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Synthesis and Characterization of Silver Nanoparticle by Chemical Route Method

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Abstract

Nanoparticles being the smallest unit, ranging between 1 to 100 nm in size play an important role in various fields and show distinct physical, chemical and biological properties from their bulk counterparts due to higher surface volume. In this work, silver Nanoparticles were synthesized by Sonication method through vibration and elevated temperature, in which silver nitrate as a metal precursor and sodium citrate as a reducing agent were used. The synthesized silver Nanoparticles were characterized by UV-visible spectroscopy and Scanning Electron Microscopy (SEM). The liquid solution containing nanoparticles were used for UV visible spectroscopy which revealed the formation of silver Nanoparticles by exhibiting the typical surface Plasmon absorption. The formation of silver nanoparticles was observed with maxima at 418–447 nm from the UV-Vis spectrum. Silver nanoparticles in powder form were used to take SEM image to study the morphological features of nanoparticles as well as it also gives the size of the nanoparticles to check whether the synthesized nanoparticles are within the Nano scale range. Observations from SEM image reveal that the nanoparticles obtained by chemical route technique are in the range between 75–90 nm.

Keywords: *Nanoparticle, UV-spectroscopy, SEM image, chemical route.*

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INTRODUCTION

In modern research, nanotechnology plays and important role in design, synthesis and manipulation of nanoparticles, nanowires, nanostructured materials, nanomaterials and so on that range between 1–100 nm in dimensions[1]. Materials developed in the nanoscale range were applied in numerous fields such as solar energy conversion, catalysts, medicine and water treatment, because the behaviors of nanomaterials were totally different when compared to that of their bulk material[2].

Nanomaterials were synthesized by two approaches namely: Top-down approach (reducing the bulk materials to nanoscale range) and Bottom-up approach (combing atoms and molecules in nanoscale range to form functional devices)[3]. Newer developments in the nanotechnology has paved the way for novel fundamental and applied frontiers by synthesizing nanoparticles to obtain a better and remarkable properties change in the optoelectronic, mechanical and electrical behavior[4]. Nanomaterials were synthesized by various methods that includes, mechanical milling, lithography, chemical route and biological reduction methods which forms the green synthesis methods[5].

Nanotechnologies deals with design, production, characterization, and application of structures, devices and

systems by controlling the shape and size of the materials at nanometer scale level. Due to the unique properties of nano-sized materials, researchers were developing various nanomaterials and are studying their properties that can be applied to various areas[6].

Based on the applications where the nanomaterials were used, generally nanoparticles are designed to meet the purpose with surface modifications[7]. From the wide chemical nature, morphology and the medium in which the nanoparticles were present and the state of dispersion of these particles, various nanoparticles can be synthesized, due to which this field is an important field in research nowadays[8].

Silver nanoparticles can be incorporated in various real time applications, particularly antifungal and antimicrobial activity due to its unique properties, which depends on size and shape of the nanoparticles produced. For synthesizing and stabilizing silver nanoparticles several physical and chemical methods were followed, which depends upon the particle size required. In chemical approach technique for synthesizing silver nanoparticles, chemical reduction route uses variety of methods such as organic and inorganic reducing agents, electrochemical techniques, physicochemical reduction, and radiolysis. Silver nanoparticle shows antifungal effects, in plaque reduction assay, antimicrobial activity, antifungal property, coatings for solar energy absorption and intercalation material for electrical batteries, and for biological implants and bone prosthesis.

LITERATURE REVIEW AND PROBLEM IDENTIFICATION

Nanoparticles that are synthesized by various routes have been characterized in order to determine the range of particle sizes by researchers, so that the nanoparticles can be applied in various fields for suitable applications. Most of the researchers nowadays are synthesizing nanoparticles by biological synthesis method but in this work we have synthesized various sized silver nanoparticles by chemical reduction method using ultrasonic mixing bath.

Sahoo *et al.*[9] synthesized silver nanoparticles by reducing silver nitrate using various sugars such as glucose, fructose, lactose, and sucrose at 55–60°C using two stabilizing agents, polyvinyl pyrolidone (PVP) and gelatin and concluded using PVP, better control of particle size was obtained, whereas a mixture of PVP and gelatin resulted in sea urchin kind of structure. Aashritha[10] synthesized silver nanoparticles in different alcoholic medium in the presence of trioctyl phosphine oxide as the capping agent at room temperature for 1 hour and found that the formation of nano products by this method is rapid, simple and stable. Alahmad[11] using wet chemistry method; synthesized silver nanoparticles, with sizes going from 16 to 47 nm using silver nitrate and dextrose as reducing agent; and PVP as a stabilizer.

Hussain *et al.*[12] discussed the effect of aniline concentrations on the growth and size of silver nano-crystals using aniline and silver nitrate as reductant and oxidant, respectively. Guzman *et al.*[13] prepared silver nanoparticles by chemical reduction method and found that the typical surface plasmon absorption maxima at 418–420 nm from the UV-Vis spectrum. Researchers have also synthesized silver nanoparticles from different biological extracts available naturally[14] and from the colloidal solutions[15–17]. Apart from silver nanoparticles, researchers have also shown interest in the synthesis of silver nanorods [18] and silver nanowires[19], which are the other forms of nanostructures[20]. Silver nanoparticles synthesized were applied mainly for antifugal and antibacterial action[21–24].

From the literature survey carried out, it is observed that previously researchers had synthesized silver nanoparticles within the range of 100 to 500 nm. In this work, chemical route method is chosen to synthesize silver nanoparticles within 100 nm range using silver nitrate and tri-sodium citrate. Instead of magnetic stirrer, ultrasonic mixing bath is used to obtain efficient result when compared to magnetic stirrer. Reduction in time taken for synthesizing nanoparticles is performed by using ultrasonic mixing bath than using magnetic stirrer and mechanical stirrer.

METHODOLOGY

Synthesis of silver nanoparticles were carried out in two step process i.e. synthesis of nanoparticles and extraction of nanoparticles. First, silver nanoparticles were prepared in liquid form by using chemical reduction method then the optical properties of prepared silver nanoparticles solution were tested in UV-Visible spectroscopic. After which the nanoparticles from the prepared solution were filtered by using whatman filter paper. The filtered nanoparticles were dried for 24 hours and the extracted nanoparticles were characterized using SEM image to find out the size of the prepared nanoparticles to check whether it is in the range of nanometer scale. If the sizes of the nanoparticles are not in the range of nanometer scale then the solutions will be prepared with various compositions and characterization is done with UV-visible spectroscopy and SEM until the nanoparticle range is obtained.

Synthesis of Nanoparticles

Silver nitrate and tri-sodium citrate were used for preparation of silver nanoparticles where the silver-nitrate as precursor and the tri-sodium citrate as reducing agent. The silver colloid was prepared by using chemical reduction method. All solutions of reacting materials were prepared in distilled water. In typical experiment, 100 ml of 0.02 M $AgNO_3$ was heated and vibrated in an ultrasonic mixing bath for 15 min, with this solution 25 ml of 0.2 M tri-sodium citrate was added drop by drop. During the process, solutions were mixed vigorously and heated until change of color was evident pale yellow. The mechanism of reaction could be expressed as follows:

$$4Ag^{+} + C_6H_5O_7Na_3 + 2H_2O \rightarrow 4Ag^{o} + C_6H_5O_7H_3 + 3Na^{+} + H^{+} + O_2\uparrow$$

Sample Preparation

Initially five sample solutions – A, B, C, D and E were prepared. These solutions were obtained by varying the mole concentration in the sample and the mixing ratio is varied: for example mole concentrations taken as 0.02 M $AgNO_3$ with 0.2 M tri-sodium citrate and 0.04 M $AgNO_3$ with 0.4 M of tri-sodium citrate. The mixing ratio in percentage is 100, 10, and 25, which is provided in Table 1.

Table 1: *Prepared Combination of Sample Solutions.*

Solution	$AgNo_3$		Tri-sodium citrate	
	Mole	(ml)	Mole	(ml)
A	0.04	100	0.4	100
B	0.02	200	0.2	200
C	0.02	100	0.2	10
D	0.04	100	0.4	10
E	0.02	100	0.2	25

Initially, 100 ml of 0.02 M silver nitrate solution was taken in the beaker and is heated and stirred by using ultrasonic mixing bath for 15 min with temperature range of 55–65°C. The prepared solution of 10 ml of 0.2 M tri-sodium citrate was added and maintained at the same temperature range and stirred until the color of the solution changed into golden yellow color. Then the solution was taken out from the ultrasonic mixing bath and stirred up until room temperature is reached, for sample A. Similarly by using the same procedure, four different types of samples B, C, D and E were prepared by varying the mixing ratio and mole concentration in these samples.

The golden yellow color in the solution indicates the formation of silver nanoparticles. The final yellow color solution is filtered by using watt man filter paper and the settled nanoparticles in wet condition, is dried in room temperature for 24 hours or with the help of oven and finally silver nanoparticles will be obtained in powder form.

Characterization of Silver Nanoparticles

The prepared nanoparticles were characterized by using UV visible spectroscopy and SEM. The liquid solution is used for UV visible spectroscopy and the powder form of silver nanoparticles is used for capturing SEM image to obtain the structural image of the prepared nanoparticles and to determine the size of the nanoparticles.

UV-Visible Spectroscopy

To check the surface, Plasmon resonance property of nanoparticle synthesized from chemical reduction method, it is necessary to for UV-Visible spectrum analysis, which reveals the specific type of nanoparticle absorbing a specific wavelength of light. This property can distinguish silver nanoparticle from others and can also state that whether the nanoparticles is present in the solution or not. UV-Visible spectroscopy works on the principle of light absorption, depending on the concentration of particles in the solution. Silver nanoparticle has a unique property of Surface Plasmon Resonance. Here, the electron on the metal surface has its own frequency due to oscillation against the electro positive nuclei. In the case of nanoparticles SPR is known as localized Surface Plasmon Resonance. By using this UV-Visible spectroscopy, we get graph which gives absorption *Vs* wavelength of nanoparticles. It gives the wavelength range of the silver nanoparticles.

Scanning Electron Microscopy

After the synthesis, nanoparticles were analyzed under scanning electron microscopy (SEM) VEGA3 TESCAN, which gives the clear image of the synthesized nanoparticle. It reveals the morphological features of nanoparticles. Scanning electron microscopy image not only gives the structural image, also gives the size of the nanoparticles in the sample to identify whether the nanoparticles are within the nanoscale range or not. SEM images of five samples were captured, which shows various sized nanoparticles in the sample so that the exact size of the prepared silver nanoparticles can be determined.

RESULT AND DISCUSSION

The solution of silver nitrate and tri-sodium citrate was mixed in a beaker and kept in ultrasonic mixing bath (Sonicator) as shown in Figure 1. After some time, the solution changes to golden yellow color which represents the formation of silver nanoparticles in the prepared solution. After the formation, the silver nanoparticles were segregated from the liquid solution through filtration technique using whatman filter paper. Silver nanoparticles for various combinations of silver nitrate and tri-sodium citrate were synthesized, as five samples, which is given in Figure 1.

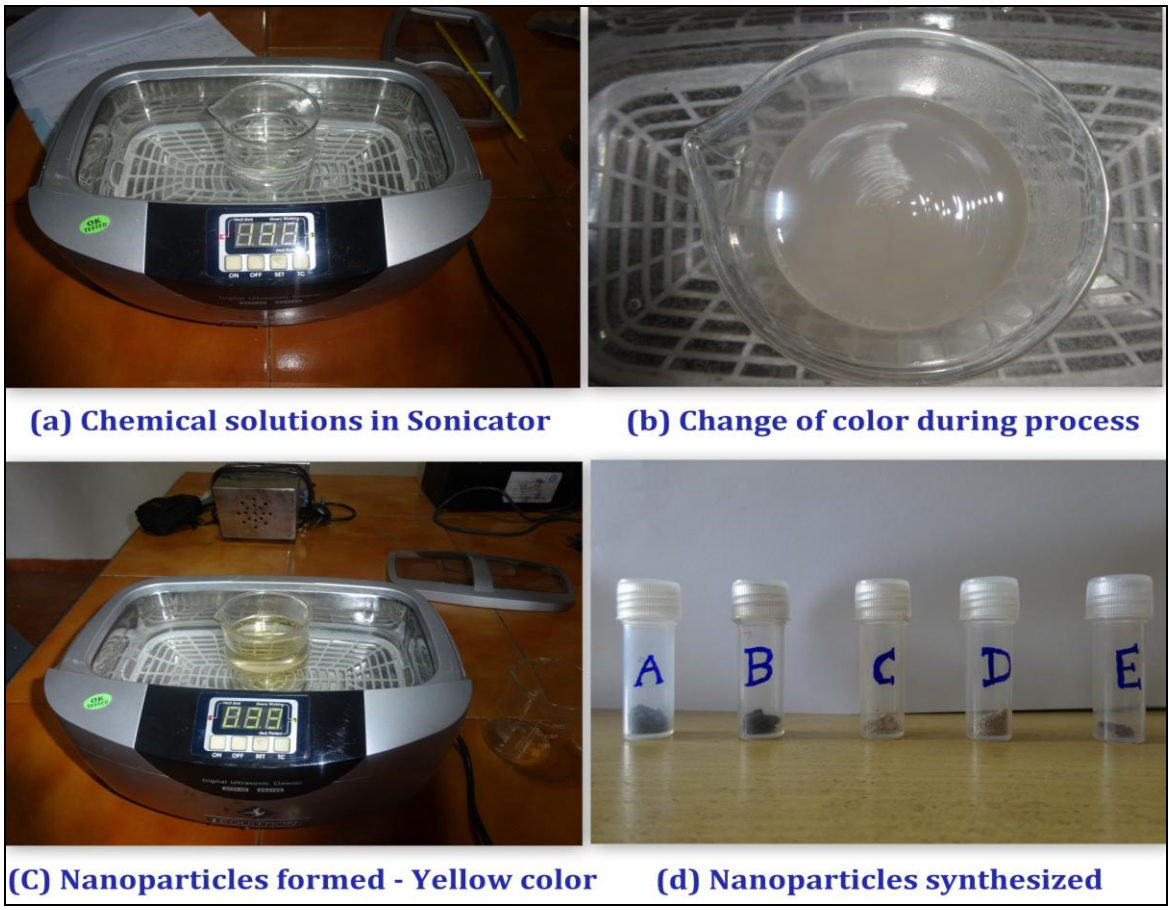

Fig. 1: *Preparation of Silver Nanoparticles in Sonicator and Resultant Nanoparticles.*

SEM images of the synthesized silver nanoparticles were captured to determine the particle size of the nanoparticles. Figure 2 displays the SEM image of 0.04 M concentration of 100 ml silver nitrate and 0.4 mole concentration of 100 ml tri-sodium citrate. It shows the synthesized particles are in the flakes form because the prepared solution was oxidized, because of which these structure were formed. Its size ranges from 380–700 nm. Figure 3 shows the SEM image of 0.02 M concentration of 200 ml silver nitrate and 0.2 M concentration of 200 ml tri-sodium citrate. It shows the synthesized particles are in the flakes form because the prepared solution is oxidized so this structure is formed. Its size ranges from 400–500 nm. Figure 4 displays the SEM image of 0.02 M concentration of 100 ml silver nitrate and 0.2 M concentration of 10 ml tri-sodium citrate. The SEM images also show that the particles are not agglomerated. The size of the nanoparticles does not varying much. It ranges from 75–120 nm. Figure 5 displays the SEM image of 0.04 M concentration of 100 ml silver nitrate and 0.4 M concentration of 10 ml tri-sodium citrate. It shows the synthesized particles are nano-spheres and the size variation is not large. The nanoparticles are not agglomerated and the size of the nanoparticles ranges from 85–95 nm. Figure 6 displays the SEM image of 0.02 M concentration of 100 ml silver nitrate and 0.2 M concentration of 25 ml tri-sodium citrate. The size of the nanoparticles does not varying much, which ranges from 75–90 nm.

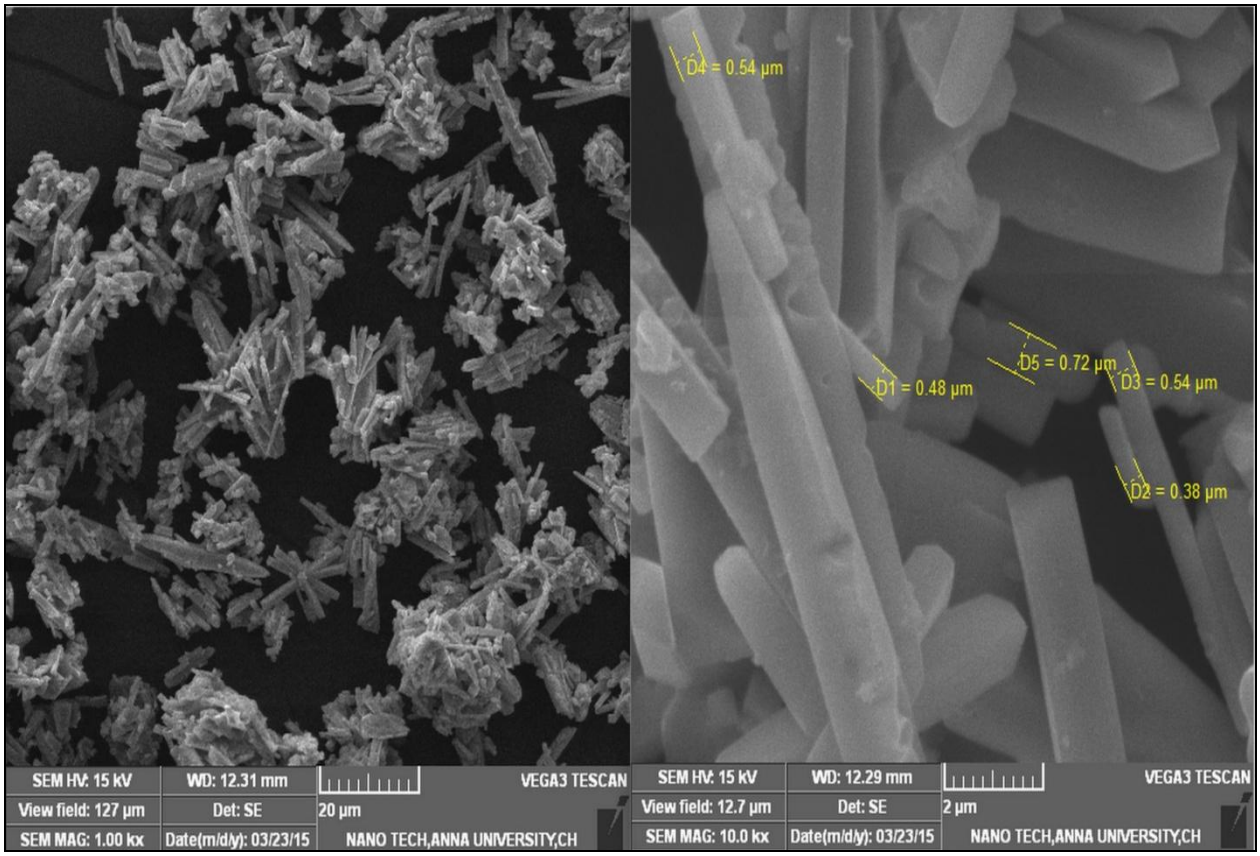

Fig. 2: *SEM Images of Sample A.*

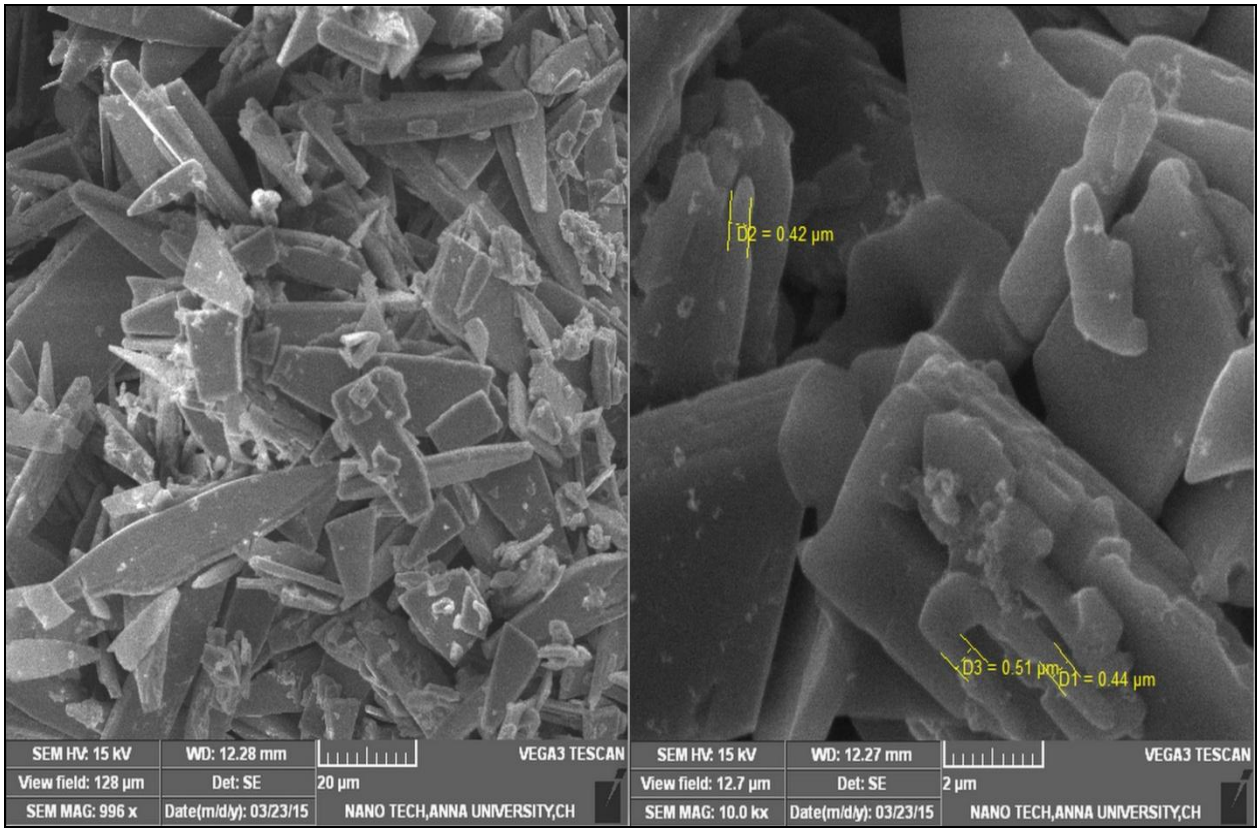

Fig. 3: *SEM Images of Sample B.*

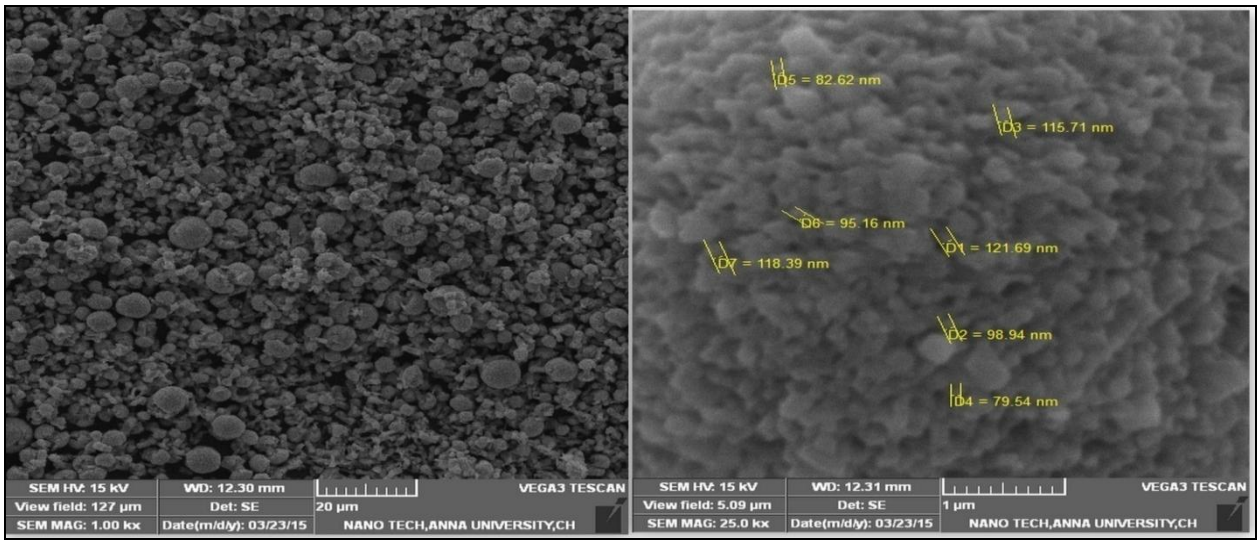

Fig. 4: *SEM Images of Sample C.*

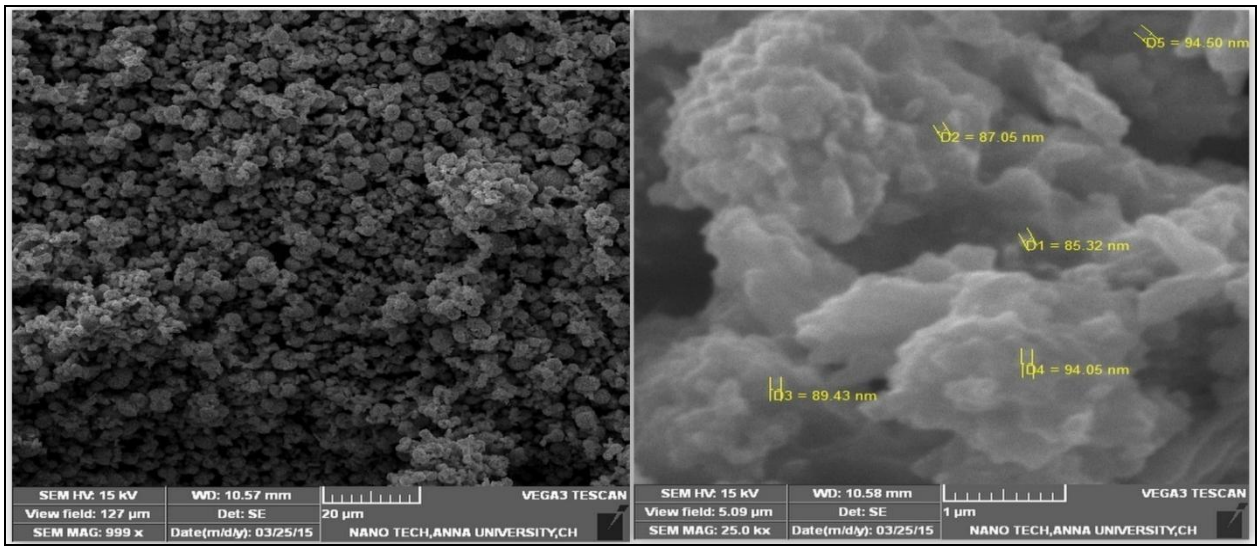

Fig. 5: *SEM Images of Sample D.*

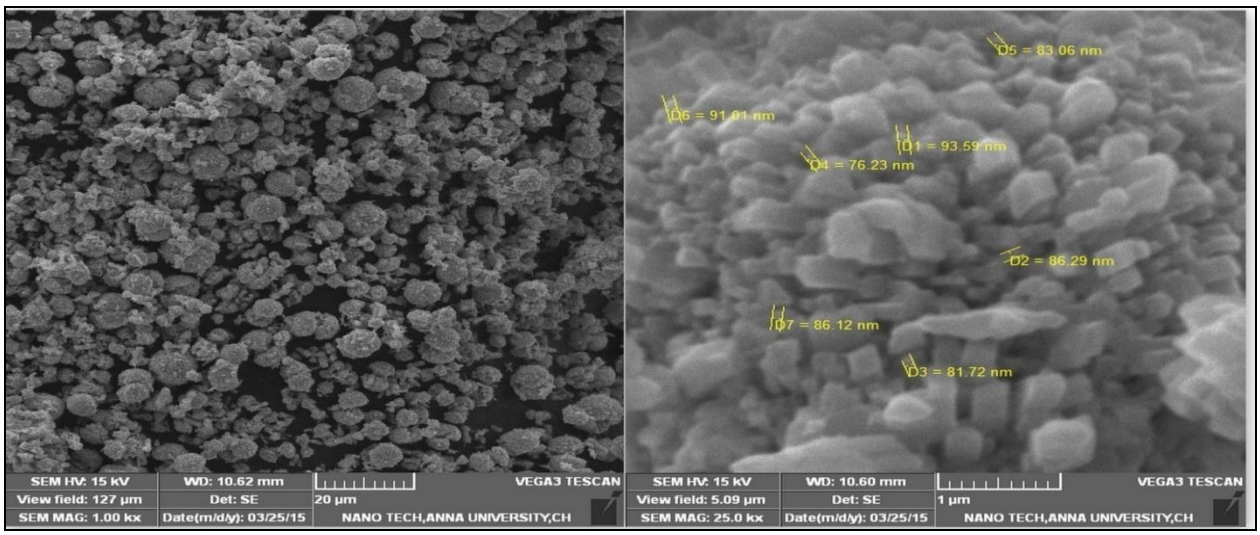

Fig. 6: *SEM Images of Sample E.*

Reduction of silver ions into silver nanoparticles was carried out by adding reduction agent tri-sodium citrate, which was eventually observed as a result of the color change. The color change is due to the Surface Plasmon Resonance phenomenon. The metal nanoparticles have free electrons, which give the SPR absorption band, due to the combined vibration of electrons of metal nanoparticles in resonance with light wave. The sharp bands of silver nanoparticles were observed around 418–447 nm which is shown in the Figure 7. From different literatures, it was found that the silver nanoparticles show SPR peak at around 420 nm. From our studies, we also found that the SPR peak was also at the same range confirming the formation of silver nanoparticles in the prepared solution. The plots of absorbance at λ_{max} (i.e., at 420 nm) *versus* time of reaction is shown in Figure 7. Most absorption spectroscopy of organic compounds is based on transitions of n or n electrons to the π^* excited state. This is because the absorption peaks for these transitions fall in an experimentally convenient region of the spectrum (200–700 nm). These transitions need an unsaturated group in the molecule to provide then electrons.

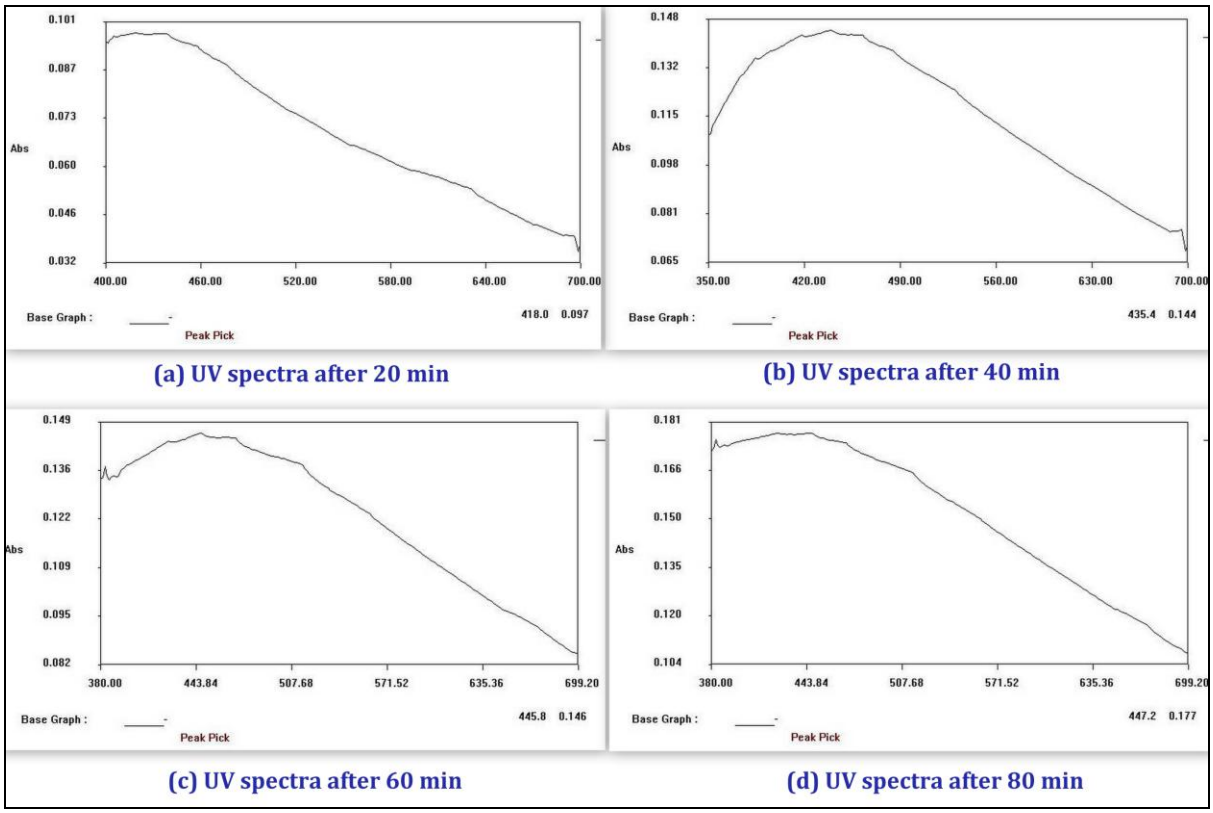

Fig. 7*: UV-Visible Spectroscopy for 0.02 M of $AgNO_3$ and 0.2 M Tri-sodium Citrate.*

The wavelength obtained from the UV-spectroscopy for 0.02 M concentration of silver nitrate and 0.2 M concentration of tri-sodium citrate after 20 min has a maximum wavelength of 418 nm, which falls in the range of silver nanoparticles. The wavelength obtained from the UV spectroscopy for 0.02 M concentration of silver nitrate and 0.2 M concentration of tri-sodium citrate after 40 min has a maximum wavelength of 435.4 nm, which also falls in the range of silver nanoparticles. The wavelength obtained from the UV spectroscopy for 0.02 M concentration of silver nitrate and 0.2 M concentration of tri-sodium citrate after 60 min, has a maximum wavelength of 445.8 nm, which falls in the range of silver

nanoparticles. The wavelength obtained from the UV spectroscopy for 0.02 M concentration of silver nitrate and 0.2 M concentration of tri-sodium citrate after 20 min, has a maximum wavelength of 447.2 nm, which falls in the range of silver nanoparticles. Hence, from the UV-visible spectroscopy spectrum, it is obvious that the synthesized nanoparticles are within the nanoscale range.

CONCLUSION

In this work, silver nanoparticles were synthesized by chemical route method by using ultrasonic mixing bath. The synthesized silver nanoparticles were characterized by UV-visible spectroscopy and the structure and size ranges were obtained by scanning electron microscopy. From the results obtained, the following conclusions were arrived.

1. The clear solution changes into golden yellow color indicating the formation of silver nanoparticles in the prepared solution.
2. When preparing the solution with composition of 1:1 silver nitrate and tri-sodium citrate the obtained particles in the range of 380–700 nm and the structure obtained in the forms of flakes.
3. When preparing the solution with composition of 100:10 and 100:25 silver nitrate and tri-sodium citrate the obtained particles are in the range of 70–120 nm and the structure obtained are not varying much.
4. Impact of concentration of $AgNO_3$ and tri-sodium citrate is inevitable in the formation of silver nanoparticles.

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