

Chemo-bio synthesis of silver nanoparticles

Abstract

Silver nanoparticles have a lot of ways of synthesis like physical and chemical methods; some of these methods use a lot of chemical substances and are very hazardous for humans and environment, so a novel, great, environmental friendly, cheap and easy to use world of green chemistry has been used. A number of characterization techniques such as UV-visible spectroscopy, Fourier transformation infrared spectroscopy, X-ray diffraction study and scanning electron microscopy revealed that silver nanoparticles have been used. Thus the different response of the functional groups and the difference in the peaks and UV-visible data was studied and then compared to understand and know the way these different reducing agents react to the same starting material. The green synthesis had a UV-visible peak at 446 nm while the one with chemical synthesis had a peak at 395 nm. FTIR results of silver nanoparticles synthesis by trisodium citrate (TSC) showed a peak at 1505 cm^{-1} which shows that the compound has a stretching of the $-\text{C}=\text{C}-$ bond. In another case, which was done by using Sodium borohydride (NaBH_4) a peak at 1695 cm^{-1} showed a $-\text{C}=\text{O}-$ bond indicating stretching and a weak absorption intensity. Another peak was present which indicates a $-\text{O}-\text{H}$ bond formation and presence which is a strong bond are found to exist. A notable peak came for synthesis by orange peel at 1517 cm^{-1} which represents a $-\text{C}=\text{C}-$ bond stretching as in aromatic compounds. Another peak at 1732 cm^{-1} indicates the $-\text{C}=\text{O}-$ bond. The XRD results on one of the silver sample prepared by green methods showed silver nanomaterials formed which had a average particle size of around 42 nm. FE-SEM results revealed that silver nanomaterials were formed and had a flake like appearance in one of the results. All the overall comparison showed that different modes of synthesis of silver nanomaterials and different reducing agents give same materials but with different peaks and intensities. All this data provided knowledge about the fact that an alternative method can be used to create new nanoparticles if one of the previously considered or tried method fails thus helping in extending the broadways for research.

Keywords: Green synthesis, Silver nanoparticles, Green chemistry

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Jagpreet Singh, Rajat Bajaj, Harpreet Kaur,
Harjot Kaur, Navneet Kaur, Sukhmeen Kaur,
Mohit Rawat

Department of Nanotechnology, Sri Guru Granth Sahib World
University, India

Correspondence: Mohit Rawat, Department of
Nanotechnology, Sri Guru Granth Sahib World University,
Fatehgarh Sahib - 140406, Punjab, India
Email mohitnano.nit@gmail.com

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Introduction

Nanotechnology is defined as the branch of modern science dealing with the study and applications of materials at very small and minute nanosized levels. Modern science defines nanotechnology as the manipulation of matter with at least one dimension sized from 1 to 100 nanometres, there are many new methods to synthesize nanoparticles. These include physical, chemical, sol-gel methods and biologically friendly methods. The chemical methods maybe hazardous to nature as their synthesis procedure are using a number of harmful chemicals.^{1,2} The most communal methodology for synthesis of metal nanoparticles is chemical reduction by organic and inorganic reducing agents such as Sodium Borohydride,³ Hydrazine,⁴ Ascorbic acid,⁵ and Poly(ethylene glycol).⁶ etc. The phytochemical presents in plant are terpenoids, aldehydes, flavones, ketones, carboxylic acids and amides. Eugenol, Flavones, organic acids, quinones is water-soluble phytochemical that are responsible for immediate reduction of the ions.⁷ In various studies huge number of medicinal plants such as *Acorus calamus*,⁸ *Alternanthera dentata*,⁹ *Ocimum Sanctum*,¹⁰ *Azadirachta indica*.¹¹

Material and methodology

Materials

Plant leaves were collected from the nearby garden and washed methodically with distilled water to remove the dust particles and were then air dried for one hour to eliminate all the water content. The dried leaves were then cut into smaller pieces.

Methodology

Preparation of leaf extract: In a 250 ml beaker, 100 ml distilled water was poured and about 5g of the finely sized leaves were added

into the beaker. It was then boiled for about one hour. The extract was then filtered thoroughly by using Whatman No: 1 filter paper to eradicate particulate matter and to get a clear solution which is further stored in the refrigerator to be used for various characterizations and future work.

Preparation of silver nitrate solution: In 100 ml of distilled water, 10^{-4} M silver nitrate was added to get a fresh solution of Silver Nitrate (Stock solution).

Synthesis of silver nanoparticles

Synthesis of Ag NPs using Tri Sodium Citrate (TSC): This process uses trisodium citrate as a reducing agent which helps in the formation of silver nanoparticles 0.084 gm of silver nitrate AgNO_3 was weighed and then added to 500 ml of boiling distilled water. The solution was mixed well and then continued to boil. Now a 1% solution of trisodium citrate was prepared. This was done by dissolving 1 gm of TSC in 100 ml of distilled water. After this 5ml of 1% TSC was added drop wise slowly by using a pipette. Then the solution was kept to heating only until up to 2 hrs after which a reddish green solution is formed which resemble silver nanoparticles as in research papers. The solution was allowed to cool at room temperature and then sent for characterization

Synthesis of Ag NPs by using Sodium Borohydride (NaBH_4): This process uses sodium borohydride as a reducing agent. In this process 30 ml of 0.002M sodium borohydride (NaBH_4) was added to an Erlenmeyer flask. After that a magnetic stir bar was taken and the flask was placed in an ice bath on a stir plate. Ice bath was used to slow down the reaction and give better control over final particle size/shape by maintaining the temperature of the reaction. The liquid was stirred and cooled for about 20 minutes. 2 ml of 0.001M silver

nitrate (AgNO_3) was dripped into the stirring NaBH_4 solution at approximately 1 drop per second. The stirring was stopped as soon as all of the AgNO_3 was added. By mixing both solutions silver nitrate was reduced to silver and the sample was sent for characterization after centrifugations repeated over 3-4 times. The resultant solution formed was brownish in colour.

Synthesis of Ag NPs using orange peel extract: This method used green concept to synthesize silver nanoparticles of a good quality. Orange peel was crushed to a fine extracts using a knife, segments of colored peel were carefully cut away from the fruit and then further cut into small pieces. About 0.2 g of orange peel was washed with de-ionized water, after that grinding was done using a blender for about 18 minutes in 50 ml of water. Now the aqueous extract was filtered through a muslin cloth at ambient temperature. Now a 1M AgNO_3 stock solution was prepared. After that 5% starch solution was prepared by adding 1 gm of starch in 100 ml of distilled water. Now 200 micro litre of 1M AgNO_3 was taken in nearly 7.5 ml of the starch solution. A little bit of KOH solution was added to the solution till a brownish black colour was formed. This confirmed the formation of silver nanoparticles which were sent for further characterization after series of centrifugations at nearly 1500 rpm. After that UV-visible analysis and FE-SEM was done as a part of characterization.

Characterization of bioreduced silver nanoparticles: UV-vis spectra were measured in a quartz cuvette using Shimadzu-UV 2600 spectrophotometer by analyzing the sample in the range of 200-800nm. The peak of the Silver nanoparticles prepared by green synthesis lies between the range 420-480nm. To examine the role of molecules and presence of capping agent in the synthesis of silver nanoparticles, the FTIR spectra were measured in the range of 4000-400 cm^{-1} in Bruker Alpha-T spectrophotometer. XRD is a very decisive experimental technique that has been long used to address all issues related to the crystal structure of solids, including lattice constants and geometry, identification of unknown materials, orientation of single crystals, preferred orientation of poly-crystals, defects, stresses, etc. Morphology and size of synthesized biogenic silver nanoparticles were investigated by Field emission secondary electron microscopy (FE-SEM)

Results and discussion

UV-visible characterization

Figure 1 consists of a combined depiction of UV-visible data peaks representing silver nanoparticles synthesized by TSC, grapes and NaBH_4 . The graph has three different peaks depicted by three different colours. The blue coloured peak represents silver nanoparticles synthesized by sodium borohydride and the black coloured peak represents silver nanoparticles synthesized by using grape fruit extract which is a green method of production. The lowermost peak in red represents silver NPs synthesized by using TSC. Sodium borohydride (NaBH_4) has a value at 395 nm and the red lowermost peak representing TSC has a value at 425 nm. The one which is black has an intense peak at 446 nm. One of the main reasons for the difference in the peaks for different peaks can also be due to the different concentration used as the bio-reducing agent. It is also possible that generally bio-reducing agents are used in higher concentration as compared to chemical reducing agents. In some cases faster nucleation may occur which is usually followed by a slower rate of growth of nanoparticles. Also the contrasting nature of the reducing agents used is responsible for these differences in the peaks because different agents show different surface Plasmon resonance for silver.

UV-visible of Silver NPs by TSC, orange extract and NaBH_4 .

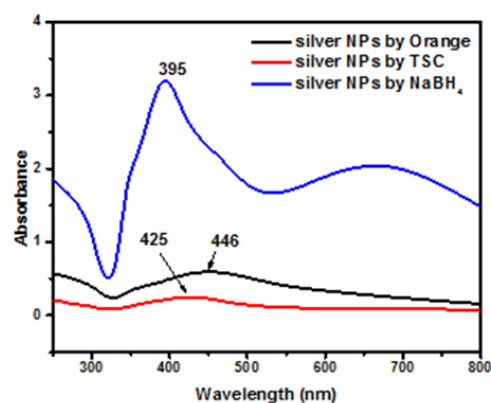


Figure 1 UV-visible of Silver NPs by TSC, orange extract and NaBH_4 .

FTIR analysis

In Figure 2 a comparison has been made and three FTIR results have been plotted against each other for the silver nanoparticle synthesis by three different modes of synthesis. These include synthesis by trisodium citrate, sodium borohydride and orange peel extract. The red colored lines indicate silver nanomaterials synthesized by sodium borohydride (NaBH_4) while the black one represents the FTIR peak of the process which used orange fruit extracts containing citric acid as a reducing agent. The blue FTIR with a couple of sharp peaks reveal the synthesis by using trisodium citrate (TSC) as the reducing agent. The comparison shows the notable difference in the peaks formed by using the different reducing agents. For instance the 3312 cm^{-1} peak of the TSC FTIR show amine stretching with medium absorbance while the 3611 cm^{-1} peak of NaBH_4 shows stretching of the alcohol group with a strong peak. Since orange extract has citric acid as the reducing agent, therefore it shows an amine (N-H) bond stretching at 3304 cm^{-1} and at 1517 cm^{-1} it shows a carbon double bond stretching as in case of aromatics. The difference in three peaks of these FTIR results come due to the intensity due to which the infra- red radiation interacts with these substances. The intensity of the peaks is all due to the different functional group region tends to include motions which are mostly stretching vibrations. The difference of the way the stretching is accomplished is the main reason for the change of intensity peaks as we change the methods of formation of nanoparticles, since each method here involves different parameters such as concentration of the reducing agent and the different temperature which is used for the preparation of the nanomaterials. Since the end product in all the above cases is silver nanomaterials thus the peaks only vary due to the different reducing agents used and also due to the unique nature of the infra-red peaks to show stretching for the respective functional groups used.

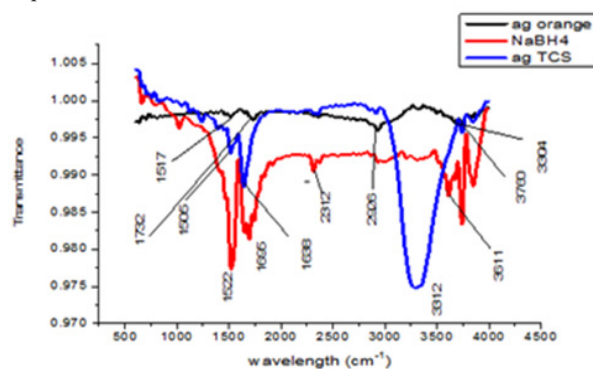


Figure 2 Comparison of FTIR of silver NPs by TSC, NaBH_4 , and Orange extract.

XRD results

The sample was characterized using Siemens X-ray diffractometer. Prepared nanoparticles were UV analyzed and then dried after several centrifugations. The generator was operated as 30 kV and with a 20 mA current. The scanning range was selected from 30° to 80° angles. Dried powder was used as an internal standard Figure 3 shows a XRD graph of a sample. The XRD pattern has been compared with JCPDS data sheet/ICDD no. 04-0783. The average particle diameter of silver nanoparticles came out to be around 42 nm and was calculated from the XRD graph according to Scherrer equation. The corresponding diffraction signals gave patterns which had their peaks at (1 1 1), (2 0 0), and (3 1 1) planes and an irregular poly-crystalline natured silver nanoparticles crystalline structures.

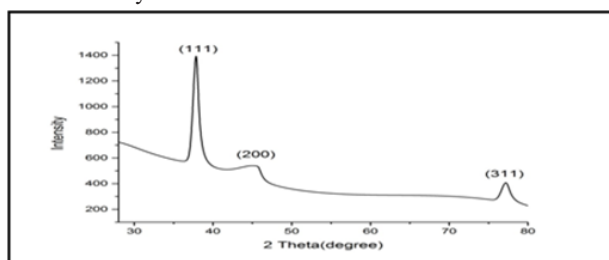


Figure 3 XRD pattern of synthesized silver nanoparticles by green synthesis.

FE-SEM analysis

The Figure 4 shows the formation of very minute and irregular flake like nanostructures. These irregular flakes were arranged in a disturbed fashion as visible in the above extremely magnified image. Thin irregular layers of silver nanoparticles have been thus confirmed by FE-SEM.

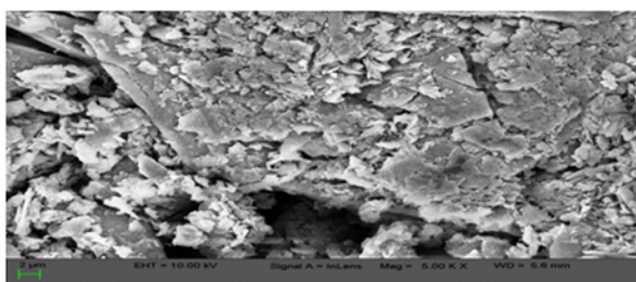


Figure 4 Shows flake like silver nanostructures characterized from FE-SEM.

Conclusion

Silver nanoparticles have a lot of ways of synthesis like physical and chemical methods; some of these methods use a lot of chemical substances and are very hazardous for humans and environment. Silver nanoparticles were prepared from a variety of chemical methods and green methods and a comparative study was done between them. The UV peak of Ag NPs synthesized by using trisodium citrate (TSC), sodium borohydride (NaBH_4) and orange peel as a reducing agent was found out to be 495 nm, 395 nm and 385 nm. XRD analysis showed

a polycrystalline nature form with size at around 42 nm for the Ag nanomaterials formed. FE-SEM images showed that flake like silver nanomaterials were formed which had an irregular type structures.

Acknowledgments

None.

Conflicts of interest

None.

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