



REVIEW

Controlled Synthesis of Silver Nanoparticles with different Shapes and Their Applications – A Review

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(Received 20 June 2024; revised manuscript received 19 October 2024; published online 30 October 2024)

Nowadays noble metal nanoparticles occupy a prominent position in science and technology owing to their facile synthesis, ease of surface modification and excellent biocompatibility which offers countless applications in numerous fields of science. Though several noble metals are used for a variety of applications, silver nanoparticles is of great attentiveness due to its unique physical and chemical properties like optical, electrical, thermal, biological, and catalytic properties. Most of these properties depends on the shape and size of the synthesized silver nanoparticles. The manufacturing of silver nanoparticles with numerous shapes is very common today, so that we can control various properties, especially in the field of medicine by many researchers. In this article, we present a review of the synthesis of silver nanoparticles of different shapes through different methods and their peculiar applications.

Keywords: Silver, Nanoparticles, Shape.

DOI: [10.21272/jnep.16\(5\).05019](https://doi.org/10.21272/jnep.16(5).05019)

PACS numbers: 61.46.Df, 78.67.Bf

1. INTRODUCTION

Nanoscience engages researchers to study new behaviors and properties of materials with dimensions at the nanoscale. A significant area of current research is nanotechnology, which is concerned with the creation, synthesis, and modification of particle structures with sizes between about 1 and 100 nm. The ability of nanoparticles to cross the gap between bulk materials and atomic or molecular structures makes them of significant scientific interest. Nanotechnology is the research and development of material device systems and products by manipulating shapes and sizes at the nanoscale with at least one new property. The synthesis of nanoparticles with various chemical compositions, sizes, morphologies, and regulated dispersities is a significant field of research in nanotechnology. Because of its many uses, nanotechnology has emerged as a fundamental branch and ushered in a new era in material science that is gaining international attention. The exploratory use of nanoparticles in biological systems led to the development of this multidisciplinary method, which involves the fields of biology, biochemistry, chemistry, engineering, physics, and medicine.

Synthesis of metal nanoparticle gains growing attention in the scientific community due to its unique optical property arising from the collective oscillation of conducting electrons named surface plasmon resonance (SPR) which finds application in biological and chemical detection/sensing, in Surface-Enhanced Raman Scattering (SERS) [1] etc. Due to their high surface to volume ratio and antibacterial qualities, metal nanoparticles exhibit the greatest promise among other types of nanoparticles. The physical and chemical characteristics of

the nanoparticles can alter if the composition or size of the particles vary. Research has demonstrated that the adsorption processes of stabilizing agents with metal nanoparticles, the kinetics of metal ion interaction with reducing agents, and the experimental conditions all have a significant impact on the size, morphology, stability and chemical and physical properties of the metal nanoparticles. Noble metal nanoparticles can enhance the specificity of detection, which greatly impacts biosensing. They also show distinctive physiochemical properties like the high surface area to volume ratio and ease of functionalization which provide additional applications such as fluorescence, IR and Raman spectroscopy, etc. Furthermore, the creation is a safe, non-toxic, and environmentally acceptable processes for the synthesis and assembly of metal nanoparticles.

The unique physical and chemical behaviors of silver nanoparticles [2] have allured a lot of attention for various applications including biological labeling, catalysis, optoelectronic bactericide, Surface-Enhanced Raman Scattering, contrast-enhancing agents, near-field optical probes, etc. These properties are strongly based on the shape of the silver nanoparticles. Nanoparticles will undergo changes in their electrical, chemical, and physical properties as they reach a specific size range of 1–100 nm. The size and features of silver nanoparticles determine their properties, which include melting temperature, magnetic behaviour, redox potential, and colour controllable by size and shape modifications. The unique tunable optical properties (SPRs) of silver nanoparticles play an important role in most of their applications. Due to their good conductivity, chemical stability, and catalytic activity, silver nanoparticles have obtained

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a lot of attention in recent years. Its application is in various fields, including medical science, food, textile, water treatment, etc. Various applications, including surface-enhanced Raman scattering, (SERS) plasmonic sensing, catalysis, metamaterials, and bio-nanotechnology, where silver nanocubes have been used. The mono-dispersing property of Ag nanorods equips them with narrow plasmonic bands, which can be tuned in the near-infrared region, which helps to facilitate application in therapeutic techniques and biological analysis. Silver nano prisms are an example of 2D nanomaterials, which have gained great attention because of their application in the biomedical field. Triangular silver nanostructures are used for high-sensitivity quantitative detection techniques like surface-enhanced Raman scattering (SERS).

The size, shape, and chemical environment of nanoparticles influence their optical, electrical, magnetic, and catalytic capabilities. New techniques for creating non-spherical nanoparticles that are three-dimensional (cubic, pyramid, etc.) and planar (triangles, 5 or 6 diagonal, round surfaces, etc.) have been developed in recent years. The principal product of the reduction of one-capacity silver ions under regulated thermodynamic conditions will be spherical nanoparticles because spherical particles have the least surface area for a given volume, making them thermodynamically more stable. It has been shown that, despite sharing the same characteristic dimensions, nanoparticles with varied shapes have fundamentally diverse spectra. The acquired results can be applied to the development of a spectroscopic protocol for the identification of metallic nanoparticles' morphology and the generation of quantitative estimations of their distinctive dimensions [3]. Nanoparticles with controlled shapes carry definite surfaces and morphologies as their nucleation and growth are managed at the molecular level thereby developing well-defined model systems for a specific study. Shape control in noble metal nanoparticles will help to optimize their effectiveness for different kinds of applications. In the latest years, numerous techniques have been introduced for the synthesis of silver nanoparticles with different shapes [2]. The types of synthesized silver nanoparticles depend on the interaction with the stabilizer and surrounding medium and also on the method of preparation, which means that the reaction rate affects the shape of the synthesized silver nanoparticle. Results of the study revealed that the rate of reaction in cubic nanoparticles is 14 times higher than that in triangular nanoparticles and four times higher than in hemispherical nanoparticles [3]. In this review paper, a broad picture of differently shaped silver particles is presented, with a special focus on chemical synthesis.

Synthesis methods for the silver nanostructures having different shapes.

2. SILVER NANOCUBES

A number of differently shaped silver nanoparticles were synthesized so far; among them, silver nanocubes have gained great attention because of their unique morphology. They have unique optical, chemical, and electrical properties and hence they have been used for a different range of applications like sensing, plasmonics,

SERS, catalysis, etc. The following are the various synthesis methods adopted for the synthesis of silver nanocubes. The polyol process is a highly recommended method for the synthesis of silver nanoparticles with different shapes because this method is highly tunable and can control the geometry and size of the synthesized nanoparticles. Silver nano cubes were synthesized by modifying the ordinary polyol process with the addition of HCl [1]. In the typical polyol process, AgNO_3 was reduced by EG to produce Ag atoms. When the amount of silver atoms in the solution reaches supersaturation value, they start to nucleate and grow to nanoparticles dimension. By the addition of HCl into the solution, more HNO_3 was formed and which activates the backward reaction that tends to dissolve the initially formed solid silver. The explanation of the formation of perfect single-crystal nano cubes is as follows. The reduction of AgNO_3 by EG leads to the formation of both single crystal and twinned Ag seeds. The twinned Ag seeds are most abundant in the solution because of their ease of formation due to their lower surface energy. With the addition of HCl, the formation of HNO_3 increases and dissolves the initially formed twinned nanoparticles owing to its relative abundance. As the reaction progresses the concentration of HNO_3 in the solution decreases and the dissolution of Ag nanoparticles reduces and finally stops. Then the reaction enters the second stage of nucleation. As the nanoparticles grow in dimension either single crystal or twinned morphology were formed. The lower overall surface energy of twinned particles results in lattice distortion and defects and hence they exhibit stronger reactivity. So, they are highly susceptible to etching. As a result of the selective etching by HNO_3 on twinned Ag seeds, single silver nanocubes of high yield were produced.

In another method, silver nanocubes were synthesized with truncated corners and high yield by reducing the AgNO_3 by a modified polyol method by adding a trace amount of NaCl [4]. Here the reaction temperature is 148 °C. The nanoparticle produced in this process is relatively mono-dispersive in both shape and size. The dimension of the synthesized nanoparticle can be controlled between the range of 20 to 80 nm. Like the first method, the reduction of AgNO_3 by EG results in the production of Ag nuclei with single crystal and twinned particles. The addition of NaCl gives Cl ions into the solution, which enhances the selective etching of twinned particles and leaves the single-crystal particles only in the solution which were monodispersed in shape and size. By adjusting the time the size can be varied from 20 to 80 nm. By further optimization of reaction conditions more wide collection of sizes and shapes of nanoparticles can be obtained.

Silver nanocubes can also be prepared by modifying the polyol method by adding a small amount of sodium sulfide or sodium hydrosulfide [2]. We can shorten the reaction time significantly to 3-8 min from 16-26 h. Monodispersed silver nanocubes with 25-45 nm were rapidly produced on a large scale by adjusting the reaction time. Sulfide ions strongly interact with silver ions leading to the creation of Ag_2S , when the Ag_2S seed concentration is above the micromolar level, which acts as a catalyst for the reduction of Ag^+ similar to the autocatalytic reduction of the Ag cluster. The enhanced rate of reduction

leads to the fast growth of single-crystal Ag resulting in the evolution of Ag nanocubes rapidly. The progress of the growth of the Ag nanocube can be easily monitored by the color change of the solution from purple to black.

Silver nanocubes with high reproducibility can be synthesized by conducting the polyol process in dark conditions using HCl etchant [5]. Several investigations were made to reveal the reason for the poor reproducibility of silver nanocube synthesis by the same ingredients and under the same circumstances. Finally, they discovered the forgotten fact, the presence of sunlight. They tried to synthesize silver nanocubes by polyol process in the presence of HCl with daylight, cloudy daytime, and nighttime. They succeeded in synthesizing silver nanocubes with a high degree of reproducibility by simply blocking all the exposed light. This is because AgCl nanoparticles formed in the solution under the addition of HCl were photo reduced to Ag and which results in the production of non-cubic Ag nanocrystals. On the other hand, cubic, silver nanocrystals were produced by blocking the exposure of light. This method gives a simple idea to produce Ag nanocubes on large scale and reproducibility is very high.

One of the major drawbacks of Ag nanocrystals by the polyol process is that it is very subtle to the presence of impurities such as the small amount of Cl^- and $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions, amount of O_2 and water contents which causes the difficulty in replicating the synthesis process. There reported an effortless method of silver nanocubes in an aqueous environment by mixing CF_3COOAg with CTAC in the presence of ascorbic acid [6]. In the early stages of the synthesis AgCl nano, octahedra were formed as the source of elemental Ag. The reaction was performed at a low temperature of 60°C . In the interior and on the surface of AgCl octahedra, Ag nuclei were generated and which evolved to single crystal seeds and finally to Ag Nanocube. In this process, silver nanocubes with pointed corners and edges were synthesized due to the specific capping of Cl^- ions on the (100) facet. If FeCl_3 ions were present in the solution they act as the oxidative etchant to selectively remove twinned NPs which again facilitated the formation of high morphology yield Ag nanocubes.

Silver nanocubes were synthesized by adding a small amount of NaBH_4 and hydrochloric acid to the polyol method of synthesizing silver nanoparticles [7]. This is a rapid way to prepare silver nanocubes with uniform distribution. In the traditional polyol process, the reaction time was 16 to 24 h but here the addition of HCl and NaBH_4 increases the reaction rate, and the reaction time is reduced to 4-5 h. Also, this method increases the production rate, and uniformity in the shape of the monodispersed silver nanocubes with an average diameter of 40, 60, and 70 nm. The results of the study show that the size of the synthesized silver nanocubes strongly depends on the reaction time. When the reaction time was 240, 260, and 300 hours, the synthesized silver nanocubes have an edge length of 40, 60, and 70 nm, respectively. The mechanism of formation of AgNCB can be explained as when AgNO_3 in EG is injected into the EG solution containing HCl/NaBH_4 at a temperature of 140°C , EG will quickly reduce Ag^+ ions to Ag nucleus due to the increased reaction rate by the presence of $\text{Cl}^-/\text{NH}_4^+$ ions in the solution. PVP plays an important role

in shaping the synthesized Ag NPS. PVP molecules strongly bind with the formed silver nucleus.

In another method, silver nanocubes were synthesized by the silver mirror reaction modified with HTAB at 120°C [8]. The shape of the thus formed silver nanoparticle into a cubical one was accomplished by the introduction of HTAB. With the addition of HTAB, the Br^- ions reacted with $\text{Ag}(\text{NH}_3)_2$ to form AgBr through a reversible reaction with an equilibrium constant of 1.63×10^5 at 120°C . This resulted in a cathodic shift of $[\text{Ag}(\text{NH}_3)_2]^+/\text{Ag}$ reduction potential and hence the reaction could be proceeded more controllable at high temperatures to form silver nanocubes.

Silver nanocubes synthesized by different methods as mentioned above has a wide spectrum of applications. The Ag NCB synthesized by the fifth method is good for biological applications also they are used in SERS-based sensing and plasmonic applications due to the aqueous environment. Silver nanocubes synthesized by the 6th method are used in the SERS technique to detect the presence of Rd_3B with a LOD of 10-14. It shows that Ag nanocubes have promising applications in the biomedical field for the detection of biomolecules.

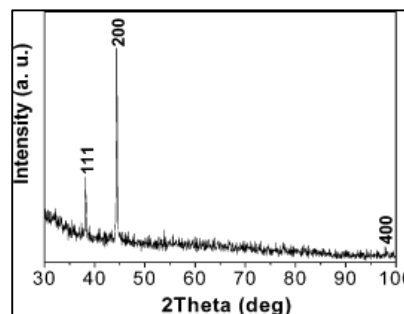


Fig. 1 – A typical XRD pattern of the Ag nanocubes [8]

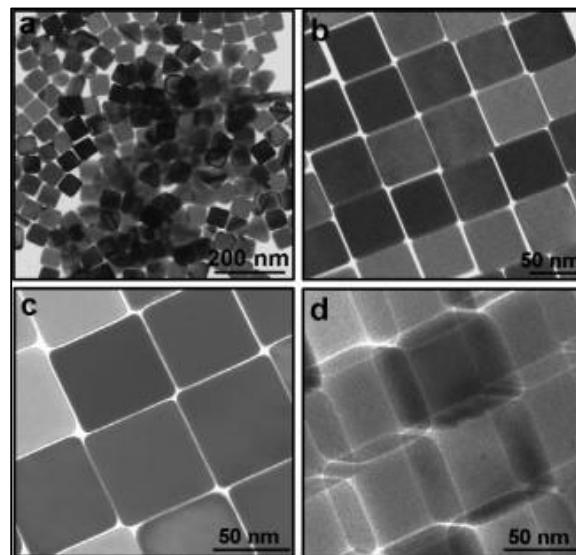


Fig. 2 – TEM images of Ag nanocubes: (a) with low magnifications; (b-d) with higher magnifications. Images c and d were recorded almost from the same several cubes, but image d was recorded after rotating the cubes by an angle of 30° [8]

3. SILVER NANORODS

One-dimensional silver nanostructures like silver rods and wires gain special interest because of their high electrical and thermal conductivity compare to their bulk counterpart. Silver is also used in a large variety of commercial products and its performance could be significantly and potentially enhanced by transforming them into one-dimensional nanoparticles of well-controlled dimension and aspect ratios. So many methods are reported for the production of silver nanorods of which chemical method for reduction is feasible and yields a large variety of morphologies and sizes. The following are different approaches adopted for the production of silver nanorods.

Silver nanorods were mainly produced by a growth process in the presence of metal seeds. In this growth process, small metal (silver) seeds were prepared first, and then it was used for the preparation of nanorods. In this method, silver nanorods were synthesized in two steps [10]. Firstly silver seeds of spherical shape were produced by reducing silver ions by NaBH_4 in the presence of TSC (trisodium citrate) to stabilize the prepared particles. In the second step, these prepared silver seeds were introduced into a solution containing more concentration of silver salt and a weak reducing agent ascorbic acid and CTAB surfactant. In explaining the mechanism of formation of Ag nanorods, since the ascorbic acid, a weak reducing agent cannot reduce Ag salt into Ag, the presence of Ag seed is needed. The role of CTAB surfactant is to block the growth of nanorods along its length by forming a bilayer structure around the nanorods in the growing phase. Two main concepts are reasonable in explaining the formation of rod-shaped and faceted particles. The first one is that the growth rate varies at different planes of the particle and the second one is that the growth process completes by the capping action of the stabilizer. The method is repeated at different temperatures and pH which control the aspect ratio and uniformity of the nanorods. The optimum value of pH and temperature for the synthesis of silver nanorods with monodispersity and high aspect ratio is pH 10.56 and 30 °C.

Silver nanorods having a high aspect ratio can be synthesized by plasmonic excitation of spherical silver seed particles with low energy light of 600 to 750 nm in a solution containing silver ions and TSC [11]. In this synthesis process, firstly spherical silver seed particles were produced by illuminating with the light of wavelength 254 nm into an aqueous solution containing silver nitrate precursor, bis(p-sulfonatophenyl)phenyl phosphine dihydrite dipotassium salt (BSPP), TSC and NaBH_4 . Spherical nanoparticles with pentagonal twin structures were produced by this method. Secondly, silver nanorods were prepared from these seed particles by adding these particles into an aqueous solution containing a mixture of AgNO_3 and trisodium citrate and then irradiating it with the light of wavelength 600-750 nm for 24 h. This light-mediated reaction yields silver nanorods of diameter about 67 nm and a length of about 350 nm these nanorods are having pentagonal cross-sections and they multiply twinned along their length.

High-quality silver nanorods with diameters less than 30 nm were prepared by using small pyramidal or decahedral seeds (Au) in a specific location of nanorods.

The silver nanorods synthesized by this method are highly tunable with low size distribution and have an aspect ratio of 2.5-11. This is also a two-step process [12], in the first step, Au bipyramids or decahedra with different dimensions were prepared by the already reported method [13]. Next, the silver nanorods were grown in these Au seeds by the reaction of AgNO_3 and ascorbic acid at 60 °C in the presence of CTAC. The dimensions of the nanorods can be varied by changing the amount of AgNO_3 in the solution and there is a linear increase in the length of nanorods with the amount of AgNO_3 added. The formation of silver nanorods was confirmed by taking the UV-Vis-NIR absorption spectra and there is a redshift in the LSPR peak with an increase in aspect ratio. When we use bipyramidal seeds, they are located at the center of the silver nanorods while decahedral seeds are at the tip and all the obtained nanorods are having a pentagonal cross-section.

Thermal regrowth in an aqueous solution of decahedral silver nanoparticles by using citrate as a reducing agent at 95 °C gives faceted pentagonal, monodispersed size-controlled silver nanorods [14]. The diameter of nanorods depends only on the size of the decahedral seed and the length depends on the amount of newly added silver into the solution. The silver nanorods are synthesized in two steps as follows. In the first step, decahedral Ag nanoparticles were prepared by mixing sodium citrate, L-arginine AgNO_3 in deionized water and which is reduced by the strong reducing agent NaBH_4 with continuous stirring, and then it was exposed to blue light for 2 to 15 h [14]. In the second step, these prepared decahedral seeds were separated from the solution and added to a reacting solution containing sodium citrate, water, and PVP at 95 °C with continuous stirring and followed by the immediate addition of AgNO_3 . The volume of this added silver nitrate decides the length of the nanorod. A very small increment in the volume of added AgNO_3 results in a large change in aspect ratio. In this growth process, the function of PVP is to improve the stability and yield of the nanorods. The formation of nanorods can be visualized by the color change of the solution from orange or red to yellow or yellow-orange and which could be confirmed by the LSPR peak shift towards the longer wavelength side.

Silver nanorods of varying aspect ratios can also be prepared by a seed-mediated approach to growth using spherical silver nanoparticles [15]. In the first part of this process, spherical silver seed particles of 4nm diameter were produced by the chemical reduction of silver nitrate by NaBH_4 and sodium citrate, which act as the stabilizer of the nanospheres. To make nanorods of varying aspect ratios, in the second step, AgNO_3 was reduced by ascorbic acid, a weak reducing agent in the presence of CTAB (the micellar template) and NaOH. The concentration of seed particles and the relative concentration of base and silver ions determine the aspect ratio of the nanorods. The function of CTAB is to produce nanorods with high yields. The pH of the solution should be higher than 11.8, the pKa of ascorbic acid, for the production of nanorods, that is why NaOH is used in this synthesis process. The formation of Ag nanorods was confirmed by a redshift in the UV-vis absorption spectra due to the longitudinal LSPR band of nanorods. The aspect ratio of nanorods increases with a decrease in seed

concentration. This method helps us to produce silver nanorods with high reproducibility and varying aspect ratio (2.5 to 15).

The aspect ratio and diameter of the silver nanorods can be controlled effectively by another synthesis method [16]. This is a seedless template-less approach to producing high-quality Ag nanorods at moderate temperatures (100 °C). In this method, silver nanorods were synthesized by reacting AgNO_3 and TSC along with of a capping/stabilizing agent, sodium dodecyl sulfonate (SDSN) which controls the diameter and aspect ratio.

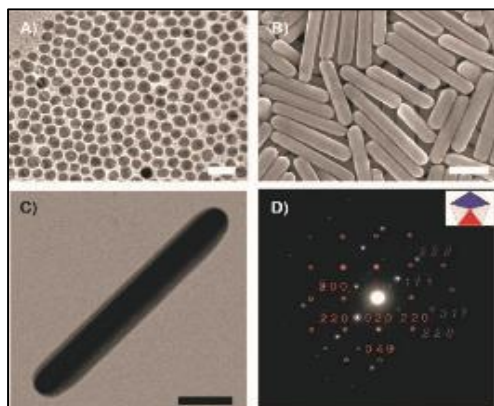


Fig. 3 – (A) TEM image of the silver seed nanoparticles. (B) SEM and (C) TEM images of silver nanorods synthesized with a bandpass filter centered at 600 (20 nm). (D) Selective-area electron diffraction (SAED) pattern of a single silver nanorod, showing the interpenetrating [100] (red) and [112] (blue) zone patterns. (Scale bars: 100 nm [11])

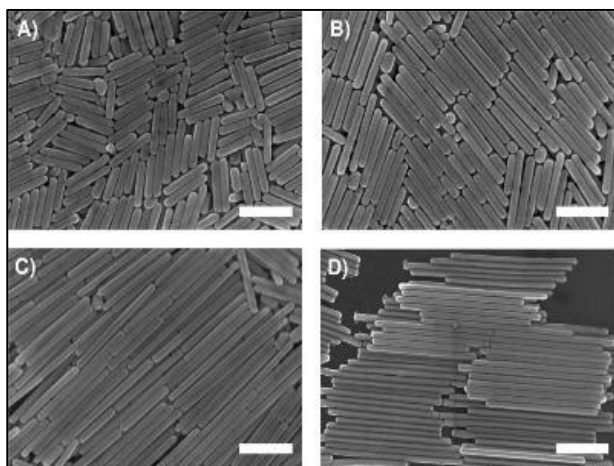


Fig. 4 – SEM images of the silver nanorods (scale bars: 400 nm) generated with the bandpass filter centred at (A) 600 ± 20 , (B) 650 ± 20 , (C) 700 ± 20 , and (D) 750 ± 20 nm [11]

Silver nanowires can also be synthesized from this method by controlling the concentration of TSC. However, the concentration of SDSN is very important in shaping the nanorods. At a very low concentration of SDSN, nanoparticles aggregate easily and at a very high concentration, the nanoparticles became spherical in geometry. That is the concentration of SDSN is the key factor determining the aspect ratio and diameter of nanorods. By increasing the concentration of SDSN the average diameter of nanorods decreases while the quantity increases. Another important factor is that the resulting

nanorods have a crystalline structure which means that the presence of SDSN in the solution dynamically controls the growth process of nanorods.

Because of their prominent optical properties, silver nanorods have diverse optical applications in plasmonics, sensing and calorimetric detection, and metal-enhanced fluorescence. They are also used as SERS substrates in determining dye molecules. Silver nanorods have some biological applications including cytotoxic coatings, in improving the quality of milk and have some antimicrobial applications.

4. SILVER NANOWIRES

Silver nanowires are one-dimensional nanostructures with diameters between 5-100 nm and several micrometers in length. They have a high aspect ratio, of the order of 400. They have excellent electrical conductivity and hence they are used in electronic, nanoelectromechanical, and optoelectronic devices. They are also used for metallic interconnections [17].

Silver nanowires were synthesized by the polyol method [18] in the presence of NaCl. The morphology of the nanowires depends on the reaction temperature, the molar ratio of PVP and AgNO_3 , the amount of NaCl stirring rate, etc. In this typical synthesis process, EG solution of PVP was prepared and then NaCl was added to it and the solution is heated to 170 °C. At the same time, EG solution of AgNO_3 was prepared and added drop by drop into the first solution by using an injection pump with continuous stirring. The mechanism of formation of Ag nanowire can be explained as during the introduction of silver ions into the solution, they are reduced and Ag atoms start to nucleate homogeneously. The PVP molecules present in the solution start to adsorb on the as-synthesized silver nanoparticles and they tend to remain on the nanoscale. The process continues and some of them start to solvate into the solution and then grow to larger nanoparticles via Ostwald ripening [19]. Thus, formed nanoparticles mainly have two planes viz (100) and (111). PVP passivate the (100) multi-twin facet by binding it and leaves the (111) plane active and they grow anisotropically along the (110) plane. The formation of the nanowire was confirmed visually by the change of color of the solution. Along with nanowires some nanocubes and pyramids were also formed during synthesis.

A parametric study reveals the following information. The effect of temperature on the synthesis process was studied and it is found that there is a critical temperature (170 °C) for the synthesis of high aspect ratio nanowires and below which low aspect ratio nanowires are synthesized. At a very high temperature, the synthesis process results in the formation of very few high aspect ratio nanowires (of length 60 μm) and a large amount of low aspect ratio nanowires. The injection rate also affects the morphology of nanorods. A slow and fast injection rate leads to the evolution of micro silver particles along with nanowires. The high PVP/ AgNO_3 molar ratio leads to undesired silver structures along with nanowires. In the absence of NaCl, only silver nanoparticles were formed and an excess amount of NaCl in the solution resulted in oversaturation, and micro-sized particles starts to grow dominantly in addition to nanowires. Slower and faster stirring also leads to an undesired result.

Silver nanowires were synthesized on large scale by polyol process with seed(Ag/Pt) mediated growth process [20]. This synthesis technique produces silver nanowires having diameters ranging from 30-40 nm. The morphology and aspect ratio can be varied by controlling reaction conditions like reaction temperature, the molar ratio of reactants, seeding conditions, etc. The nanowire synthesis involves two steps viz formation of Ag/Pt seeds and followed by growing of nanowires. In the first step, Ag/Pt nanoparticles were formed by reducing $\text{AgNO}_3/\text{PtCl}_2$ by EG at 160 °C. Thus formed Ag/Pt nanoparticles function as seeds for growing silver nanowires through heterogeneous nucleation. In the second step, silver nanowires are synthesized by the reduction of AgNO_3 with ethylene glycol in the presence of PVP and Ag/Pt seeds. In the typical reaction process, Ag/Pt seed solution is taken and ethylene glycol solution of AgNO_3 and PVP is taken separately and added to it dropwise simultaneously with continuous heating at 160 °C and stirring. Color change of the solution indicates the formation of nanowires. The formation mechanism of nanowires in this technique is almost similar to the first one. Here the function of the metal seed is to determine the diameter of nanowires and it acts as the nuclei for the following growth of silver nanowires. Parametric influences are i) the increase in temperature reduces the aspect ratio of nanowires ii) the increase in the number of seeds slightly reduces the diameter of nanowires iii) at higher PVP/ AgNO_3 molar ratio (~ 18) silver nanoparticles of size about 20 nm were formed as the main product and nanorods or wires were not obtained.

In another method, silver nanowires can be produced by a seed-mediated polyol process in the presence of CTAB [21]. In this method, the author also tries to investigate the growth mechanism and supporting evidence. In this typical synthesis procedure, silver seeds of 3-5 nm were added to the solution containing CTAB[21], along with AgNO_3 . With the addition of reducing agents like Ascorbic acid into this solution, metal seeds act as a nucleation site and nanowires begin to grow under CTAB confinement which maintains the growth of silver nuclei in one dimension. The cross-section of nanowires formed by this method is pentagonal. The mechanism of nanowire growth is the same as explained above. Two critical components of this growth process are decahedral multi-twin particles and PVP. Silver nanorods produced by this method have a pentagonal cross-section and 5-fold twin structure and they are believed to be evolved from decahedral MTP with the help of PVP. The proper concentration of PVP and maintenance of the pentagonal symmetry of twin structures is important in the formation of silver nanowires. The parameters which influence the morphology of nanowires include concentration, temperature, etc. When concentration is relatively high, quasi-spherical NPs were obtained because high PVP concentration was not favorable to produce decahedral MTP and it also results in the development of a thick coating over MTP's entire surface. When the temperature was lower than 110 °C, no nanowires were obtained. The optimum temperature for the transformation of MTPs into nanowires was found to be about 160-170 °C.

Large-scale production of uniform diameter silver nanowires with and various aspect ratios were produced

by the self-seeding polyol process [22]. In this process, silver nanowires were produced by reducing AgNO_3 by EG, which acts as both reducing agent and solvent in the presence of PVP. In the first step, ethylene glycol was heated in an oil bath to 160 °C and then EG solution of AgNO_3 and PVP were injected into it dropwise simultaneously with stirring. The solution color changes gradually from yellow to a turbid gray color indicating the formation of Ag nanowires. The reaction mechanism is the same as that mentioned above. The aspect ratio and morphology of the produced Ag nanowires depend on the PVP/ AgNO_3 molar ratio. The length of nanowires decreases with an increase in molar ratio and yield became lower. It is also found that temperature play a crucial role in the production of Ag nanowires. At high temperatures, silver nanowires having a low aspect ratio would be formed. At very high temperatures, irregular-shaped silver nanoparticles were produced.

Crystalline silver nanowires can also be prepared in water even in the unavailability of surfactant or polymer and external seed [23]. In this process, silver atoms were reduced from silver ions by the reaction between AgNO_3 and sodium citrate at 100 °C in the presence of NaOH. In this typical experiment, first, prepare an aqueous solution of AgNO_3 and NaOH and to this solution freshly prepares TSC in water is added quickly, with heating and continuous stirring. Another solution of AgNO_3 and NaOH in water with different volume and molarity were prepared and boiled. Both the solutions were mixed and heated to 60 °C with stirring. The change of color of the solution indicates the formation of the nanowire. NaOH is an important factor that determines the morphology of nanowires. KOH or NH_4OH also plays the same role as NaOH in this process. This means that the presence of OH^- ion rather than the Na^+ ion controls the nanowire growth. An increase in the amount of NaOH decreases the nanowire yield. Because by adding more NaOH, the pH of the solution increases above the pKa of citrate (6.4) they were monoprotonated and leading to a weak complexing agent and allowing nanoparticles to agglomerate.

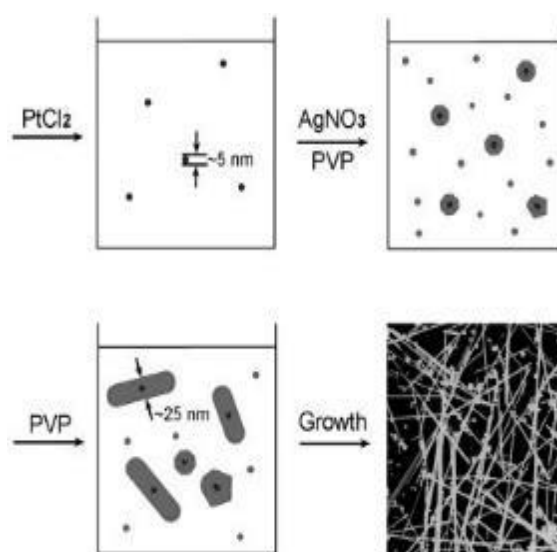


Fig. 5 – Schematic illustration of the experimental procedure that generates silver nanowires through a Pt-seeded polyol process [20]

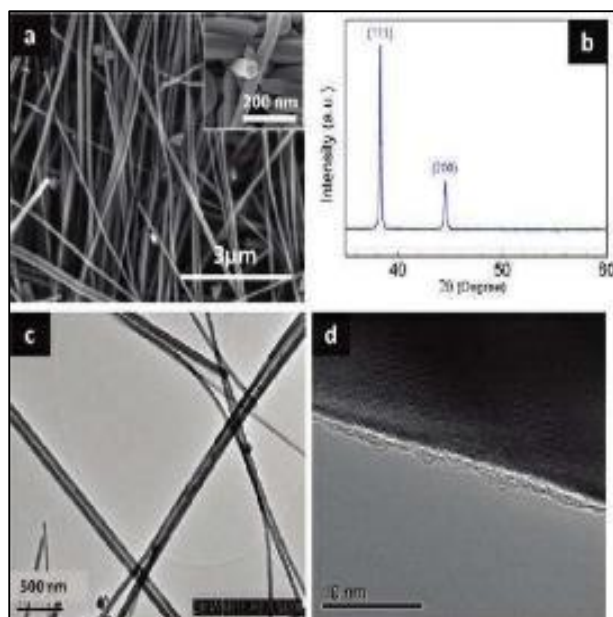


Fig. 6 – (a) SEM image of silver nanowires, inset shows their pentagonal crosssection. (b) XRD pattern for the nanowire (c) low and (d) high-resolution TEM image [18]

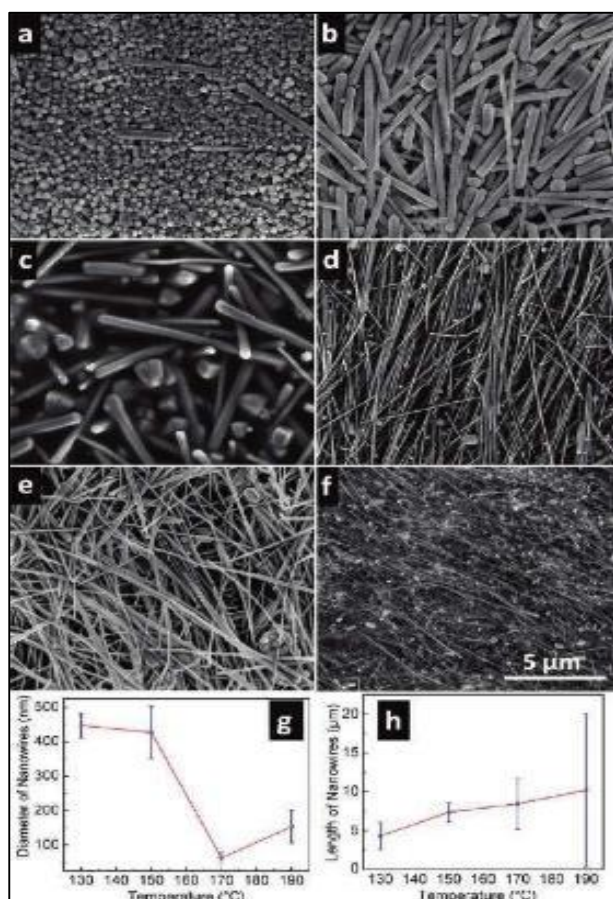


Fig. 7 – SEM images of Ag nanowires synthesized with different injection rates of (a) 1, (b) 3, (c) 5, (d) 6, (e) 8, and (f) 300 mL/h. All scales are the same. Changes in (g) nanowire diameter and (h) length with injection rate are also shown [18]

In comparison with other silver nanoparticles, silver nanowires are extremely different in nature. They have

unique thermal, electrical and optical properties. They have remarkable absorption and reflection of light. They are highly conductive and can be dispersed in water, EG and ethanol IPA, etc. They are highly conductive and hence they are used in computer boards, touchscreen displays, high-intensity LEDs, etc. they have antimicrobial properties so they are used in sterile equipment, clothing, bandages, cosmetics, and paints because of their unique optical properties they were used in Raman spectroscopy, optic limiters, medical imaging, solar films, surface plasmons, etc.

5. SILVER NANOTRIANGLES

Silver nano triangles come under the category of two-dimensional nanoparticles known as nanoplates. They exhibit unique optical properties by showing intense surface plasmon peaks which differs them from silver nanorods or spheres. They are widely used in optical and pharmaceutical devices and are also used in chemical and molecular detections, in the area of optical sensors, chemical analysis, etc. The following are various synthesis routes developed for the production of silver nano triangles.

Silver nano triangles were synthesized by the reaction of AgNO_3 , ascorbic acid and PVP by bearing silver seeds in the solution at room temperature [24]. The silver seeds act as a nucleation site and PVP as a capping agent and both of them play a crucial role in determining the shape and edge length of the triangle. The typical synthesis process involves two steps. In the first step, silver seed particles were synthesized by the reducing of AgNO_3 with NaBH_4 in the presence of trisodium citrate in water. Secondly, AgNO_3 , PVP and seed solution were mixed with continuous stirring, and ascorbic acid was added dropwise to it. The edge length of the nanotriangle depends on the ratio of PVP and AgNO_3 and also on the amount of silver seed. When the volume of silver seed increases the average edge length decreases and it gradually turned to hexagonal truncated nanoplates and even turned to circular Nano discs. The varying dosage of PVP also tunes the edge length, which decreases with an increase in the PVP/ AgNO_3 molar ratio. This is because, at high PVP concentration, the (100) facets of silver seeds were selectively bounded by a large number of PVP molecules and which inhibit the growth of nanocrystals. The edge length of nano triangles synthesized by this method can be tuned from 50 to 260 nm. The SPR peak of silver nano triangles varied with edge length and shows three distinct bands which correspond to the in-plane dipole, quadrupole, and out-plane quadrupole plasmon resonance (Wu et al., 2015).

The fast and simple production of silver nano triangles was done by the chemical reduction of AgNO_3 with NaBH_4 and sodium citrate followed by irradiation of light [25]. In this synthesis procedure, firstly NaBH_4 solution was added drop by drop to a solution containing citrate and AgNO_3 with vigorous stirring. Then it was irradiated by a sodium vapor lamp ($\lambda = 589 \text{ nm}$). The pH of the solution was adjusted by adding various amounts of NaOH. The detailed investigation of this procedure was done under different reaction conditions and from which it is concluded that the formation of silver nano triangles was significantly affected by NaBH_4 concentration and the limiting value is 0.25 nM, below which no

triangles were formed. The absorption spectra of samples prepared at different pH values were taken and from which it is clear that a pH 9 is most suitable for silver nanotriangle formation. The experiment was performed at different wavelengths of light irradiation and it is found that reduction without light irradiation leads to the formation of spherical nanoparticles. The shapes of nanoparticles formed varied with the wavelength of light and it is observed that the yellow light (sodium lamp) is most suitable for nanotriangle formation. In total, the optimum condition for the production of silver nano triangles by this method is a 0.25 mM concentration of NaBH_4 , pH9, and yellow light irradiation.

In another procedure, silver nano triangles were produced by seed-mediated growth in water by the reaction between AgNO_3 and ascorbic acid [26]. In this method, some modifiers such as PVA, citrate, polystyrene sulfonate, etc were used. Thus, formed silver nano triangles have well-defined SPR peaks which can be easily tuned from visible to NIR region. In this synthesis process, firstly spherical silver seeds were prepared by the reduction of AgNO_3 with NaBH_4 in the presence of sodium citrate, which was then used as a catalyst for the reduction of AgNO_3 by ascorbic acid in an aqueous solution in the presence of PVA/PVP. The formation of silver nanotriangle depends on the ratio of Ag^+/Ag seed and the concentration of PVA. A parametrical study shows that citrate ions play a vital role in the formation of nanoplates because at high concentrations they bind the (111) plane of particles and prevent its growth. The concentration of PVP does not play a major role in forming Triangular SNPs. The Triangular SNPs prepared at higher temperatures were more stable than that prepared at a lower temperature. The disadvantage of this method is that the sample contains both triangular and spherical particles. This problem was resolved by adding polymers (polystyrene sulphonate) during seed preparation time. This polymer-treated seed-mediated reduction produces triangular nanoparticles only. Due to the tunability of SPR peaks of nano triangles prepared by this method they are widely used in optical applications like biological sensing.

Truncated silver nano triangles were prepared by the reduction of silver nitrate by hydrazine in an aqueous solution in presence of sodium citrate [27]. Both triangular and spherical nanoparticles were formed in this method and the spherical ones turned triangular by aging. In this typical synthesis process, an aqueous solution of silver nitrate and sodium citrate was made, to which hydrazine solution was added dropwise with vigorous stirring. The color of the solution first became yellow and then it turned green indicating the formation of truncated triangular nanoparticles. The absorption spectrum analysis in the UV-Vis region shows that there are four distinct peaks of which peaks at 334 nm, 672 nm, and 740 nm region correspond to out-of-plane quadrupolar resonance, in-plane dipolar, and in-plane quadrupolar resonance respectively. The fourth intense peak at 404nm corresponds to spherical particles.

When the concentration of AgNO_3 increases the synthesis leads only to the production of spherical particles which turns into triangular one by aging. The effect of citrate concentration on the formation of TSNPs was studied and it is found that they were formed at any concentration of citrate. The effect of the pH of the solution

in the synthesis process was also studied at pH ranging from 2-12 and it shows that at very low pH, no triangles are formed and when pH increased from 4-8, the formation of nano triangles increases, further increase in pH reduce the production of nano triangles. With the increase in hydrazine concentration, a greater number of smaller nano triangles were formed.

The unique optical property of silver nano triangles arises from their sharp corners and edges. Due to this, it shows that the SPR of three distinct peaks corresponds to an in-plane dipole, quadrupole, and out-plane quadrupole plasmon resonance. These peaks can be shifted toward shorter or longer wavelength sides by decreasing or increasing their edge length and which can be easily done by adjusting reaction conditions and parameters during the synthesis process. This easy tuning of SPR peak finds application in the field of optical sensing, SERS detection of biological molecules, calorimetric detection of heavy metals, etc. They also have applications in the detection of volatile compounds like chlorides. They have catalytic activity in the shape-dependent reduction of CO_2 and CO.

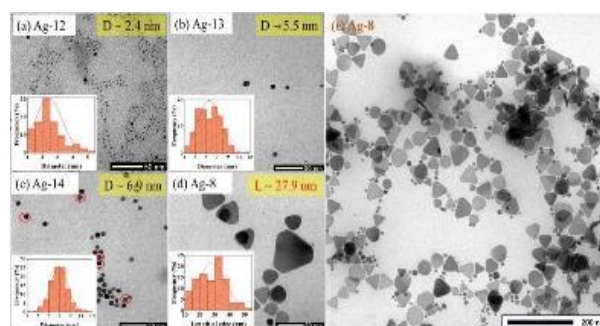


Fig. 8 – TEM images of Ag NPs solutions under different light irradiations: without light (a), UV light (b), solar light (c), and sodium lamp light (d-e) with the particle size distributions have inserted [25]

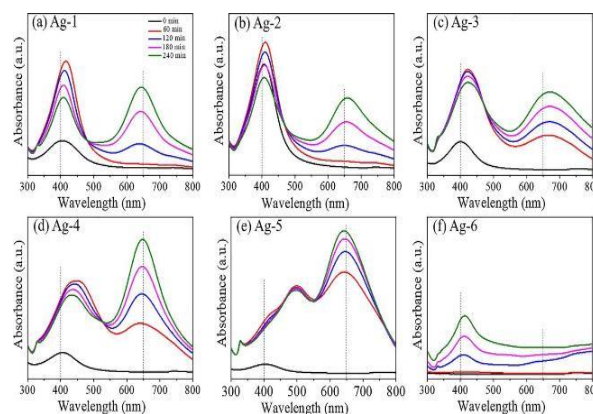


Fig. 9 – Absorption spectra of Ag NPs versus photoreduction time at various NaBH_4 concentrations: 10 mM (a), 5 mM (b), 1 mM (c), 0.5 mM (d), 0.25 mM (e), and 0.125 mM (f). T.H.N. Nguyen, et al. Colloids and Surfaces A 594 (2020) 124659 [25]

6. SILVER NANOSPHERES

Spherical and quasi-spherical silver nanoparticles have been gaining the interest of the scientific community due to their optical properties and applications. They are available in sizes in the range of 10-100 nm and

correspondingly their SPR peaks vary from 390-490 nm. There are so many synthesis routes adopted in their preparation, the following are a few of them.

There is a new route for the synthesis of silver nanospheres by polyol process in which PEG is used to reduce silver salt in the presence of PVP [28]. Here PEG acts as both solvent and reducing agent and PVP acts as a capping/stabilizing agent. In this synthesis process, a solution of silver nitrate in water was injected into a hot PEG solution of PVP at 80 °C under stirring. The solution's color changes from colorless to light yellow. After completion of the reaction, it is transferred to an autoclave and heated to 260 °C for 24 h, then it was cooled at room temperature in the air. In this method, the shape and size of the nanoparticles can be changed by adjusting the temperature. At high temperatures (200-260 °C) the nanospheres were dominated in the solution and narrow size distribution. On reducing the temperature, the number of nanospheres in the solution decreases and irregularly shaped nanoparticles in the solution increase, and size distribution also gradually tends to widen on decreasing temperature. Extinction peak is blue shifted on decreasing temperature. The optimum PVP/AgNO₃ molar ratio for the preparation of silver nanosphere in this method is 8 for uniform distribution of size. On increasing the molar ratio, the uniformity was lost and the size distribution became wider. On lowering the molar ratio, the product contains nanospheres and some irregularly shaped nanoparticle.

Another reported method of synthesis of silver nanospheres in CTAB/NH₃ is by reducing an aqueous solution of silver nitrate with L-ascorbic acid [29]. In the typical reaction procedure, a solution of AgNO₃ in water was vigorously stirred at room temperature, then CTAB solution was rapidly injected into it with stirring, the solution's color changed to milky blue, and ascorbic was then slowly introduced into it and the color changes to deep green indicating the formation nanospheres, nanoparticles were separated from the solution by centrifuging. The mean diameter of the nanospheres thus formed is of the order of 30 nm. The function of ammonia in this reaction is to neutralize the acidic effect contributed by CTAB in the reaction environment and to vary the pH of the solution.

Single-crystal silver nanospheres were prepared with a modified polyol process by adding a small amount of NaCl into the reaction medium [30]. In this process, PEG serves as both a reducing agent and solvent of precursor. Single crystal nanospheres were obtained by oxidative etching and dimerization with the help of added NaCl. The amount of NaCl imparts a vital role in the growth of nanospheres. When the amount of NaCl is too low, both single crystal particles and twinned particles were formed, but a larger amount of NaCl addition results in the clustering of particles and results in the reduced yield of nanospheres.

In another method, silver nanospheres were produced by a simple procedure of reducing silver nitrate with trisodium citrate without the help of any capping or stabilizing agents [31]. In this reaction mechanism, they tried to analyze the effect of the amount of citrate on the formation of nanospheres by simply noting the color change of the solution and also by taking XRD and

UV-vis spectra of samples. Here the molar ratio of citrate to AgNO₃ was kept constant (10:1). The solution's color changes from light yellow color to dark orange on increasing the amount of TSC in the solution and the TEM image shows that the size of nanoparticles increases from 20-30 nm on an increase in the amount of TSC. The particles formed were more spherical when the amount is larger.

The UV-Vis absorption spectrum of spherical nanoparticles shows maximum absorbance at about 400nm and thus they can be used as a substrate in SERS. They have powerful toxic behavior toward microorganisms and thus they are extensively used in the field of biomedical research, in drugs, and used as antimicrobial agents [31]. They are also used to treat burns and infections. Spherical silver nanoparticles can also be used as bioimaging labels for finding human cancer cells. They have some photocatalytic activity when it is on some metal oxides like zinc.

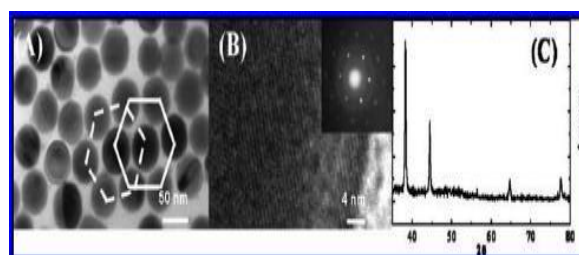


Fig. 10 – (A) TEM and (B) HRTEM images of the silver nanospheres prepared at 260 °C for 24 h with molar ratio of PVP to AgNO₃ of 8, and the SAED pattern (inset) of an individual silver nanosphere with a diameter of about 50 nm. (C) Powder XRD pattern taken from the same batch of sample [28]

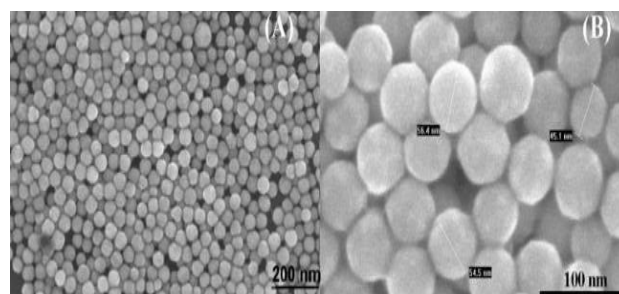


Fig. 11 – (A) Low- and (B) high-magnification SEM images of the silver nanospheres prepared at 260 °C for 24 h with molar ratio of PVP to AgNO₃ of 8 [28]

7. SILVER NANO DECAHEDRONS

Silver nano decahedrons were prepared by the photochemical method by the irradiation of a blue light-emitting diode. The evolution of nano decahedrons was studied at different irradiation times (0-72 h) and the results of this study indicated that silver nano decahedrons evolved from silver seeds after 6 hours of light-emitting diode irradiation. In the synthesis process AgNO₃, TSC, PVP, and L Arginine were mixed with Milli Q water and stirred magnetically. Then to this mixture, NaBH₄ was added rapidly. The solution color rapidly changes to light yellow color and, then yellow color, indicating the formation of AgNPs. The as-synthesized AgNPs solution was exposed to blue LEDs for 6, 12, 24, 48, and 72 h, and the color of the solution changed from

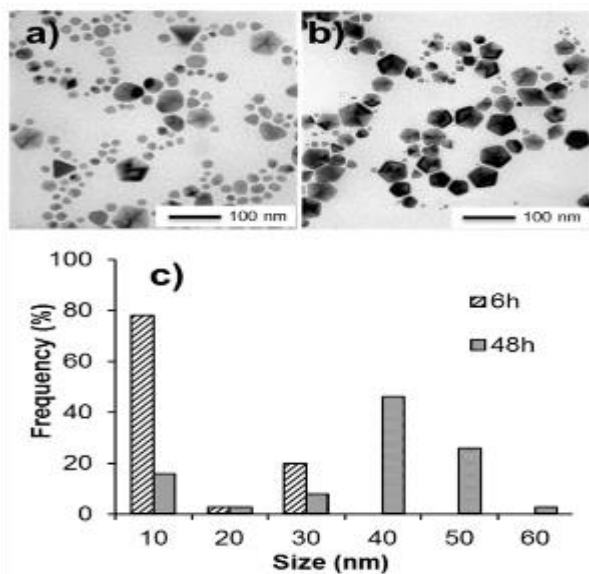


Fig. 12 – (a, b) TEM images and (c) particle size distribution of silver nanoparticles after 6 h and 48 h of irradiation [32]

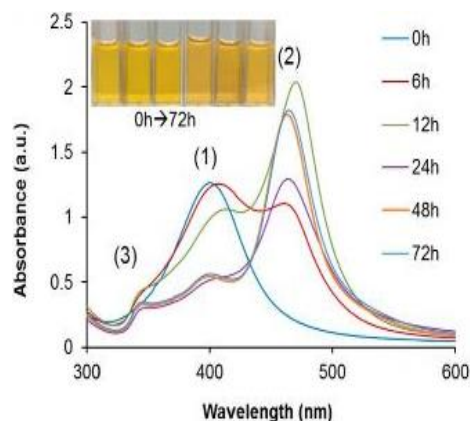


Fig. 13 – UV Vis spectra of silver nanoparticles at different LED irradiation times [4]

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Контрольований синтез наночастинок срібла різної форми та їх застосування – огляд

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Нині наночастинок благородних металів займають важливе місце в науці та техніці завдяки їх легкому синтезу, легкості модифікації поверхні та чудовій біосумісності, що пропонує незліченну кількість застосувань у багатьох галузях науки. Хоча благородні метали використовуються для різноманітних застосувань, наночастинок срібла викликають велику увагу завдяки своїм унікальним фізичним і хімічним властивостям, таким як оптичні, електричні, теплові, біологічні та каталітичні властивості. Більшість цих властивостей залежить від форми та розміру синтезованих наночастинок срібла. Виробництво наночастинок срібла з різними формами сьогодні дуже поширене, так що ми можемо контролювати різні властивості, особливо в галузі медицини, як вважають багато дослідників. У цій статті ми представляємо огляд синтезу наночастинок срібла різної форми різними методами та їх специфічне застосування.

Ключові слова: Срібло, Наночастинка, Форма.