of 4-nitrophenol to 4-aminophenol, and has been tried in different laboratories. Aromatic nitro compounds are found to have toxic effect on various life forms. Among these, nitrophenols are regarded as one of the most widespread and versatile organic pollutant. These pollutants are chemically very stable and so traditional water treatment methods are usually ineffective in removing them from water. Therefore, developing an efficient method for their removal is of immense importance. Nanocatalysis is a fast developing area of research in which metal nanoparticles are used as catalysts for wide range chemical reactions. Several research groups have investigated the reduction of nitrophenols using a number of noble metal nanoparticles as catalyst. Nano Silver colloidal catalysis is influenced by many factors like shape, ligand capping, material of the nanoparticles and pH value. For example in colloidal nanoparticles the ligand capping affects strongly the catalytic capability as was found for many nanoparticles. The complex strong interaction between ligand, pH-value and nanoparticle (its size, shape, and surface morphology) covers the activity of silver nanoparticles.
in the reaction. So stabilization and dispersion of silver nanoparticles is essential for the better
catalytic activity.

The reduction conversion of 4-NP with sodium borohydride catalyzed by Ag nano
catalysts to 4-aminophenol is of industrial and environmental importance. Since then, this
reaction has been used as a benchmark reaction for the activity of nanoparticles. This reaction is
easily followed by UV-vis spectroscopy due to the fact that p-nitrophenol shows a distinctive
absorption peak at 400 nm in alkaline solution. The product, p-aminophenol, exhibits a weak
absorption peak at around 300 nm. In the UV-vis spectra of the reaction several isosbestic points
confirm that there are no side reactions and that only one product is formed. Without the catalyst
the reduction of p-nitrophenol does not proceed. From the vanishing intensity of the absorption
at 400 nm, the reaction rate can be calculated by a pseudo first order reaction, if an excess of
sodium borohydride is used. This rate constant can be further analyzed to gain the activation
energies of the reaction. Even though this reaction is often applied to verify and to compare the
activity of different metal nanoparticles, the reaction mechanism has never been analyzed in
detail. Zhang et al. suggested that the borohydride transfers a surface hydrogen species which
reacts with the p-nitrophenol to produce p-aminophenol, while Khalavka et al supposed that
“hydrogen” adsorbs onto the surface, which reacts with the p-nitrophenol from solution. But
neither of the authors provides any evidence for this suggestion. Thus a detailed mechanistic
study of this model reaction is essential for a full understanding of the catalysis.
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Chapter 2

Facile synthesis of silver nanoparticles using a novel benzene thiol derivative and cationic surfactant

2.1. Introduction

In the research field of nano materials, the recent exponential growth of “nano silver” or colloidal silver nanoparticles is due to their distinct optical, electrical, magnetic and fascinating catalytic properties.\(^1\)\(^-\)\(^3\) The plasmon resonance of silver nanoparticles (AgNps) are scientifically significant and has been an area of intriguing research. This is due to their potential application in different areas of next generation technologies.\(^4\)\(^-\)\(^6\) In particular, AgNps have been successfully used in many fields, such as catalysis, sensing, photovoltaics, nanophotonics, optoelectronics, biosensing and molecular diagnostics.\(^7\)\(^-\)\(^13\) Undoubtedly, advanced research applications will require silver nanoparticles of specific size, shape and surface modification surrounding the nanoparticle.\(^14\)\(^-\)\(^16\) This led to their simple, facile and high performance fabrication with manipulated morphology and size.\(^17\)\(^-\)\(^19\) Substantial research is underway to achieve monodispersity and stability of silver nanoparticles without perturbing the desired properties.\(^20\)\(^-\)\(^21\) The stabilization of AgNps against agglomeration is usually accomplished by surface passivation using different functional molecules bound to the surface of nanoparticles.\(^22\)\(^-\)\(^24\) The specific passivating functional molecules control the growth kinetics of nanoparticles and thus prevent them from aggregation.\(^25\)\(^-\)\(^26\) Various methodologies have been so far reported to reduce and stabilize Ag and Au nanoparticles by thiol (SH) functional groups.\(^27\)\(^-\)\(^29\) Interaction of thiol (SH) provide the beneficial organic surrounding and thus control the growth of nanoparticles and formed highly disperse narrow size nanoparticles.\(^30\)\(^-\)\(^32\) The choice of the organo sulfur functional...
group with chain length play an important role for the reduction and stabilization of nanoparticles depends on the intended application. 33 The metal-sulfur interaction is strong enough to immobilize the thio groups on the surface of metal nanoparticles. For example, the chemisorption energy between silver and sulfur is estimated at 126 kJ mol\(^{-1}\). 34 Alkane thiols are widely explored as reductive stabilizer of metal nanoparticles.\(^{35-37}\) However, much attention has not been paid to the formation of AgNps using short chain benzene thiol derivatives. Although, fundamentally aromatic thiols exhibited superior physical and chemical properties compared with saturated alkane systems. In aromatic thiols (SH) both sulfur and benzene moieties were involved to the surface adsorption, changing the R-group imparts different functionality to the particles that can be manipulated according to the intended applications. 38 In TBSH due to the presence of short methylene chains and symmetrical distances, electrons moves faster through delocalized system than saturated system and conjugated molecules are rigid compared with saturated flexible molecules. These unique properties of TBSH attributed to relative ease of ligands (SH) bounded with the nanoparticles surface within short span of time and with superior stability by compact and rigid network.

From this view point, we incorporated 1,3,5-triazine moiety with mercaptobenzoate as a thiophenol derivative (scheme 1 ). Triazine unit is a remarkable unit, able to interact with other organic moiety through coordination bond, hydrogen bonding, electrostatic charge transfer and aromatic staking with applications in host guest chemistry, catalysis, anion recognition, sensors, electronics and magnetism.\(^{39}\) Qin et al have synthesized AgNps decorated with 2,4,6-tris (2-pyridyl)-1,3,5-triazine nanobelts and their application for \(\text{H}_2\text{O}_2\) and glucose detection.\(^{40}\) Nasr-Esfhani have reported several triazine based dendimers in their research work and they used them to stabilize Cu (11) containing nano silicates triazine dendrimers.\(^{41}\) We synthesized (4,6-
dimethoxy-1,3,5-triazin-2-yl)-4-mercaptobenzoate (TBSH), in which the time span of synthesis decreases while maintaining the green chemistry parameters at the same time. In TBSH compound, the strong covalent binding with silver nanoparticles is easily formed with interactions of mercapto group. It is well known that colloidal silver nanoparticles may oxidized easily and undergo irreversible aggregation upon chemisorptions of organo thiol compounds. Aggregation process is easy to observe as the yellow color of silver colloid solutions turns to black after few hours, especially in case of AgNPs > 20 nm in diameter, aggregate after some time of addition.\textsuperscript{42-43} To increase the stabilization, aggregation of nanoparticles can be avoided by the addition of cationic or anionic surfactants, such as CTAC, CTAB and SDS.\textsuperscript{44-46} Surfactants properties have attracted growing attention for use in biological and chemical research applications. The surfactant coating on nanoparticles changes their aggregation behavior due to changed interparticle potential. Therefore, different types of surfactants, depending upon their molecular structures, may tune the interparticle interactions to different extent and hence have distinctive tendency to prevent the nanoparticles aggregation.\textsuperscript{47} The most interesting aspect of this present study is to investigate the unique functionality formed by the TBSH and cationic surfactant network as combine stabilizer capped the nanoparticles.

Choice of surfactant as an additional capping agent is also very crucial because it greatly influence the final shape and size of the nanoparticles. Number of authors attempted using a cationic surfactants, cetyltrimethylammonium bromide (CTAB) and cetyltrimethylammonium chloride (CTAC), as the stabilizer to produce spherical shape poly disperse AgNps.\textsuperscript{48-49} The influence of surfactant on nanoparticles either by strong absorption of stabilizer would occupy the nanoparticle growth site, thus reducing the growth rate of nanoparticles or a full coverage of stabilizer.
Adding a new dimensions in nano material chemistry, we developed the striking route to synthesize silver nanoparticles by using a new type of trainzine benzene thiol (4,6-dimethoxy-1,3,5-triazin-2-yl)-4-mercaptobenzoate (DMTMB) as reductive stabilizer in combination with cationic surfactant. Moreover, we compared the role of two surfactants, such as cetyltrimethylammonium chloride (CTAC) and cetyltrimethylammonium chloride (CTAB), having same hydrocarbon chain length but head groups containing different halide ions. CTAB with bulkier head group, having bromide as a counter ion, the micelles are much bigger in size as compared to their counterpart CTAC micelles. The fact that ionic radius of bare Br⁻ is 0.195nm compare to radius thickness of bare Cl⁻ ion is 0.18 nm, this suggests that most of the condensed Br⁻ ions resides in a monolayer of counter ions around the micelle. This shows that compared to Cl⁻ ions, Br⁻ tend to stay closer to the micelle. Br⁻ ions have less affinity to water. Thus, one expects that Br⁻ ions in CTAB micellar solution will be less dispersed in water as compared to Cl⁻ ions in CTAC solution. These properties of two surfactants would be helpful in developing new insight about size controlling capabilities of the surfactant. Based on the present results, we propose the molecular structure and stability of silver nanoparticle (AgNps).
2.2. Experimental

2.2.1. Materials

All starting materials of analytical grade were commercially available from Wako Pure Chemical Industries, Ltd., Sigma Aldrich Co. and Nakarai Tesque and were used without further purification. All atmosphere-sensitive reactions were performed under nitrogen gas. Double distilled water was used throughout the experiments. $^1$HNMR spectra were recorded on a JEOL GSX-400 spectrophotometer. Absorption and FTIR spectra were recorded on a Hitachi U-2900 spectrophotometer and a Perkin Elmer Multiscope FTIR spectrophotometer, respectively. Hg lamp used was UVL-400HA, RIKO medium pressure lamp. X-ray photoelectron spectroscopy (XPS) was obtained on an ESCA-1000 Shimadzu electron spectrometer. The incident radiation was the MgK X-ray line (1253.6 eV) with a source power of 180W (15 kV, 12mA). The analysis chamber was maintained at a steady base pressure of $<6 \times 10^{-9}$ Torr during samole analysis. Survey scans were carried out at an analyzer pass energy of 32.5 eV with 1.0 Ev steps and a dwell time of 300 ms. The Binding energy (BE) scale was calibrated using the C1 s peak with a BE set at 285.0 eV as reference for all XPS peak positions to compensate for energy shifts due to the spectrometer work functions. Samples were prepared as a film on silicon playe which had been thoroughly cleaned using ethanol, rinsed with Milli-Q water dried with nitrogen. Transmission electron microscopic (TEM) images were recorded on a JEOL JEM-3010 VII operating at 300 kV. A drop of dilute solution containing a suspension of the as prepared silver nano particle was placed on a copper grid with a carbon foil and the solvent evaporated under reduced pressure at room temperature in an incubator for a week. Approximately 200 particles were counted and then size distribution of AgNps was determined.
2.2.2 Synthesis of \((4,6\text{-dimethoxy-1,3,5-triazin-2-yl})\)4-mercaptobenzoate (TBSH).

4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (304 mg, 1.1 mmol) was added to a 10 mL MeOH solution of 4-mercaptobenzoic acid (154 mg, 1.0 mmol) (10mL) at 20°C. The mixture was stirred to give (4,6-dimethoxy-1,3,5-triazin-2-yl)-4-mercaptobenzoate (1) as a white precipitate within 30 minutes (Scheme1). The mixture was filtered and then the precipitate was dried in vacuo to obtain in excellent yield (>95%). mp 235-238.\(^1\)H NMR (400MHz, DMSO-\(d_6\)): \(\delta=3.83\) (s, 6H, OCH\(_3\)), 7.74 (d, 2H, \(J=8.0\)Hz, ArH), 7.99 (d, 2H, \(J=8.0\)Hz, ArH).\(^{13}\)C NMR(100MHz, DMSO-\(d_6\)): \(\delta=55.2\)(OCH\(_3\)), 129.8, 131.7, 132.4, 134.9 (ArC), 166.7(C=O), 17.08, 182.7 (Triazin-C). MS: \(m/z\) 292 (M\(^+\)-H), HRMS (EI): Calculated for \(C_{12}H_{10}N_3O_4S\) (M\(^+\)-H) 292.0392, found 292.0391.

2.2.3. Synthesis of TBSH surfactant stabilized AgNps.

The AgNps solution was prepared by the following procedure. 10 ml of aqueous CTAB solution (1.3mM), adjusted to pH 10 by using Na\(_2\)CO\(_3\) (50mM) under stirring. To this solution AgNO\(_3\) (50m M, 80 µL) was added. After that TBSH (2.5mM, 50 µL in THF) was added. Then the solutions were irradiated by Hg-lamp for 6-7 hours. The color of the sample solution changed from transparent to blackish yellow.

10 ml of various concentrations of CTAC (0.3 ~ 2.0mM),adjusted to pH 10 by using Na\(_2\)CO\(_3\)(50mM) under stirring and then AgNO\(_3\) solution (50m M, 80 µL) was added to each sample solution. After that TBSH (2.5mM, 50 µL in THF) was added. Then the solutions were irradiated by Hg-lamp for 4-5 minutes. The color of the solution changed from transparent to yellow.
2.3. Results and Discussion

Figure. 1(A), shows the UV-vis absorption spectra of TBSH-Ag-Surfactants systems after UV irradiation. The formation of AgNps attributed to the reducing capacity of the terminal thiol groups of TBSH under UV irradiation. We investigated the role of two cationic surfactants systems, cetyltrimethylammonium bromide (CTAB) and cetyltrimethylammonium chloride (CTAC), having the same hydrocarbon chain length of C18 but different head groups due to the presence of different counter ions (CTAB-Br⁻ and CTAC Cl⁻ counter ions). The spectra shows a maximum absorbance at 419 and 430 nm for CTAC and CTAB, respectively, characteristic of silver surface plasmon resonance (SPR). Both CTAB and CTAC have different cmc values in the same system, so for uniform comparison, above cmc concentration[1.3mM] were used at alkaline pH 10. The pH of the reaction medium plays a key role. After doing several trials it was found that acidic pH suppresses the silver nanoparticles formation due to over nucleation and within short span of time resulted in fast agglomeration and large size of nanoparticles. Whereas, at alkaline pH i.e. 9 or 10 the nucleation process is moderate and resulted in smaller size of silver nanoparticles with higher stability. When CTAB was used as a capping agent, the reaction mixture turned from transparent to turbid with the addition of AgNO₃ and TBSH. After 6~7 hours of UV irradiation the turbid sol color changed to blackish yellow and no clear SPR band were found (Figure. 1A ). This change could be ascribed to the formation of large quantity of silver bromide (AgBr) from AgNO₃ (Ag⁺) and CTAB (Br⁻). In this system, CTAB did not work well as a capping agent, due to the formation of large quantity of water insoluble AgBr precipitates, hindered the reduction of Ag⁺ ions to Ag⁰ by TBSH. This is supported by the fact that the solubility of AgBr in CTAB (described by the constant of solubility equilibrium, Ksp=7.7x10⁻¹³) is much lower than that of AgCl (Ksp=1.56x10⁻¹⁰) in CTAC at 25°C. In case of
CTAC, the reaction mixture after addition of AgNO$_3$ and TBSH were transparent before UV irradiation after irradiation of 4~5 minutes turned to yellow with no turbidity (Figure. 1B).

CTAC counter chloride ions, due to small size and low polarizibility always solvated by water molecules and more disperse, hence TBSH easily reduced Ag$^+$ ions to zero valent Ag$^0$. The absorption spectra were followed as a function of time after UV irradiation (Figure. 1B).

Scheme 1. Synthesis of (4,6-diethoxy-1,3,5-triazin-2-yl)-4-mercaptopbenzoate (TBSH).
Figure 1. (A) UV-visible absorption spectra of TBSH-AgNps-Surfactant systems. (a) CTAC and (b) CTAB. [Surfactant = 1.3mM] (B) Plots of absorbance of TBSH-AgNps-surfactant systems against reaction time of 11 hours.
The role of CTAC as an additional stabilizer in TBSH-AgNps-CTAC system were further studied, at three different concentrations below cmc, at cmc and above cmc, while keeping the TBSH and AgNO₃ concentrations and other parameters same as mentioned in the experimental section 2.3. Figure 2(A), shows the UV-visible absorption spectra of TBSH-Ag-CTAC systems below cmc [0.3 mM], at cmc [0.6 mM], and above cmc [2.0 mM] of CTAC. After the UV irradiation of 4~5 minutes the reaction mixture exhibited yellow color due to excitation of surface plasmon resonance band in the visible absorption region. The spectra shows an initial peak at about 255 nm (Ag⁺) for all samples. As the time increases the peak of Ag⁺, centered at 255 nm decreases with a corresponding increase in intensity of zero valent silver (Ag⁰) with peaks of 407, 410 and 418 nm for below cmc [0.3], at cmc [0.6] and above cmc [2.0] at pH 10. The sharp absorption peak in this region corresponds to the signature peaks of AgNps. UV visible absorption spectra explain the factor of time-dependent formation of silver nanoparticles. As the time duration increased, the nanoparticles formation and in turn intensity also increased (Figure 2B). After 11 hours, the maximum wavelength (λ max) stabilized indicating that all the Ag⁺ ions in solution has been reduced to Ag⁰, representing the completion of AgNps formation process. This behavior was the same for all the samples.

Figure 3, summarizes λ max TBSH-AgNps-CTAC systems against various CTAC concentration below cmc [0.3, 0.5 mM], at cmc [0.6 mM] and above cmc [1-2 mM]. The red shift of λ max with increase in concentration of CTAC i.e. above cmc, indicated the formation of a large size of silver nanoparticles (AgNps) because above cmc of CTAC, there were increased aggregation of micelles due to increase in number of as formed micelle.
Figure 2. (A) Absorption spectra of TBSH-AgNps-CTAC. [CTAC] above cmc (a), at cmc (b) and below cmc (c). (B) Plots of absorbance of TBSH-AgNps-CTAC systems against reaction time. [CTAC] below cmc (○), at cmc (●) and above cmc (●).
Figure 3. TBSH-AgNps-CTAC systems maximum absorbance wavelength ($\lambda_{\text{max}}$) against [CTAC].

The growth of TBSH-CTAC stabilized AgNps was further confirmed by TEM (Figure 4). The nanoparticles size and shape evaluation was obtained by processing TEM micrographs of different samples of TBSH-CTAC-AgNps. The TEM correlated with time dependent spectroscopic observations, confirmed the presence of AgNps in all tested solutions. TEM images of colloidal solution of silver nanoparticles exhibiting spherical shapes and polydisperse in nature. The average particle sizes of below cmc [0.5mM], at cmc [6.0 mM] and above cmc [2.0 mM] of CTAC were as follows, 25.6 ± 6, 26.3 ±5 nm  32.1± 6 nm respectively, (Figure 4 A,C,D). The histogram was obtained by measuring the size of about 200 AgNps and their diameter is given in (Figure 4 B,D, E). Figure 5, shown the average nanoparticle size against various CTAC concentrations. The average size of the AgNps ranged from 25 to 35 nm and wider size distribution from 10-58 nm were measured.
Figure 4. TEM images and histogram of TBSH-AgNps-CTAC systems. Histogram of corresponding particle size distribution of [CTAC]= below cmc (A), at cmc (C) and above cmc (E).
Figure 5. TBSH-AgNps-CTAC system average nanoparticle size and distribution against [CTAC].

FTIR spectroscopy was used to probe the conformational changes and lateral chain-chain interaction of stabilizers with AgNps surface. The formation of new bands and shift in existing bands confirms the presence of binding of thiols to the silver nanoparticles and adsorption of CTAC alkyl chains on the AgNp surface. The FTIR spectra recorded in the spectral region of 3200–600 cm$^{-1}$ (Figure 6) and their frequency assignment are given in Table 1. The spectra of the TBSH-AgNps-CTAC systems below, at and above cmc colloidal solutions are almost similar to one another, however, a slight difference in their peaks intensities were found, indicating that the organic molecules have indeed become a part of the silver nanoparticles.

In pure TBSH the presence of SH stretching mode at 2549 cm$^{-1}$ is absent in TBSH-AgNps-CTAC systems. (Table 1). This suggests that SH bond is broken upon binding to the AgNps surface. In addition, triazine ring (>C=N-) and carbonyl C=O stretching vibrations in TBSH is observed at 1541 cm$^{-1}$ and 1683 cm$^{-1}$ and its corresponding TBSH-AgNps-CTAC systems these signals shifted to 1559 cm$^{-1}$ and 1742 cm$^{-1}$ respectively (Table 1). The resonance at 2918 and 2850 cm$^{-1}$ in TBSH and CTAC spectrum corresponds to the characteristic C-H asymmetric and
symmetric stretching modes of methylene groups in TBSH and alkyl chain of CTAC. Figure 6d, clearly shown that these intensities shifted to higher frequencies for below cmc [0.3 mM] and (Figure 6a) lower frequencies at cmc [0.6 mM] and (Figure b,c) above cmc [1.6-2.0 mM] concentrations of CTAC in TBSH-AgNps-CTAC systems also mentioned in Table 1. These peaks of 1487, 1464,961 and 728 cm\(^{-1}\) are assigned asymmetric, symmetric, stretching and rocking mode of head group of CTAC (CH\(_3\)-N\(^+\)) respectively. These peaks are all the same as those of CTAC itself, therefore alkyl chains of CTAC are adsorbed on the surface of AgNps and head groups point outward in the reaction mixture.

It has been well known that the symmetric \(\nu_{as}(\text{CH}_2)\) and asymmetric \(\nu_{s}(\text{CH}_2)\) vibrations are sensitive to the gauche/ trans conformer ratio of CTAC on AgNps. Figure 7 shows the [CTAC] dependence of both vibrational bands of CH\(_2\) stretching symmetric and symmetric vibrations and provide information about the degree of characteristic conformational order to disorder or gauche to trans conformers ratio in the methylene chain structure in TBSH-AgNps-CTAC systems. It is known that conformational ordered state (trans) is characterized by a asymmetric and symmetric CH\(_2\) stretching mode frequency below 2919 and 2850 cm\(^{-1}\), while the conformational disorder (gauche) results in a rising of these frequencies by several wave numbers. The observed \(\nu_{as}(\text{CH}_2)\) stretching vibration modes below cmc is (2921-2926) cm\(^{-1}\) and for \(\nu_{s}(\text{CH}_2)\) at (2851-2856) cm\(^{-1}\) suggesting a higher population of gauche conformers and poor chain packing around AgNps. These frequencies shifted to lower frequency for \(\nu_{as}(\text{CH}_2)\) at cmc and above cmc (2920-2916) cm\(^{-1}\) and \(\nu_{s}(\text{CH}_2)\) at (2850-2849) cm\(^{-1}\), confirming the presence of all trans conformers and ordered alkyl chain packing around AgNps.
### Table 1. Assignment of vibrational bands in FTIR spectra for TBSH, CTAC and TBSH-AgNps-CTAC systems.

<table>
<thead>
<tr>
<th>Assignment of vibrational modes</th>
<th>TBSH cm(^{-1})</th>
<th>CTAC cm(^{-1})</th>
<th>TBSH-AgNps-CTAC cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu) s (CH(_2)) stretching</td>
<td>2918</td>
<td>2918</td>
<td>2926</td>
</tr>
<tr>
<td>(\nu) s (CH(_3)) stretching</td>
<td>2850</td>
<td>2850</td>
<td>2856</td>
</tr>
<tr>
<td>(\nu) s (S-H) stretching</td>
<td>2549</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\nu) (C=O) stretching</td>
<td>1683</td>
<td></td>
<td>1741</td>
</tr>
<tr>
<td>(\nu) (CHN) stretching</td>
<td>1541</td>
<td>1559</td>
<td>1560</td>
</tr>
<tr>
<td>(\nu) s (N(^{+})-CH(_3)) headgroup methylene</td>
<td>1487</td>
<td></td>
<td>1487</td>
</tr>
<tr>
<td>(\nu) s (N(^{+})-CH(_3)) headgroup methylene</td>
<td>1464</td>
<td></td>
<td>1464</td>
</tr>
<tr>
<td>(\nu) (C-O)</td>
<td>1353</td>
<td>1367</td>
<td>1351</td>
</tr>
<tr>
<td>(\nu) (C-N(^{+})) stretching</td>
<td>961</td>
<td>964</td>
<td>961</td>
</tr>
<tr>
<td>(\delta) (CH(_2)) rocking</td>
<td>728</td>
<td>728</td>
<td>727</td>
</tr>
</tbody>
</table>

**Figure 6.** FTIR spectra of TBSH-AgNps-CTAC systems. [CTAC] at cmc [0.6 mM] (a), above cmc [1.6, 2.0 mM] (b,c) and below cmc [0.3 mM] (d).
Figure 7. FTIR frequencies (cm$^{-1}$) of C-H asymmetric (A) and C-H symmetric (B) TBSH-AgNps-CTAC systems. [CTAC] = below cmc, at cmc and above cmc.

XPS spectroscopy was used to further probe the chemical bonding between the sulfur atom of TBSH and AgNps surface. (Figure 8), the XPS spectrum in Ag (3d) region of TBSH –
CTAC-Ag shows two peaks; these are connected to spin–orbit coupled energy states J=5/2 and 3/2. The Ag 3d$_{5/2}$ and Ag 3d$_{3/2}$ appeared at 367.8 and 373.8 eV, respectively, confirms the presence of zero valent silver (Ag$^0$). The XPS spectrum in S(2P) region showed one peak at S2p$_{3/2}$ 162.1 eV. However the signals for S of TBSH-CTAC-AgNps were weaker due to the small scattering cross-section of the S and the lower amount of material present. These results are in agreement with the results published for short chain aromatic thiols assembled on silver nanoparticles.

Figure 8. XPS spectra of TBSH-AgNps-CTAC systems at Ag 3d$_{3/2}$ and Ag 3d$_{5/2}$.

The FTIR, TEM and XPS analysis indicated the formation process of AgNps with TBSH and CTAC. Finally we can propose (Figure 9) a possible mechanism and structure of the TBSH-
CTAC-AgNps system. Because of the strong affinity of thiols with the Ag nanoparticles. It immediately formed a strong covalent bond with Ag. The structural integrity of the TBSH and CTAC capped the AgNps maintained. CTAC alkyl chains at cmc and above cmc of CTAC is not significantly perturbed because of the formation of micelles so enhanced trans conformers are present and fairly good chain packing around AgNps surface and present as “solid state”, but below cmc of CTAC there is less extension in the frequencies of long hydrocarbon tail. CTAC below cmc is present as an electrolyte and as ‘liquid state’.

Figure 9. Schematic representation of TBSH-CTAC stabilized silver nanoparticles.
2.4. Conclusion

We have developed a simple and novel synthetic method of AgNps by using TBSH thiol derivative. TBSH is remarkable powerful reductant for Ag$^+$ ions at alkaline pH. In this system, the shape and size distribution of Ag-nanoparticles strongly depend on the reduction potential of the reductant and pH of the reaction media. CTAC as an additional capping agent enhance stabilization of AgNps.
2.5. Reference


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Assembled Monolayers of Mixed Thiols on Surfaces Coated with Silver Nanoparticles.  


Chapter 3

**Novel synthesis of silver nanoparticles by using new short chain triazine disulfide derivative as stabilizer with potential application in catalysis**

### 3.1. Introduction

In the domain of colloidal nano chemistry, during the last three decades, the most prominent developments are the organo sulfur compounds such as disulfide and thiol functionalized nanoparticles.\(^1\)\(^-\)\(^3\) The organo thiol capped nanoparticles have been implied in a wide range of application including optoelectronics, biosensors, catalysis, surface enhanced Raman scattering, photovoltaics.\(^4\)\(^-\)\(^8\) The chemical nature and morphology of the organo thiol molecules shell dictate a large fraction of the particles properties. Thus it is important to investigate how organo thiol molecules capped the core of nanoparticles and prevent them from agglomeration and passivating the surface electronic properties.\(^9\)\(^-\)\(^10\)

The thiol (RSH) is unique organo sulfur group due to its multifaceted chemical and physical properties, it can be emphasized here as changing the R-group of (RSH), imparts different functionality to the nanoparticles and thus the chemical behavior of the nano particles can be manipulated according to the intended applications.\(^11\) It would be quite interesting to elucidate the role of hydrocarbon chain present in thiols with respect to their effect on the growth and stability of the nanoparticles.\(^12\) Literature is replete with the several successful reports of synthesis of thiol- stabilized silver nanoparticles (AgNps). Silver nanoparticles (AgNps) provide a new frontier for technological innovation.\(^13\)\(^-\)\(^16\) The myriad applications of silver in electronics offer an mind-boggling view into how one of the most famous metals in history has become a fore front material of the future.\(^17\)\(^-\)\(^18\) Due in part to its unique property of having the highest
thermal and electrical conductivity of all metals, silver compare to other metals, less expensive materials.\textsuperscript{19-20} As the size of the silver particles decreases down to the nanometer scale, they exhibit many unique optical, electronic, and chemical properties that cannot be observed in the bulk.\textsuperscript{21-23} Hence, silver nanoparticles (AgNps) serve as a material in the development of new generation electronic, optical and sensor devices including, photovoltaics, photonics, molecular diagnostics, optoelectronics, catalysis, sensing, surface enhanced ramen scattering and in plasmonic applications.\textsuperscript{24-34} Although an impressive amount of research work has been done for the preparation of silver nanostructures. Among these methods, chemical reduction of metal ions in a solution is still the most common preparative route.\textsuperscript{35-37} However, unprotected metal colloids are susceptible to irreversible aggregation in solution due to their small size. To solve this problem, some surface passivating layer is required to insulate the core and stabilize the nanoparticles.\textsuperscript{38-39} In recent years, aromatic thiols capped silver nanoparticles (AgNps) have come to receive attention because of their high conductivity and strong structural rigidity compared to conventional alkane thiol making them interesting for molecular electronics, molecular wires and electron transfer promotors for electro analytical sensors etc.\textsuperscript{40} It has been known that the electronic properties of capping agent strongly depend on molecular orientations, adsorption conditions and intermolecular interactions. Therefore, the control of the structural ordering of aromatic thiols capping has become a crucial issues in tailoring various capping/stabilizing properties. Aromatic compounds are of special interest in molecular transport. Their smallest highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) gap and functionalization capability make them attractive for potential molecular electronics application. It is known that, electrons move faster through shorter distances than longer distances, that electrons move faster through delocalized systems than saturated systems,
and that conjugated molecules are rigid while saturated molecules are flexible. In case of short chain aromatic thiols, other interactions, e.g., between the benzene ring and surface, between functional groups, and the intermolecular π-π interactions, can drive the strong packing structure around the core of nanoparticles. Organosulfur groups including thiols and disulfide, strongly coordinate with silver nanoparticles (AgNps). Sulfur possesses a huge affinity for metal surfaces, and organo sulfur compounds thus will chemisorbed or adsorb spontaneously. The metal- sulfur interaction is strong enough to immobilize the thiol groups on the surface of metal nanoparticles. For example, the chemisorption energy between silver and sulfur is estimated at 217 kJ mol\(^{-1}\). Thiols can interact with (AgNps) in two different ways. The first possibility is the chemisorption of the intact RSH molecule on the surface. The second possibility is the chemisorption of thiols or disulfides on metal surfaces which generates SR groups. The disulfide bond is a very valuable functional group in a variety of chemical and biological agents that display effective reactivity or biological activities. Disulfide-based functionalization for biological applications has been widely used in the development of chemosensors, prodrugs, nanomaterial carriers and etc. In deliberation of this view point, we synthesized novel short chain diphenyl triazine disulfide (bis(4,6-dephenyl-1,3,5-triazine-2-aminoethyl)) disulfide 2 (TPhSS). s-Triazine derivatives have proven their great potential in this rising area of material chemistry, both for their π-interaction abilities, and for their aptitude to be involved in intricate H-bond networks. Triazine is thermally stable unless heated to above 600 °C where it decomposes. It is a unique moiety, and many of its derivatives are used as as pharmaceutical products, herbicides or building blocks in the field of supra molecular and coordination chemistry. Presence of triazine unit in the short chain of TPhSS gives extra strength to the methylene chain of TPhSS and stability to S-Ag bond. In this present report, we opted a striking
route and developed a novel, easy and cost effective procedure to prepare silver nanoparticles. TPhSS stabilization gives unique functionality to AgNps with longer stability. The as prepared silver nanoparticles (AgNps-TPhSS) are also effective as heterogeneous catalyst system for the reduction of 4-nitrophenol to 4-amino-phenol. 46-50

3.2. Experimental

3.2.1. Materials

All starting materials of analytical grade were commercially available from Wako Pure Chemical Industries, Ltd., Sigma Aldrich Co. and Nakarai Tesque and were used without further purification. All atmosphere-sensitive reactions were performed under nitrogen gas. Double distilled water was used throughout the experiments. ¹HNMR spectra were recorded on a JEOL GSX-400 spectrophotometer. Absorption and FTIR spectra were recorded on a Hitachi U-2900 spectrophotometer and a Perkin Elmer Multiscope FTIR spectrophotometer, respectively. X-ray photoelectron spectroscopy (XPS) was obtained on an ESCA-1000 Shimadzu electron spectrometer. Transmission electron microscopic (TEM) images were recorded on a JEOL JEM-3010 VII operating at 300 kV. A drop of dilute solution containing a suspension of the as prepared silver nano particle was placed on a copper grid with a carbon foil and the solvent evaporated under reduced pressure at room temperature in an incubator for a week. Approximately 200 particles were counted and then size distribution of AgNps was determined.
3.2.2. Synthesis of bis(4,6-dephenyl-1,3,5-triazine-2-aminoethyl) disulfide \(2\) (TPhSS).

To a dry THF solution (5.0 mL) of cystamine dihydrochloride (225 mg, 1.0 mmol) was added TEA (606 mg, 6.0 mg) and a dry MeOH solution (5.0 mL) of 2-Chloro-4,6-diphenyl-1,3,5-triazine (CDPT) (535 mg, 2.0 mmol). The mixture was stirred at room temperature for 7 hours. The solvent was removed in vacuo, and then the residue was extracted with ethyl acetate (30 mL) and \(\text{H}_2\text{O}\) (30 mL), and the organic layer was dried over MgSO\(_4\). The solvent was removed in vacuo to give compound \(1\) (33% yield) as a light yellow solid. \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.51-8.60 (m, Ar-H, 8H), 7.46-7.53 (m, Ar-H, 12H), 5.94 (s, 2H, NH), 3.97 (q, \(J=6.4\) Hz, 4H), 3.05 (t, \(J=6.6\) Hz, 4H). MS: FAB\(^+\): Calcd for \(\text{C}_{34}\text{H}_{31}\text{N}_8\text{S}_2\) (\(\text{M}^+\)+H) 615.2113, found 615.2102

3.2.3. Synthesis of TPhSS stabilized AgNps.

The AgNps solution was prepared by the following procedure. In 40 ml of water under vigorous stirring, various concentration of TPhSS (0.2-0.8 mM, 20 \(\mu\)L in THF) and NaBH\(_4\) (10 mM, 500 \(\mu\)L aqueous) were slowly added respectively. To these reaction mixtures, AgNO\(_3\) (200 mM, 10 \(\mu\)L) were added. Stop stirring, the color of the sample solution changed from transparent to yellow.

In a typical experiment, the AgNps solution was prepared by the following procedure. Under vigorous stirring, TPhSS (0.425mM, 20 \(\mu\)L in THF) and NaBH\(_4\)(10 mM, 500 \(\mu\)L aqueous ) were added in 40 ml of water in three individual vials. To these reaction mixtures varying concentration of AgNO\(_3\) (200,400 and 600 mM, 10 \(\mu\)L) were added. Stop stirring, the color of the sample solution changed from transparent to yellow.
3.3. Results and Discussion

Figure 1 (A), shows the UV-vis absorption spectra of TPhSS stabilized AgNps. The formation of AgNps attributed to the reducing capacity of the terminal thiol group after the dissociation of disulfide bond in short chain di phenyl triazine disulfide bis(4,6-dephenyl-1,3,5-triazine-2-aminoethyl) disulfide 2(TPhSS). In TPhSS, the disulfide undergoes S-S bond cleavage and formed a thiolate bond (TPhSH) at the AgNps surfaces. In this system, we used sodium borohydride (NaBH₄) to dissociate a disulfide bond and formed a thiolate bond as well as to reduced Ag⁺ into Ag⁰. UV-vis absorption spectra of TPhSH-AgNps systems Figure 1(A), at various concentration (0.2-0.8 mM) of [TPhSS], while keeping the AgNO₃ and NaBH₄ concentration same as reported in the experimental section. The UV-visible absorption spectra Figure 1(A), shown a peak for all four samples at 396, 395, 393, and 391 nm for 0.2, 0.4, 0.6, and 0.8 mM [TPhSH] –AgNps system respectively, corresponding to the characteristic wavelength of AgNps surface plasmon resonance (SPR) band. The reaction mixture exhibited yellow color due to excitation of surface plasmon resonance band in the visible absorption region. The absorption spectra were followed as a function of time as shown in Figure 1(B), as the time increases the SPR peak of Ag⁰ in between (391-396) increases and becomes stabilized after 12 hours indicating the complete reduction of Ag⁺ ions into Ag⁰. This behavior is the same for all the four samples. The terminal thiol group of TPhSH stabilized AgNps very well. The blue shift of λ max with increase in concentration of [TPhSS] indicated the formation of chemisorbed thiol group TPhSH, compact and strong network around AgNps. The blue shifted narrow SPR band indicating the formation of small, mono disperse and spherical shape AgNps. The homogeneous distribution of prepared nanoparticles with the increase of concentration of [TPhSS] was also found in TEM images.
Scheme 1. Synthesis of (bis(4,6-depheny1-1,3,5-triazine-2-aminoethyl)) disulfide \( \overset{\Delta}{\rightarrow} \) (TPhSS)
Figure 1. (A) UV-visible absorption spectra of [TPhSH]-AgNps systems. (B) Plots of absorbance [TPhSS]-AgNps systems against reaction time of 12 hours. [TPhSS]= 0.825, 0.625, 0.425, and 0.225 mM.

Figure 2 (A), shows the UV-vis absorption spectra, at varying concentration (200-600 mM) of AgNO$_3$ while keeping the TPhSS (0.4 mM) and NaBH$_4$ concentration same in the reaction systems as mentioned in the experiment section. The reaction mixture exhibited yellow color due to excitation of surface plasmon resonance band in the visible absorption region. The UV-visible absorption spectra shown a peak for all three samples at 395 nm for 200, 400 and 600 mM of [AgNO$_3$] in TPhSH-AgNps systems respectively, corresponding to the characteristic wavelength of silver surface plasmon resonance (SPR) band. The absorption spectra were followed as a function of time as shown in Figure 2 (B). As time increases the SPR peak of Ag$^0$ increases and becomes stabilized after 12 hours. This behavior was the same for all the three samples.
Figure 2. (A) UV-visible absorption spectra of TPhSH-[AgNps] systems. (B) Plots of absorbance of [AgNps]-TPhSS systems against reaction time of 12 hours. [AgNps] of ■ 600, ▲ 400, ● 200 mM.
The growth of TPhSH-stabilized AgNps was further confirmed by TEM images (Figure 3). The nanoparticles size and shape evaluation was obtained by processing TEM micrographs of different samples of TPhSH-AgNps systems. The TEM correlated with time dependent spectroscopic observations, confirmed the presence of AgNps in all tested solutions. TEM images of colloidal solution of AgNPs-TPhSH systems exhibiting spherical shape and mono disperse in nature. The average particle sizes (Figure 3 A,C,E,G) of 0.2, 0.4, 0.6, and 0.8 mM [TPhSH]-AgNps system was found to be 14±4, 13±4, 10±4 and 7±2 nm respectively. These results indicate a decrease in AgNps size by increasing the concentration of the TPhSS. Our results are in total agreement by the results obtained by other researchers. The histogram was obtained by measuring the size of about 200 AgNps and their diameter is given in (Figure 3 B,D, F,H). The average size of the AgNps ranged from 7 to 14 nm and wider size distribution from 5-25 nm were measured.
Figure 3. TEM images and histogram of TPhSH-AgNps systems. [TPhSH] = 0.2 (A), 0.4 (C), 0.6 (E), and 0.8 (G) mM. Histogram of corresponding AgNps size distribution of [TPhSH] 0.2 (B), 0.4 (D), 0.6 (F), and 0.8 (H) mM.

XPS spectroscopy was used to further investigate the chemical bonding between the sulfur atom of TPhSH and AgNps surface. Photoelectrons, originating in the 3d$_{3/2}$, 3d$_{3/2}$, S2p$_{3/2}$ and S2p$_{1/2}$ orbitals were examined. The pure (bis(4,6-dephenyl-1,3,5-triazine-2-aminoethyl)) disulfide compound shown the doublet in the S2p region of disulfide peak with spin – orbit
coupled energy states J=3/2 and 1/2 connected to S2p_{3/2} and S2p_{1/2} of 161.3 and 162.6 eV respectively. The XPS (Figure 4) spectrum in Ag (3d) region of short chain TPhSH-AgNps shows two peaks these are connected to spin – orbit coupled energy states J=5/2 and 3/2. The Ag3d_{3/2} and Ag3d_{5/2} appeared at 374.1 and 368.1 eV, respectively, confirms the presence of zero valent silver (Ag^0). The XPS spectrum in S(2p) region showed a singlet peak of thiol at S2p_{3/2} 162.1 eV. No sulphur peaks above 166 eV were observed, indicating that no oxidized sulfur is present at the surface.

Figure 4. XPS spectra of TPhSH-AgNp systems at Ag 3d_{5/2}, and Ag3d_{3/2}.
To further confirm that TPhSH chemisorbed with AgNps, FTIR characterization performed on each of the samples. The spectrum not only supports the presence of thiol- AgNps but also reveals the nature of the interactions of the molecules of short chain diphenyl triazine thiol (TPhSH) with AgNps. The spectra of the TPhSH-AgNps systems colloidal solutions are almost similar to one another, however, a slight difference in their peaks intensities were found, indicating that the organic molecules have indeed become a part of the AgNps. In pure TPhSS the presence (Figure.5 a) of S-S stretching mode at 572 cm\(^{-1}\) is absent in TPhSH-NaBH\(_4\) (Figure.5 b) and TPhSH-AgNps (Figure.5 c) systems.

The presence of thiol stretching mode at 2322 cm\(^{-1}\) in TPhSH-NaBH\(_4\) (Figure.5 b) is absent in TPhSH-AgNps (Figure.5 c) systems suggest that the S-H bond is broken upon binding to the AgNps surface, this conforming the formation of TPhSH capped AgNps. In addition, in pure TPhSS, the N–H symmetric stretching vibration frequency at 3276 cm\(^{-1}\), asymmetric \(\nu_{as}(\text{CH}_2)\) and symmetric \(\nu_{s}(\text{CH}_2)\) vibrations at 2956 and 2871 cm\(^{-1}\) of methylene group and triazine ring (\(>\text{C} =\text{N}-\)) in TPhSS confirms the strong band near 1591,1561 and 1537 cm\(^{-1}\) corresponding to the in-plane vibrations involving the ring(Figure.5 a). In TPhSH-AgNps system these bands are shifted to higher frequency in case of asymmetric \(\nu_{as}(\text{CH}_2)\) and symmetric \(\nu_{as}(\text{CH}_2)\) vibrations at 2917 and 2850 cm\(^{-1}\) of methylene group and triazine ring (\(>\text{C} =\text{N}-\)) vibrational mode shifted to to higher frequency 1599 cm\(^{-1}\) (Figure.5 c).
Figure 5. FTIR spectra of (a) pure TPhSS (b) TPhSH-NaBH$_4$ (c) TPhSH-AgNps.
3.4. Conclusion

In summary, a facile, scalable and environmentally friendly route has been developed for the fabrication of AgNps by using new short chain aromatic thiol molecule TPhSH. TPhSH proved to be a remarkable powerful stabilizer for AgNps under an ambient temperature. In cooperating the di phenyl ring with traizine gives strength to the back bone chain of TPhSH, which in turn give higher stability and disperse AgNps. TPhSH is powerful stabilizer for AgNPs. In this system, the shape and size distribution of Ag-nanoparticles strongly depend on the reduction potential of the reductant NaBH₄ and stabilizer TPhSH. The time span of synthesis is very short and its very cost effective and can be easily scale up with possible applications in catalysis gas sensors and photovoltaics.
3.5. Reference


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Facile synthesis of silver nanoparticles by using novel short chain triazine diphenyl disulfide derivative as reductive stabilizer

4.1. Introduction

Silver nanoparticles (AgNps) having fine or ultrafine sizes have attracted great scientific interest because of their unique optical, electrical, thermal, and mechanical properties. Silver nanoparticles (AgNps) due to their quantum size and surface effects reveal highest electrical and thermal conductivity among all metals and strong surface plasmon resonance which largely dependent on their size and shape. The surface plasmon resonance (SPR) properties of silver nanoparticles are of particular importance for application related to biolabeling, surface enhance Raman scattering (SERS), surface enhanced fluorescence (SEF), sensing and fabrication of nano photonic devices and circuits. Nano silver shows different colors due to light absorption and scattering in the visible region based on surface plasmon resonance, the frequency at which conduction electrons oscillate in response to the alternating electric field of incident electromagnetic radiation. The color of metal nanoparticles depends on the shape and size of the nanoparticles and dielectric constant of the surrounding medium. In the past decade, nanoparticle fabrication by a size and shaped controlled methods has become a new and interesting area of research. Due to the growth process of nanoparticles controlled by the stabilizers, it is possible to manipulate the shape and size of nanoparticles by choosing different stabilizing or capping agents. Thus, the stabilizer used may be different with distinct shapes and size of nanoparticles depends on the requirement of the intended application. The enhanced stability of noble metal nanoparticles capped with ligands has been attributed mainly to the relatively strong chemical bond at the interface between the capping agent and the transition
The use of organo sulfur compounds for modifying noble metal nanoparticles properties is one of the most developed methods, because organo sulfur groups strongly coordinate to various metals, such as Ag, Au, Cu, Pt, or Fe. Sulfur possesses a huge affinity for metal surfaces, and organosulfur compounds such as thiol or disulfide capped nanoparticles can be prepared by two methods. First, the sulfur compounds can be grafted on the surface of pre-synthesized nanoparticles covered by solvent molecules which then replaced by the sulfur containing ligands. The second method is to synthesize an organo sulfur-capped nanoparticle in a one-step process, where the metal precursor and the capping ligand are reacted simultaneously. In this case, two processes compete with each other. The first is the growth of the particles leading to a reduction of the total surface. At some point, coordination of the ligands to the surface atoms of the clusters becomes more favorable and stops further growth. The choice of the organo sulfur ligand and the variation of its concentration lead to a control of the particle size. It is well known that the optical and electrical properties of metal nanoparticles are size-dependent. Since the size of the nanoparticles can be controlled by varying the capping ligand concentrations, an important influence of the nature and concentration of the ligand on the nanoparticle properties exists which in turn arrests the growth of nanoparticles. Among organo sulfur compound, thiols can interact with metal nanoparticles in two different ways. The first possibility is the adsorption of the intact RSH molecule on the surface. The second possibility is chemisorption of thiols or disulfides on metal surfaces which generates SR groups. Chemisorption of thiols on the metal surface occurs with concomitant cleavage of the S–H bond. Conjugated molecular structures, such as aromatic thiols, due to their structure and chemical reactivity, provides the essential features to allow strong capping on silver nanoparticles.
Short chain aromatic thiol or disulfide derivative with their small highest occupied molecular orbital- lowest unoccupied molecular orbital (HUMO-LUMO) gap make then outstanding candidate for various molecular electronic applications. Movement of electrons are much faster, in aromatic systems due to the shorter distances and presence of delocalization, $\pi$ electrons are delocalized throughout an extended $\pi$ system in aromatic thiol or disulfide compounds. Structurally aromatic compounds with their conjugation are rigid, while alkane compounds are flexible. In case of short chain aromatic thiols, other interactions, e.g., between the benzene ring and surface, between functional groups, and the intermolecular $\pi-\pi$ interactions, can drive the strong packing structure around the core of nanoparticles.\textsuperscript{19-21} Large number of research was published regarding the chemical reduction methods for the synthesis of stable and various shapes of silver nanoparticles in water by the use of different reducing agents including sodium borohydride ($\text{NaBH}_4$), hydrazine, ascorbic acid, ammonium formate and others. Among them an efficient preparative technique based on the reduction of $\text{AgNO}_3$ by $\text{NaBH}_4$ in the presence of thiol or disulfide compounds.\textsuperscript{22-24}

Adding fascinating features, to the short chain aromatic thiol stabilized AgNps. New short chain amino phenyl triaizne diphenyl disulfide derivative (TAPhSS), as a stabilizer for AgNps were synthesized. In this system, increasing aromaticity in the molecular backbone of (TAPhSS), by the addition of phenyl and triazine rings effects the size and shape of silver nanoparticles. Phenyl groups, enhanced stability of AgNPs in comparison to equivalent bonding in aliphatic (non-aromatic) groups. This increased stability is due to the unique properties of aromatic molecular orbitals. Phenyl groups are found in many organic compounds, both natural and synthetic. Most common among natural products is the amino acid phenylalanine which contains a phenyl group. Many drugs as well as many pollutants contain phenyl rings. In
addition 1,3,5-Triazine derivatives have been known for a long period of time. They have found widespread applications in the pharmaceutical, textile, plastic, and rubber industries, and are used as pesticides, dyestuffs, optical bleaches, and surface active agents. s-triazine or 1,3,5 triazine aromatic structure provide a strong rigidity to the back bone chain or TAPhSS compound which in turn capped the AgNPs through strong chemisorption of terminal thiol group. The present work aim, to investigate the induction \(^{26}\) and growth time \(^{27}\) period of AgNps and how does it will reflect the size AgNps under an ambient conditions. The time between the creation of super saturation and the initial changes in the physical properties of the system due to the formation of the solid phase is defined as induction time. Induction time cannot be regarded as a basic property of the system since its value depends on the procedure used to detect the nanoparticles. Nonetheless, the induction time is experimentally accessible and contains information about the kinetics of new phase nucleation. Induction time is estimated by the time needed for several different events, such as the time needed to reach a quasi-steady state distribution of clusters, a brief time for the formation of stable nuclei, and the time needed for the nuclei to grow to detectable size. Induction time depends on super saturation, temperature and interfacial tension, among them, super saturation is the most influential factor with an inverse effect on it. Another factor that has important effect on induction time is temperature, and in most cases induction time decreases with increasing temperature. The induction and growth time of silver nanoparticles were observed by using very low concentrations of (TAPhSS) as stabilizer and very low concentration of sodium borohydride (NaBH\(_4\)) (0.06, 0.12, 0.2, 0.5, 1 mM) as reductant for both Ag\(^+\) ions to Ag\(^0\) and (TAPhSS) into amino phenyl triazine diphenyl thiophenol (TAPhSH). It has been demonstrated that short chain aromatic thiol (TAPhSH) capping, remarkably enhanced the stabilization of AgNps by increasing the number
of benzene rings in the short molecular back bone chain of (TAPhSS) resulting a very rigid and symmetrical packing around the nanoparticles. The particular advantage of using TAPhSH is, simple synthesis and a very low concentration of the TAPhSH (0.05, 0.3, 0.6 mM) easily stabilized the nascent silver nanoparticles by terminal thiophenol. The as-formed TAPhSH-AgNps are long-lived with promising potential applications in catalysis and photovoltaics.
4.2. Experimental

4.2.1. Materials

All starting materials of analytical grade were commercially available from Wako Pure Chemical Industries, Ltd., Sigma Aldrich Co. and Nakarai Tesque and were used without further purification. All atmosphere-sensitive reactions were performed under nitrogen gas. Double distilled water was used throughout the experiments. $^1$HNMR spectra were recorded on a JEOL GSX-400 spectrophotometer. Absorption and FTIR spectra were recorded on a Hitachi U-2900 spectrophotometer and a Perkin Elmer Multiscope FTIR spectrophotometer, respectively. X-ray photoelectron spectroscopy (XPS) was obtained on an ESCA-1000 Shimadzu electron spectrometer. The incident radiation was the Mg K X-ray line (1253.6 eV) with a source power of 180W (15 kV, 12mA). The analysis chamber was maintained at a steady base pressure of $<6 \times 10^{-9}$ Torr during sample analysis. Survey scans were carried out at an analyzer pass energy of 32.5 eV with 1.0 Ev steps and a dwell time of 300 ms. The Binding energy (BE) scale was calibrated using the C1 s peak with a BE set at 285.0 eV as reference for all XPS peak positions to compensate for energy shifts due to the spectrometer work functions. Samples were prepared as a film on silicon playe which had been thoroughly cleaned using ethanol, rinsed with Milli-Q water dried with nitrogen. Transmission electron microscopic (TEM) images were recorded on a JEOL JEM-3010 VII operating at 300 kV. A drop of dilute solution containing a suspension of the as prepared silver nano particle was placed on a copper grid with a carbon foil and the solvent evaporated under reduced pressure at room temperature in an incubator for a week. Approximately 200 particles were counted and then size distributions of AgNps were determined.
4.2.2. Synthesis of (bis(4,6-dianilino-1,3,5-triazine-2-aminophenyl) disulfide 1) (TAPhSS).

4-Aminophenyl Disulfide (993 mg, 4 mmol) and TEA (404 mg, 4 mmol) was added to a dry THF solution (20 mL) of Cyanuric chloride (1.47 g, 8.0 mmol) and stirred at 0 °C for 1 hr. The solution was filtered. Aniline (745 mg, 1.49 g) and DIPEA (2.07 g, 16 mmol) was added to the filtrate, and then stirred at 40 °C for 24 hrs. The resulting solution was extracted with saturated sodium bicarbonate solution (100 mL) and CH$_2$Cl$_2$ (100 mL). The aqueous layer was extracted with CH$_2$Cl$_2$ (50 mL) and then the organic layers were combined and dried over MgSO$_4$. The solvent was removed under reduced pressure to give compound 1 (10.0% yield) as a light yellow solid. Scheme 1. $^1$H-NMR (400 MHz, CDCl$_3$): δ 7.04 (t, $J$=7.3 Hz, 4H, aniline-Ar-4H), 7.26 (dd, $J$=6.4, 9.2 Hz, 8H, aniline-Ar), 7.35-7.44 (m, 14H, aniline-Ar-8H, NH-6H), 7.48 (d, $J$=7.6 Hz, 8H, disulfide-Ar), MS: FAB$^+$: Calcd for C$_{42}$H$_{35}$N$_{12}$S$_2$ (M$^+$+H) 771.2554, found 771.2552.

4.2.3. Synthesis of TAPhSS stabilized AgNps.

The AgNps solution was prepared by the following procedure. In 15 ml of water under vigorous stirring, added AgNO$_3$ (3 mM, 80 µL). To this solution various concentration of TAPhSS (0.05, 0.3, 0.6 mM, 20 µL in THF) and NaBH$_4$ (0.0625, 0.125, 0.25, 0.5, 1 mM, 100 µL aqueous) were added respectively. Stop stirring, the color of the sample solution changed from transparent to yellow.
4.3. Result and Discussion.

Figure. 1(A), shows the UV-vis absorption spectra of (bis(4,6-dianilino-1,3,5-triazine-2-aminophenyl) disulfide) (TAPhSS)-AgNps systems. The formation of AgNps attributed to the reducing capacity of the terminal thiol group after the dissociation of disulfide bond in short chain triazine bearing diphenyl disulfide derivative (TAPhSS). In this system, sodium borohydride (NaBH₄) played the dual role, it’s dissociate a disulfide bond and formed a thiolate bond (TAPhSH) as well as reduced Ag⁺ in to Ag⁰. Figure. 1(A), shows the UV-vis absorption spectra, at various concentration of [TAPhSS = (0.05(a), 0.3(b) and 0.6(c)mM)] with [NaBH₄ = (0.0625 mM)] while keeping the AgNO₃ concentration same as reported in the experimental section. The UV-visible absorption spectra of all tested sample exhibited the characteristic AgNps surface plasmon resonance (SPR) band (Figure.1 A) at 408,411, and 410 nm for [TAPhSS = (0.05(a), 0.3(b) and 0.6(c)mM)] with [NaBH₄ = (0.0625 mM)] respectively. The reaction mixture exhibited yellow color due to excitation of surface plasmon resonance band in the visible absorption region. The absorption spectra were followed as a function of time, as shown in Figure. 1(B), as the time increases the surface plasmon resonance (SPR) peak of Ag⁰ in between (408-411nm) increases and becomes stabilized after 11 hours indicating the complete conversion of Ag⁺ in the solution reduced to Ag⁰. This behavior was the same for all the tested samples.
Scheme 1. Synthesis of bis(4,6-dianilino-1,3,5-triazine-2-aminophenyl) disulfide (TAPhSS).
Figure 1. (A) UV-vis Absorption spectra of TAPhSH-AgNps systems. [TAPhSS = 0.05 (a), 0.3 (b), 0.6mM (c)] with [NaBH₄ = 0.0625 mM]. B) Plots of absorbance of TAPhSH-AgNps systems against reaction time of 11 hours. [TAPhSS = 0.05 (●), 0.3 (▲), 0.6 (●)]

Further, the effect of varying concentration of reductant sodium borohydride [NaBH₄ = 0.125, 0.25, 0.5 and 1mM] were investigated carefully while keeping [TAPhSS = 0.05 (a), 0.3(b) and 0.6 mM (c)] same. Increase in the concentration of freshly prepared reductant sodium borohydride [NaBH₄] at 25°C leads to blue shift of SPR peak of AgNps which indicates the smaller AgNps particle size. These experiments reiterate the vital role of NaBH₄ in the formation of TAPhSH-AgNps. Figure 2, demonstrated λ max of TAPhSH-AgNps systems against various NaBH₄ concentrations. Figure 2, UV-visible absorption spectra of (C) with 403, 399 and 408 nm for [NaBH₄ = 0.125 ], (E) with 398, 408, 403 nm for [NaBH₄ = 0.25 ], (G) with 397, 402, 395 nm for [NaBH₄ = 0.5], and (I) with 398, 396 and 397 nm for [NaBH₄ = 0.1 mM] for [TAPhSS =
(0.05(a), 0.3(b) and 0.6(c) mM) demonstrated the signature surface plasmon resonance (SPR) band of AgNps. UV visible absorption spectra explain the factor of time-dependent formation of silver nanoparticles. As the time duration increased, the nanoparticles formation and in turn intensity also increased (Figure 2, (D), (F), (H) and (J). After 11 hours, the maximum wavelength ($\lambda_{\text{max}}$) stabilized indicating that all the Ag$^+$ ions in solution has been reduced to Ag$^0$, representing the completion of AgNps formation process. This behavior was the same for all the samples.
(D) Absorbance vs. Time (hr)

(E) Absorbance vs. Wavelength (nm)
Figure 2. UV-vis Absorption spectra of TAPhSH-NaBH₄-AgNps- systems. [ TAPhSS=0.05(a), 0.3 (b), 0.6 ( c) mM] and [NaBH₄0.125 (C), 0.25 ( E ), 0.5 ( G) and 1mM ( I ). (B) Plots of absorbance of TAPhSH-AgNps systems against reaction time of 11 hours. [TAPhSS= 0.05 (●), 0.3 (▲),0.6 (●)] and [NaBH₄ 0.125 (D), 0.25 ( F ), 0.5 ( H) and 1mM ( J )].

The induction and growth time period of AgNps stabilized by TAPhSH was further confirmed by TEM (Figure. 3). The nanoparticles size and shape evaluation was obtained by processing TEM micrographs of different samples of TAPhSH-AgNps. The TEM correlated with time dependent spectroscopic observations, confirmed the presence of AgNps in all tested solutions. TEM images of colloidal solution of silver nanoparticles exhibiting spherical shapes and monodisperse in nature. We investigated the formation of AgNps stabilized by TAPhSH during induction time period, which was within 5 minutes, after the addition of freshly prepared sodium borohydrirde (NaBH₄) in the precursor (AgNO₃) and TAPhSS reaction mixture. The average size of the
TAPhSH- AgNps (Figure. 3A) during induction time for [TAPhSS = 0.05mM] with [NaBH₄ = 0.0625mM] was 5 ± 2 nm. The induction time is before super saturation or initial stages of nanoparticles nucleation. When the growth of the AgNps didn’t start to detectable size. During the induction time the size of the AgNps were very small. After brief induction time period of AgNps, the growth of the AgNps started and completed after 11 hours. The average size of the TAPhSH- AgNps (Figure. 3 B) after 11 hours for [TAPhSS = 0.05mM] with [NaBH₄ = 0.0625mM] was 11 ± 4 nm. In order to confirm the active role of NaBH₄ as reductant and TAPhSH as stabilizer for AgNps and how does their increasing concentration reflect on AgNPs size. Figure.3(C), shown the histogram of average nanoparticle size against various NaBH₄ concentrations. The average size of the AgNps ranged from 11 ± 4 nm with size distribution from 5-20 nm were measured.
Figure. 3. TEM images and histogram of TAPhSH-AgNps systems. [TAPhSS =0.05mM with [NaBH₄]= 0.0625mM]. Induction time of TAPhSH-AgNps systems within 5 minutes (A). (B) Growth of TAPhSH-AgNps systems after 11 hours. (C) with corresponding histogram of particle size distribution.

We measured, few more TEM images with increasing concentration of reductant (NaBH₄) and stabilizer (TAPhSH). The average size of the TAPhSH- AgNps (Figure. 4 (A) and (D) during induction time for [TAPhSS = 0.3mM and 0.6mM] with [NaBH₄]= 0.25 and 1mM] was 4 ± 1 and 3 ± 1 nm respectively. The average size of the TAPhSH- AgNps (Figure. 4(B) and (E)) exhibited the growth of nanoparticles after 11 hours for [TAPhSS = 0.3 and 0.6mM] with [NaBH₄= 0.25 and 1mM] was 10 ± 4 and 9 ± 3 nm. These results would indicate that growth proceeds until the monomer concentrations (Ag⁰) reaches the solubility equilibrium level. However, this will usually result in larger size and shape distribution due to
ostwald ripening (i.e. the growth of larger nanoparticles at the expense of smaller nanoparticles. Therefore growth is usually terminated after reaching to equilibrium.\textsuperscript{28} Figure 4(C) and (F), shown the histogram of average nanoparticles with size distribution from 5-20 nm were measured.
Figure 4. TEM images and histogram of TAPhSH-AgNps systems. Induction time of TAPhSH-AgNps systems within 5 minutes. [TAPhSS =0.3 (A) and 0.6 (D)] with [NaBH₄= 0.25 (A) and 1(D) mM]. Growth of TAPhSH-AgNps systems after 11 hours (B), and (E) with corresponding histogram of particle size distribution (C) and (F).

XPS spectroscopy was used to further probe the chemical bonding between the sulfur atom of TAPhSH and AgNps surface.(Figure 5), the XPS spectrum in Ag (3d ) region of TAPhSH –AgNps shows two peaks these are connected to spin – orbit coupled energy states J=5/2 and 3/2. The Ag 3d₅/₂ and Ag3d₃/₂ appeared at 368 and 374 eV, respectively, confirms the presence of zero valent silver (Ag⁰). The pure bis(4,6-dianilino-1,3,5-triazine-2-aminophenyl) disulfide 1 shown the doublet in the S 2P region of disulfide peak with spin – orbit coupled energy states J=3/2 and 1/2 connected to S2p₃/₂ and S2p₁/₂ of 161.3 and 162.6 eV respectively. The XPS spectrum in S(2P) region showed a singlet peak of thiol at S2p₃/₂ 162.1 eV. No sulphur
peaks above 166 eV were observed, indicating that no oxidized sulfur is present at the surface of AgNps.

Figure 5. XPS spectra of TAPhSH-AgNp systems. Ag 3d $\frac{5}{2}$, and Ag3d $\frac{3}{2}$.

To further confirm that TPhSH chemisorbed with AgNps, FTIR characterization performed on each of the samples. The spectrum not only supports the presence of thiol- AgNps but also reveals the nature of the interactions of the molecules of short chain of (TAPhSH) with AgNps. The spectra of the TAPhSH-AgNps systems colloidal solutions are almost similar to one another, however, a slight difference in their peaks intensities were found, indicating that the
organic molecules have indeed become a part of the silver nanoparticles. In pure TAPhSS the presence (Figure. 6 a) of S-S stretching mode at 597 cm\(^{-1}\) is absent in TAPhSH-NaBH\(_4\) (Figure. 6 b) and TAPhSH-AgNps (Figure. 6 c) systems.

The presence of thiol stretching mode at 2274 cm\(^{-1}\) in TPhSH-NaBH\(_4\) (Figure 6 b) is absent in TPhSH-AgNps (Figure 6 a ad c) systems suggest that the S-H bond is broken upon binding to the AgNps surface, this conforming the formation of TPhSH capped AgNps. In addition, in pure TPhSS, the N–H symmetric stretching vibration frequency at 3276 cm\(^{-1}\) asymmetric \(\nu_{as}(\text{CH}_2)\) and symmetric \(\nu_s(\text{CH}_2)\) vibrations at 2970 and 2870 cm\(^{-1}\) of methylene group and triazine ring (\(>\text{C}=\text{N}-\)) in TPhSS confirms the strong band near 1594,1547 and 1503 cm\(^{-1}\) corresponding to the in-plane vibrations involving the ring(Figure 6 a). In TPhSH-AgNps system these bands are shifted to higher frequency in case of asymmetric \(\nu_{as}(\text{CH}_2)\) and symmetric \(\nu_s(\text{CH}_2)\) vibrations at 2925 and 2853 cm\(^{-1}\) of methylene group and triazine ring (\(>\text{C} =\text{N}-\)) vibrational mode shifted to to higher frequency 1653 cm\(^{-1}\) (Figure 6 c).
Figure 6. FTIR spectra of (a) pure TAPhSS (b) TAPhSH-NaBH₄ (c) TAPhSH-AgNps.
4.4. Conclusion.

In this study the novel synthesis method of silver nanoparticles was presented by using new short chain \((\text{bis}(4,6\text{-dianilino-1,3,5-triazine-2-aminophenyl})\text{ disulfide derivative})\) (TAPhSS). In Increasing aromaticity in TAPhSS through the addition of triazine and diphenyl disulfide strongly stabilized AgNps. The induction time is experimentally accessible and contains information about the kinetics of nucleation. Mono disperse, small size TAPhSH-AgNps nanoparticles were obtained during induction time, which followed by growth of the nanoparticles during which the size of the AgNps increased. The time span of synthesis is very short and its very cost effective and can be easily scale up. The as prepared TAPhSH-AgNps have promising application in catalysis, photovoltaics and sensors.
4.5. References


Triazine benzene thiol and disulfide derivatives stabilized silver nanoparticles catalyst application in the reduction of 4-nitrophenol to 4-aminophenol

5.1. Introduction

Silver nanoparticles (AgNps) has already showed their promise in different fields of scientific and technological research.\(^1\)-\(^3\) Now the world of catalysis involving AgNps has been revolutionized and awaiting a progress.\(^4\)-\(^6\) In recent years, metal nanoparticles have been investigated extensively to understand their physical and chemical properties, not only for scientific knowledge but also for technological applications. In the nano size regime, metal nanoparticles show remarkable changes in their electrical, optical, and catalytic properties.\(^7\)-\(^9\) Size and shapes of nanoparticles plays a crucial role, to act as an effective catalyst in different fields. An important change in reduction potential is observed for metal nanoparticles of different sizes in comparison to bulk metals as the Fermi potential of nanoparticles becomes more negative.\(^10\) This specific property allows them to act as catalysts in various electron transfer processes. Furthermore, nanoparticles have been applied to easy, low-energy routes for manufacturing industrially important products. Another significant application of nanoparticles is in environmental remediation utilizing nanoparticle-based technologies. Thus, currently impregnation of nano catalysts on renewable and nonhazardous materials has been of immense importance.

To study the efficacy of silver nanoparticles in a catalytic process it is important to find a model reaction. The reaction must be appealing, reliable and should have a universal attraction so that the reaction can be studied with certainty using a simple experimental set up. At present,
only one reaction stands out and has been qualified to study AgNp catalyzed reaction, that is an aqueous phase reduction reaction of 4-nitrophenol to 4-aminophenol, and has been tried in different laboratories.\textsuperscript{11-13}

Nitroaromatic compounds including nitro phenols are widely used in the manufacture of pharmaceuticals, pigments, dyes, plastics, pesticides and fungicidal agents, explosives and industrial solvents. Manufacturing of many analgesic and antipyretic drugs, such as paracetamol, phenacetin, and so on, needs 4-aminophenol as a potent intermediate. However, these compounds are highly hazardous on release in environment and have strong toxicity toward humans, animals and plants. Among them, 4-nitrophenol has been classified as a top priority pollutant by US Environmental Protection Agency (EPA), which is stable in the environment and resists biodegradation.\textsuperscript{14-16} Therefore, it is highly desirable to develop the environmentally clean technology for treating such compounds in aqueous medium.

The reduction conversion of 4-NP with sodium borohydride catalyzed by Ag nano catalysts to 4-aminophenol is of industrial and environmental importance. Silver nanoparticles in colloidal solutions so far were used several times to investigate their catalytic capabilities.\textsuperscript{17} However, AgNps colloidal catalysis is influenced by many factors like shape, ligand capping, material of the nanoparticles and pH value. For example in colloidal nanoparticles the ligand capping affects strongly the catalytic capability as was found for many nanoparticles. The complex strong interaction between ligand, pH-value and nanoparticle (its size, shape, and surface morphology) covers the activity of silver nanoparticles in the reaction. So stabilization and dispersion of silver nanoparticles is essential for the better catalytic activity.\textsuperscript{18} The dispersion and aggregation of metal nanoparticles crucially depends on their surface chemistry, and for a number of materials, a surface passivation layer is required to protect the core of
nanoparticles from the environment and stabilize the metal nanoparticles. Recently, much attention has been devoted to the development of new strategies for metal nanoparticles stabilization. The capping molecules play a dual role: on one hand, they stabilize the metal nanoparticles; on the other hand, they can be opportunely selected to functionalize the metal cluster, making the resulting system better suited for different applications. The higher stability of capped nanoparticles has been attributed mainly to the relatively strong chemical bond at the interface between the capping agent and the transition metal. The particular passivating functional molecules control the growth kinetics of nanoparticles and thus prevent them from aggregation. Voluminous methods has been reported to reduce and stabilize Ag and Au nanoparticles by thiol (SH) or disulfide functional groups. Interaction of thiol (SH) or disulfide provide the specific organic surrounding and thus control the growth of nanoparticles and formed highly disperse narrow size nanoparticles.\textsuperscript{19-20} Reduction and stabilization of nanoparticles mainly depend on the organo sulfur functional group with chain length play an important role. The metal-sulfur interaction is strong enough to immobilize the thio groups on the surface of metal nanoparticles. Aromatic thiols shown significant physical and chemical properties compared with saturated alkane systems. In aromatic thiols (SH) both sulfur and benzene moieties were involved to the surface adsorption, imparts different functionality to the particles that can be utilized according to the required applications.\textsuperscript{21} We, synthesised silver nanoparticles by using three Triazine bearing short chain benzene thiol and disulfide derivatives, namely (4,6 di methoxy 1,3,5 triazine -2-yl-4- mercaptobenzoate) and cationic surfactant (TBSH), disulfide (N,N-(disulfanediylbis (ethane-2,1-diyl)) bis( 4,6 –diphenyl-1,3,5-triazin-2-amine) (TPhSS) and , disulfide (4,6 dianimonophenyl 1,3,5 triazine -4- aminophenyl disulfide )) or aniline disulfide compound 1 (TAPhSS) . The unique properties of these three triazine bearing aromatic thiol and
disulfide derivatives are the ease of ligands (SH) bounded with the nanoparticles surface within short span of time and with superior stability by compact and rigid network. Presence of 1,3,5-triazine moiety in the short back bone chain provide the enhanced stabilization of nanoparticles. 1,3,5-Triazine derivatives have been known for a long period of time. They have found widespread applications in the pharmaceutical, textile, plastic, and rubber industries, and are used as pesticides, dyestuffs, optical bleaches, and surface active agents. The chemistry of this group of compounds has been studied intensively and has been the subject of many reviews. Triazine group easily interact with other organic compounds through coordination bond, hydrogen bonding, electrostatic charge transfer and aromatic staking with applications in host guest chemistry, catalysis, anion recognition, sensors, electronics and magnetism.

Adding novel and exclusive applications of nanosilver as heatrogenous catalyst in the reduction of nitroarena compound. To our knowledge, this is the first report of catalytic activity of silver nanoparticles stabilized by various short chain, traizine bearing benzene thiol and disulfide derivatives. The thiol and disulfide compounds used in this study for the stabilization of silver nanoparticles are (4,6 di methoxy 1,3,5 triazine -2-yl-4- mercaptobenzoate) (TBSH), disulfide (N,N-(disulfanediylbis ( ethane-2,1-diyl)) bis( 4,6 –diphenyl-1,3,5-triazin-2-amine) (TPhSS) and , disulfide (4,6 diaminophenyl 1,3,5 triazine -4- aminophenyl disulfide )) or aniline disulfide compound 1 (TAPhSS) respectively. The spectroscopic results and surface morphology of as prepared silver nanoparticles (AgNps) by using various triazine bearing benzenethiol and disulfide derivatives resulted in the monodisperse and smaller size of AgNps. The short backbone chain of thiols or disulfide with increased aromaticity in (TBSH, TPhSS and TAPhSS) have shown a profound effect on the size of silver nanoparticles. Smaller nanoparticles exhibit larger surface area for the same volume of material resulting a larger active area of the
catalyst. We developed facile methods to apply as prepared AgNps for the reduction of 4-nitrophenol to 4-aminophenol.

5.2. Experimental

5.2.1. Materials

All starting materials of analytical grade were commercially available from Wako Pure Chemical Industries, Ltd., Sigma Aldrich Co. and Nakarai Tesque and were used without further purification. All atmosphere-sensitive reactions were performed under nitrogen gas. Double distilled water was used throughout the experiments. $^1$HNMR spectra were recorded on a JEOL GSX-400 spectrophotometer. Absorption and FTIR spectra were recorded on a Hitachi U-2900 spectrophotometer and a Perkin Elmer Multiscope FTIR spectrophotomer, respectively. Hg lamp used was UVL-400HA, RIKO medium pressure lamp. X-ray photoelectron spectroscopy (XPS) was obtained on an ESCA-1000 Shimadzu electron spectrometer. The incident radiation was the Mg K X-ray line (1253.6 eV) with a source power of 180W (15 kV, 12mA). The analysis chamber was maintained at a steady base pressure of $<6 \times 10^{-9}$ Torr during sample analysis. Survey scans were carried out at an analyzer pass energy of 32.5 eV with 1.0 Ev steps and a dwell time of 300 ms. The Binding energy (BE) scale was calibrated using the C1 s peak with a BE set at 285.0 eV as reference for all XPS peak positions to compensate for energy shifts due to the spectrometer work functions. Samples were prepared as a film on silicon playe which had been thoroughly cleaned using ethanol, rinsed with Milli-Q water dried with nitrogen. Transmission electron microscopic (TEM) images were recorded on a JEOL JEM-3010 VII operating at 300 kV. A drop of dilute solution containing a suspension of the as prepared silver nano particle was placed on a copper grid with a carbon foil and the solvent evaporated under
reduced pressure at room temperature in an incubator for a week. Approximately 200 particles were counted and then size distribution of AgNps was determined.

5.2.2. Synthesis of (4,6-dimethoxy-1,3,5-triazin-2-yl)-4-mercaptobenzoate (TBSH).

4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (304 mg, 1.1 mmol) was added to a 10 mL MeOH solution of 4-mercaptobenzoic acid (154 mg, 1.0 mmol) (10mL) at 20°C. The mixture was stirred to give (4,6-dimethoxy-1,3,5-triazin-2-yl)-4-mercaptobenzoate (1) as a white precipitate within 30 minutes (Scheme1). The mixture was filtered and then the precipitate was dried in vacuo to obtain in excellent yield (>95%). mp 235-238.\textsuperscript{1}H NMR (400MHz, DMSO-$d_6$): δ=3.83 (s, 6H, OCH$_3$), 7.74 (d, 2H, J=8.0Hz, ArH), 7.99 (d, 2H, J=8.0Hz, ArH).\textsuperscript{13}C NMR(100MHz, DMSO-$d_6$): δ C=55.2(OCH$_3$), 129.8, 131.7, 132.4, 134.9 (ArC), 166.7(C=O), 17.08, 182.7 (Triazin-C). MS: $m/z$ 292 (M$^+$-H), HRMS (EI): Calculated for C$_{12}$H$_{10}$N$_3$O$_4$S (M$^+$-H) 292.0392, found 292.0391.

5.2.3. Synthesis of TBSH surfactant stabilized AgNps.

The AgNps solution was prepared by the following procedure. 10 ml of aqueous CTAC solution at cmc (0.6 mM), adjusted to pH 10 by using Na$_2$CO$_3$ (50mM) under stirring. To this solution AgNO$_3$ (50m M, 80 µL) was added. After that TBSH (2.5mM, 50 µL in THF) was added. Then the solutions were irradiated by Hg-lamp for 6~7 hours. The color of the sample solution changed from transparent to blackish yellow.

5.2.4. Catalytic reduction of 4-Nitrophenol to 4-Aminophenol by AgNps-TBSH-CTAC.

The catalytic reduction reaction of 4-nitrophenol was performed in aqueous solution in a standard quartz cell with a 1 cm path length. The reaction procedure was as follows:

Under vigorous stirring 4-nitrophenol (1 mM, 400 µL), AgNps-TBSH-CTAC (1mL), and deionized water (1 ml) were added in a quartz cell respectively. To this immediately added
freshly prepared NaBH₄ (15 mM, 1 mL), the solution colored was changed from light yellow to dark yellow and the UV – vis absorption spectra were recorded with a time interval of 5 minutes in a scanning range of 190 – 1100 nm at ambient temperature (25° C).

5.2.5. Synthesis of bis(4,6-dephenyl-1,3,5-triazine-2-aminoethyl) disulfide 2 (TPhSS).

To a dry THF solution (5.0 mL) of cystamine dihydrochloride (225 mg, 1.0 mmol) was added TEA (606 mg, 6.0 mg) and a dry MeOH solution (5.0 mL) of 2-Chloro-4,6-diphenyl-1,3,5-triazine (CDPT) (535 mg, 2.0 mmol). The mixture was stirred at room temperature for 7 h. The solvent was removed in vacuo, and then the residue was extracted with ethyl acetate (30 mL) and H₂O (30 mL), and the organic layer was dried over MgSO₄. The solvent was removed in vacuo to give compound 1 (33% yield) as a light yellow solid. (Scheme 2). ¹H-NMR (400 MHz, CDCl₃): 8.51-8.60 (m, Ar-H, 8H), 7.46-7.53 (m, Ar-H, 12H), 5.94 (s, 2H, NH), 3.97 (q, J=6.4 Hz, 4H), 3.05 (t, J=6.6 Hz, 4H). MS: FAB⁺: Calcd for C₃₄H₃₁N₈S₂ (M⁺+H) 615.2113, found 615.2102

5.2.6. Synthesis of TPhSS stabilized AgNps.

In a typical experiment, the AgNps solution was prepared by the following procedure. In 40 ml of water under vigorous stirring, added varying concentration of AgNO₃ (200, 400 and 600 mM 10 µL). To these solutions TPhSS (0.425 mM, 20 µL in THF) and NaBH₄ (10 mM, 500 µL aqueous) were added. Stop stirring, the color of the sample solution changed from transparent to yellow.

5.2.7. Catalytic reduction of 4-Nitrophenol to 4-Aminophenol by AgNps-TPhSS.

The catalytic reduction reaction of 4-nitrophenol was performed in aqueous solution in a standard quartz cell with a 1 cm path length. The reaction procedure was as follows:
Under vigorous stirring 4-nitrophenol (1 mM, 200 µL), 1mL of AgNps (AgNps-TPhSS), and deionized water (1 ml) were added in a quartz cell respectively. To this immediately added freshly prepared NaBH₄ (15mM, 1mL), the solution colored was changed from light yellow to dark yellow and the UV–vis absorption spectra were recorded with a time interval of 5 minutes in a scanning range of 190 – 1100 nm at ambient temperature (25°C).

5.2.8. Synthesis of (bis(4,6-dianilino-1,3,5-triazine-2-aminophenyl) disulfide 1 (TAPhSS).

4-Aminophenyl Disulfide (993 mg, 4 mmol) and TEA (404 mg, 4 mmol) was added to a dry THF solution (20 mL) of Cyanuric chloride (1.47 g, 8.0 mmol) and stirred at 0 °C for 1 hr. The solution was filtered. Aniline (745 mg, 1.49 g) and DIPEA (2.07 g, 16 mmol) was added to the filtrate, and then stirred at 40 °C for 24 hrs. The resulting solution was extracted with saturated sodium bicarbonate solution (100 mL) and CH₂Cl₂ (100 mL). The aqueous layer was extracted with CH₂Cl₂ (50 mL) and then the organic layers were combined and dried over MgSO₄. The solvent was removed under reduced pressure to give compound 1 (10.0% yield) as a light yellow solid. (Scheme 3). ¹H-NMR (400 MHz, CDCl₃): 7.04 (t, \(J=7.3\) Hz, 4H, aniline-Ar-4H), 7.26 (dd, \(J=6.4, 9.2\) Hz, 8H, aniline-Ar), 7.35-7.44 (m, 14H, aniline-Ar-8H, NH-6H), 7.48 (d, \(J=7.6\) Hz, 8H, disulfide-Ar), MS: FAB⁺: Calcd for C₄₂H₃₅N₁₂S₂ (M⁺+H) 771.2554, found 771.2552.

5.2.9. Synthesis of TAPhSS stabilized AgNps.

The AgNps solution was prepared by the following procedure. In 15 ml of water under vigorous stirring, added AgNO₃ (3, 5 and 9mM, 80 µL). To this solution TAPhSS (0.6mM, 20 µL in THF) and NaBH₄ (0.5, 1mM, 100 µL aqueous) were added respectively. Stop stirring, the color of the sample solution changed from transparent to yellow.
5.2.10. Catalytic reduction of 4-Nitrophenol to 4-Aminophenol by AgNps-TAPhSS.

The catalytic reduction reaction of 4-nitrophenol was performed in aqueous solution in a standard quartz cell with a 1 cm path length. The reaction procedure was as follows:

Under vigorous stirring 4-nitrophenol (1 mM, 200 μL), 1mL of AgNps (AgNps-TAPhSS), and deionized water (1 ml), were added in a quartz cell respectively. To this immediately added, freshly prepared NaBH₄ (15mM, 1mL), the solution colored was changed from light yellow to dark yellow and the UV–vis absorption spectra were recorded with a time interval of 5 minutes in a scanning range of 190 – 1100 nm at ambient temperature (25⁰ C).

5.3. Result and Discussion

A potential application of metal nanoparticles is the catalysis of certain reactions that would otherwise not occur. We have chosen the reduction of 4-nitrophenol to 4-aminophenol as a model system, in order to evaluate the catalytic activity of (AgNps-TBSH-CTAC, AgNps-TPhSS, AgNps-TAPhSS). The reduction of 4-nitrophenol ($E^0_{(4-NP/4-AP)} = -0.076$ V) by sodium borohydride (NaBH₄) ($E^0_{(H3BO3/BH4^-)} = -1.33$ V) is thermodynamically feasible but kinetically restricted in the absence of a catalyst. Figure 1(A), addition of NaBH₄ (15mM, 1mL) to a 4-nitrophenol (1mM, 200μL), solution changes the light yellow color of the solution to intense yellow due to formation of the 4-nitrophenolate ion (Figure. 1(B)). This is due to the fact that addition of NaBH₄ changes the pH from acidic to highly basic. Accordingly, the UV-vis absorption peak of 4-nitrophenolate at 317nm (Figure. 2(a)), shifts to 400 nm indicating the formation of the 4-nitrophenolate ion (Figure. 2(b)). Absorption intensity at 400 nm for the 4-nitrophenolate ion remained unaltered in the presence of only NaBH₄ even after two days. This result indicated that the reduction does not proceed without a catalyst.
Scheme 1. Synthesis of (4,6- dimethoxy -1,3,5 triazin-2-yl)-4- mercaptobenzoate (TBSH).

Scheme 2. Synthesis of (bis(4,6-dephenyl-1,3,5-triazine-2-aminoethyl)) disulfide 2 (TPhSS)

Scheme 3. Synthesis of bis(4,6-dianilino-1,3,5-triazine-2-aminophenyl) disulfide 1 (TAPhSS).
Figure 1. (A) 4-nitrophenol aqueous solution. (B) 4-nitrophenolate.

Figure 2. UV-vis absorption spectra of 4-nitrophenol (4-NP) (a) and 4-nitrophenolate (b).
Figure 3(A), demonstrated the reduction process of 4-Nitrophenol in the presence of reductant NaBH$_4$ and (AgNps-TBSH-CTAC) as catalyst. The intense yellow color due to the formation of nitrophenolate ion (Figure.3 (B)) changed to transparent (Figure.3(C)) after the addition of AgNps as catalyst with in few minutes. The appearance of transparent color of 4-aminophenone indicating the completion of the reduction process of of 4-Nitrophenol to 4-Aminophenol.

**Figure 3.** (A) 4-nitrophenol aqueous solution. (B) 4- nitrophenolate (C) 4- aminophenol.

Figure 4(A), UV-vis absorption spectra illustrates the reduction reaction of 4-nitrophenol, observed at different time intervals using (AgNps-TBSH-CTAC) as catalyst. In the presence of (AgNps-TBSH-CTAC) and NaBH$_4$ the 4-nitrophenol was reduced, and the intensity of the absorption peak at 400 nm gradually decreased with time and after 20 minutes, disappeared. In the meantime, a new absorption peak appeared at 300 nm and progressively increased in intensity .This new peak is attributed to the typical absorption of 4-aminophenol. The UV-vis spectra in Figure 4(A), showed two isosbestic points at 288 and 317 nm. This result suggests that
the catalytic reduction of 4-nitrophenol exclusively yielded 4-aminophenol, without any other side products.

In the reduction process, the overall concentration of NaBH$_4$ was 15mM and 4-nitrophenol was 1 mM. Considering the much higher concentration of NaBH$_4$ compared to that of 4-nitrophenol, the pseudo- first-order kinetics could be applied with respect to 4-nitrophenol in order to determine the catalytic activity of (AgNps-TBSH-CTAC). The absorbance of 4-nitrophenol is proportional to its concentration in solution, the absorbance at time t ($A_t$) and time $t = 0$ ($A_0$) are equivalent to the concentration at time t ($C_t$) and time $t = 0$ ($C_0$). The rate constant (k) was determined from the linear plot of $-\ln(A_t / A_0)$ versus reduction time in minutes, and the constant was estimated to be 0.08 min$^{-1}$. 

![Graph with absorbance vs. wavelength for 4-NP and 4-AP]
Figure 4 (A). UV-vis absorption spectra of reduction of 4-nitrophenol to 4-aminophenol in the presence of (AgNps-TBSH-CTAC) as catalyst. (B). Plot of ln(A_t/A_0) against the reaction time for pseudo-first-order reduction kinetics of 4-nitrophenol to 4-aminophenol in the presence of (AgNps-TBSH-CTAC) as catalyst.

The mechanism of reduction of 4-nitrophenol to 4-aminophenol by NaBH_4 in the presence of silver nanoparticles is discussed in terms of the Langmuir-Hinshelwood (LH) model (Figure 5 (A)). Borohydride ions (BH_4^-) adsorb on the surface of the AgNps and transfer a surface-hydrogen species to the surface of the nanoparticles. This reversible step can be modeled in terms of a Langmuir isotherm. Concomitantly, 4-nitrophenol molecules are adsorbed on the surface of the nanoparticles. This reversible process can also be modeled by a Langmuir isotherm. Moreover, the adsorption/desorption equilibriums and diffusion of reactants to the nanoparticles are considered to be fast. The reduction of 4-nitrophenol, which is the rate-determining step, occurs due to the reaction of adsorbed 4-nitrophenol with the nanoparticles surface-bound hydrogen atoms. When product, 4-aminophenol, desorbs leaving free metal surface, the catalytic cycle can begin again.²²
Figure 5. Reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by NaBH₄ in the presence of silver nanoparticles (AgNps) follows the Langmuir–Hinshelwood (LH) model. Borohydride (BH₄⁻) react with silver nanoparticles (AgNps) to form silver hydride. 4-nitrophenol adsorbs on the silver nanoparticles surface and both reagents adsorption and desorption on the surface of AgNps is very rapid following the Langmuir isotherm. Reduction of the adsorbed 4-nitrophenol and then 4-aminophenol desorbs is the rate determining step.

UV-vis absorption spectra (Figure 6(A)) demonstrated the reduction reaction of 4-nitrophenol, by using (AgNps-TPhSH) as the catalyst. In this case, TPhSH stabilized AgNps very well without using any other additional stabilizer such as surfactants and others. In the presence of (AgNps-TPhSH) and NaBH₄ the 4-nitrophenolate was reduced, and the intensity of the absorption peak at 400 nm gradually decreased with time and after 15 minutes, fully disappeared. In the meantime, a new absorption peak appeared at 300 nm and progressively
increased in intensity. This new peak is attributed to the typical absorption of 4-aminophenol. The UV vis absorption spectra in Figure 6(A), showed two isosbestic points at 288 and 316 nm. This result suggests that the catalytic reduction of 4-nitrophenol exclusively yielded 4-aminophenol, without any other side products.

In the reduction process, the overall concentration of NaBH$_4$ was 15mM and 4-nitrophenol was 1mM. Higher concentration of NaBH$_4$ compared to that of 4-nitrophenol, the pseudo- first-order kinetics could be applied with respect to 4-nitrophenol in order to determine the catalytic activity of (AgNps-TPhSH). The absorbance of 4-nitrophenol is proportional to its concentration in solution, the absorbance at time $t$ ($A_t$) and time $t = 0$ ($A_0$) are equivalent to the concentration at time $t$ ($C_t$) and time $t = 0$ ($C_0$). The rate constant ($k$) was determined from the linear plot of $-\ln (A_t/A_0)$ versus reduction time in minutes, and the constant was estimated to be Figure 6 (D) 0.18 min$^{-1}$. We further investigated, the role of catalyst (AgNps-TPhSH) by synthesizing AgNPs-TPhSH with increasing concentration of precursor AgNO$_3$. UV-vis absorption spectra (Figure 6(B) and (C)) of AgNps-TPhSH systems with [AgNO$_3$]= 400mM (B) and 600mM(C)]. As the concentration of AgNO$_3$ increased, more nanoparticles formed and stabilized by TPhSH. More catalyst surfaces available for the reduction of 4-Nitrophenol to 4-Aminophenol. This will in turn decreased the time of reduction with higher value of $k$ (min$^{-1}$) as summarize in Table 1. In the reduction process, the overall concentration of NaBH$_4$ was 15mM and 4-nitrophenol was 1 mM. This is the pseudo- first-order kinetics with respect to 4-nitrophenol in order to determine the catalytic activity of (AgNps-TPhSH), due to much higher concentration of NaBH$_4$ compared to that of 4-nitrophenol. Figure 6 (E) and (F), the rate constant ($k$) was determined from the linear plot of $-\ln(A_t/A_0)$ versus reduction time in minutes,
and the constant was estimated to be 0.20 and 0.24 min⁻¹ for AgNps-TPhSH systems, [AgNO3= 400mM (E) and 600mM( F)].

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<th>Synthesis of Silver nanoparticles (AgNps )</th>
<th>TPhSH-AgNps catalytic activity</th>
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<td>Short chain Aromatic compound (TPhSS) (mM)</td>
<td>NaBH₄ (mM)</td>
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**Table: 1.** Catalytic activity of (AgNps-TPhSH ) with varying concentration of [AgNO₃= 200, 400, 600mM].
Figure 6. UV-vis absorption spectra of reduction of 4-nitrophenol to 4-aminophenol in the presence of catalyst (AgNps-TPhSH) systems. [AgNO₃= 200 (A), 400 (B), 600mM(C)]. Plot of \(-\ln(A_t/A_0)\) against the reaction time for pseudo-first-order reduction kinetics of 4-nitrophenol to 4-aminophenol in the presence of catalyst (AgNps-TPhSH) systems. [AgNO₃= 200 (D), 400 (E), 600mM (F)].

We further explore the effective role of AgNps, by increasing the aromaticity in the short chain aromatic disulfide derivative (TAPhSS). Increasing aromaticity through phenyl and triazine ring in the short back bone chain of the TAPhSS compound have a profound effect on
the stabilization of AgNps, which in turn shown the enhanced the catalytic activity for the reduction of 4-nitrophenol to 4-aminophenol.

UV-vis absorption spectra (Figure 7(A)) demonstrated the reduction reaction of 4-nitrophenol, by using (AgNps-TAPhSH) as the catalyst. In the presence of (AgNps-TAPhSH) and NaBH$_4$ the 4-nitrophenolate was reduced, and the intensity of the absorption peak at 400 nm gradually decreased with time and after 15 minutes disappeared. In the meantime, a new absorption peak appeared at 300 nm and progressively increased in intensity. This new peak is attributed to the typical absorption of 4-aminophenol. The UV vis absorption spectra in (Figure 7(A)), showed two isosbestic points at 287 and 317 nm. This result suggests that the catalytic reduction of 4-nitrophenol exclusively yielded 4-aminophenol, without any other side products. In the reduction process, the overall concentration of NaBH$_4$ was 15mM and 4-nitrophenol was 1 mM. Due to much higher concentration of NaBH$_4$ compared to that of 4-nitrophenol, the pseudo- first-order kinetics could be applied with respect to 4-nitrophenol in order to determine the catalytic activity of (AgNps-TAPhSH). The absorbance of 4-nitrophenol is proportional to its concentration in solution, the absorbance at time t ($A_t$) and time t = 0 ($A_0$) are equivalent to the concentration at time t ($C_t$) and time t = 0 ($C_0$). The rate constant (k) was determined from the linear plot of -ln($A_t/A_0$) versus reduction time in minutes, and the constant was estimated to be (Figure 7(D)) 0.17 min$^{-1}$. The role of catalyst (AgNps-TAPhSH) further explored by synthesizing AgNPs-TAPhSH with increasing concentration of precursor AgNO$_3$. UV-vis absorption spectra (Figure 7(B) and (C)) of AgNps-TAPhSH systems with [AgNO$_3$] = 5 mM (B) and 9mM(C). As the concentration of AgNO$_3$ increased, more nanoparticles formed and stabilized by TAPhSH. More catalyst surfaces available for the reduction of 4-Nitrophenol to 4-Aminophenol. This will in turn decreased the time of reduction with higher value of k (min$^{-1}$) as summarize in Table 2. In
the reduction process, the overall concentration of NaBH$_4$ was 15mM and 4-nitrophenol was 1 mM. Considering the much higher concentration of NaBH$_4$ compared to that of 4-nitrophenol, the pseudo- first-order kinetics could be applied with respect to 4-nitrophenol in order to determine the catalytic activity of (AgNps-TAPhSH). Figure 7 (E) and (F), the rate constant (k) was determined from the linear plot of $-\ln(A_t/A_0)$ versus reduction time in minutes, and the constant was estimated to be 0.23 and 0.25 min$^{-1}$ for AgNps-TAPhSH systems, [AgNO$_3$= 3mM (E), 9mM (F)].

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**Table: 2.** Catalytic activity of (AgNps-TAPhSH) with varying concentration of [AgNO$_3$= 3, 5, and 9mM].
Figure 7. UV-vis absorption spectra of reduction of 4-nitrophenol to 4-aminophenol in the presence of catalyst (AgNps-TPhSH) systems. [AgNO$_3$]=3 (A), 5 (B), and 9mM(C)]. Plot of $-\ln(A_t/A_0)$ against the reaction time for pseudo-first-order reduction kinetics of 4-nitrophenol to 4-aminophenol in the presence of catalyst (AgNps-TAPhSH) systems. [AgNO$_3$]=3 (D), 5 (E), and 9mM(F)].
5.4. Conclusion.

The present study describes, a new simple and cost effective methods for the reduction of 4-nitrophenol to 4-aminophenol in presence of AgNps as catalyst. Three types of new heterogeneous silver nanoparticle catalysts viz., TBSH-CTAC–AgNPs, TPhSH–AgNPs and TAPhSH-AgNps were synthesized by a simplified wet chemical reduction procedure. This comparative study, revealed higher rate constants values of the silver nanoparticles (AgNps) as catalyst, when stabilized by (AgNps-TBSH-CTAC,AgNps-TPhSS, and AgNps-TAPhSS) due to more bare surface of silver nanoparticles (AgNps) available for the reduction of 4-nitrophenol to 4-aminophenol. From the calculated rate of reaction k values, it was observed that the TAPhSH-AgNps catalyst was more active than TPhSH-AgNps and TBSH-CTAC-AgNps The rate of reaction k value found to increase with increasing concentration of precursor AgNO₃. The as prepared silver nanoparticles could be easily integrated into various other catalytic applications.
5.5. References.


6.1. Summary

This doctoral dissertation focuses the facile and novel synthesis of silver nanoparticles (AgNps) and their application in catalysis, sensing and photovoltaics. In this thesis, we present a series of novel experimental techniques to synthesize AgNps by using various new triazine bearing benzenethiol and disulfide derivatives as reductive stabilizer for AgNps. The optical properties of as-prepared AgNps were investigated by using UV–vis, Fourier transform infrared (FTIR), Transmission electron spectroscopy (TEM) and X-ray photoelectron (XPS) spectroscopic techniques. These spectroscopic methods also provide the detailed information regarding the molecular interaction of triazine bearing benzenethiol and disulfide derivatives with surface of AgNps. Moreover, as prepared stable AgNps first time shown very high catalytic activity.

Chapter 1, describes the general introduction about the AgNps as an attractive metal due to its highest electrical and thermal conductivity among all metals and high optical reflectivity. As the size of the Ag particles decreases down to the nanometer scale, they exhibit many unique optical, electronic, and chemical properties that cannot be observed in the bulk crystals. In addition, the versatility of capping AgNps by various aromatic sulfur compounds containing thiol and disulfide groups, and their influence on the optical properties of AgNps were also discussed.

Chapter 2, outlined the preparation methods of AgNps by using a triazine benzenethiol derivative (TBSH) as reductant and cationic surfactant as a stabilizer. A novel, short-chain benzenethiol (4,6-dimethoxy-1,3,5-triazin-2-yl)-4-mercaptobenzoate were synthesized. Under ambient conditions, TBSH with its terminal thiol functional group reduced and stabilized AgNps. Cationic surfactant, such as cetyltrimethylammonium chloride (CTAC) was used as an additional
surface modifier which hindered the growth of AgNps. The optical properties of the as-prepared AgNps were analyzed by using UV–vis, Fourier transform infrared (FTIR), and X-ray photoelectron (XPS) spectroscopic techniques. Transmission electron microscopy (TEM) images shown morphology of AgNps with average size of 30 nm. CTAC–concentration dependence of FTIR spectra indicates that the combination of rigid and compact network of TBSH and CTAC capped on AgNps significantly affects the size and shape of AgNps and also exhibit the presence of enhanced gauche conformers below the critical micellar concentration (cmc ~ 0.6 mM) and trans conformers at cmc and above cmc of CTAC. Based on the present results, we propose the model of molecular structure and stability of silver nanoparticles (AgNps).

Chapter 3, reports a facile synthesis of AgNps using a novel triazine bearing disulfide derivative such as (N,N’-disulfanediylbis(ethane-2,1-diyl))bis(4,6-diphenyl-1,3,5-triazine-2-amine))(TPhSS) as a stabilizer for AgNps. In this system sodium borohydride (NaBH₄) was used as a reductant of disulfide bond to thiol and Ag⁺ ions to Ag⁰. UV-visible absorption spectra exhibited the surface plasmon resonance (SPR) band of AgNps. The XPS spectra showed two peaks at Ag 3d₅/₂ and Ag 3d₃/₂ confirms the presence of zero valent silver (Ag⁰). Moreover, FTIR spectra also illustrated the presence of thiol stretch in pure compound of (TPhSS) and the absence of an S–H stretching mode in the spectrum of TPhSH- AgNps systems suggests that the S–H bond is broken upon binding to the AgNps surface, thus conforming the formation of TPhSH capped AgNps. TEM images show the as-prepared AgNps have spherical in shape with average size of 15 nm.

Chapter 4, outlined the effects of increasing aromaticity by synthesizing amino phynel triazine diphenyl disulfide derivative (bis(4,6-dianilino-1,3,5-triazine-2-aminophenyl) disulfide TAPhSS) as a stabilizer for AgNps. This chapter also highlighted the benefits of increased
aromatic properties of the compound (TAPhSS) which results in enhanced hydrophobicity and generates very small size of AgNps capped by (TAPSH). In order to investigate the induction and growth time, formation of AgNps at very low concentrations of TAPhSS as stabilizer, NaBH₄ as reductant, for the reduction of both Ag⁺ ions to Ag⁰ and diphenyl disulfide bond into thiophenol has been carried out. Mono disperse, small size TAPhSH-AgNps nanoparticles were obtained during induction time, which followed by growth, resulted in increased size AgNps capped by TPSH. The time span of synthesis is very short and its very cost effective and can be easily scale up. By measuring UV-visible, XPS and FTIR spectra, the formation mechanism of AgNps stabilized by TAPhSH discussed in detailed.

Chapter 5, summarizes the present results in order to discuss that how the molecular structure of various benzenethiol and disulfide derivatives bearing triazine group reflect, on the particle size of AgNps. Three types of new heterogeneous silver nanoparticle catalysts viz., TBSH-CTAC–AgNPs, TPhSH–AgNPs and TAPhSH-AgNps were synthesized by a simplified wet chemical reduction procedure. All the three catalysts were characterized by various spectroscopic techniques. The catalytic activity was inspected using the reduction of 4-nitophenol to 4-aminophenol as a model reaction system keeping under pseudo-first order reaction conditions. From the calculated rate of reaction k values, it was observed that the TAPhSH-AgNps catalyst was more active than TPhSH-AgNps and TBSH-CTAC-AgNps. The rate of reaction k value found to increase with increasing concentration of precursor AgNO₃. The as prepared silver nanoparticles could be easily integrated into various other catalytic applications.
In chapter 6, the results of facile synthesis of AgNps by using varios benzenethiol and disulfide derivatives bearing groups are finally summarized.