



The Influence of Silver Precursor Concentration on Size of Silver Nanoparticles Grown by Soft Chemical Route

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Abstract

We demonstrated the morphology and size control on the nanoparticles by varying the silver precursor concentration. Silver nanoparticles are synthesized using Tri sodium citrate as reducing agent and PVA as capping agent. Different concentrations of silver precursor are used to study its effect on the size of the nanoparticles. Broadened XRD peaks confirmed the formation of nanosized silver nanoparticles with face centred cubic structure and is consistent with FESEM studies. Further XRD results revealed the increase of mean particle size with increase of silver nitrate concentration. FESEM images showed the formation of spherical silver nanoparticles in nanometre regime. EDAX analysis confirmed the presence of elemental silver without any further impurities in the prepared nanoparticles. PL study ascertains the decrement of luminescence intensity with increase of silver precursor concentration due to increase of particle sizes.

Keywords: Silver nanoparticles, XRD, FESEM, Photolumiscene.

Introduction

Nanotechnology is the creation of functional materials, devices and system through control of matter on the nanometer length scale, exploiting novel phenomena and properties present only at that length scale. In its original intellect, nanotechnology refers to the projected ability to construct items from the bottom up, using techniques and tools being developed today. Nanotechnology entails the application of fields of science as diverse as surface science, organic chemistry, molecular biology, semiconductor physics, micro fabrication etc.

Design and synthesis of novel nanomaterials for varying size and shape is one of the emerging areas of material science. The properties of the nanomaterials depend on the particle morphology and hence demands for the tailoring of size and shape of the nanostructures. Two principal factors cause the properties of nanomaterials to differ significantly from other materials: increased relative surface area, and quantum effects. Metal nanoparticles have received considerable attention due to their remarkable electrical and optical properties. In particular, metal nanoparticles of noble elements such as silver are well studied because of their applications in surface-enhanced Raman scattering (SERS), plasmonics etc¹⁻².

Silver nanoparticles (Ag NPs) have been a subject of immense interest among scientists due to their remarkable properties such as good conductivity, catalytic and antibacterial effect³⁻⁶. Ag nanoparticles can be synthesized using various methods: chemical, electrochemical, γ -radiation, photochemical, laser ablation etc⁷⁻¹⁰. We have prepared through chemical reduction method due to certain advantages: readily produce bulk quantities of nanoparticles, process can easily scaled up to meet

mass manufacturing needs, relatively cheaper compared to other methods. Tan et al. prepared Ag NPs using sodium citrate as a reducing agent in the presence of aniline¹¹. However, using this method they have resulted with large-sized and a bit aggregated Ag nanoparticles between the ranges of 35 and 100 nm. Sileikaite et al. reported 100 nm sized Ag nanoparticles from AgNO₃ salt, using sodium citrate as reducing agent¹².

We have investigated the dependence of size on silver precursor concentration using Tri-sodium citrate as reducing agent and PVA as capping agent. Our results showed that by varying the silver precursor concentration it is possible to control the particle size and hence the optical properties of Ag nanoparticles.

Material and methods

All the chemicals were of analytical reagent grade and were used without any further purification. The Ag NPs were prepared by soft chemical method. In a typical synthesis process, 0.01 M of silver nitrate (AgNO₃) solution is prepared with ethanol. Then 0.1 M of Tri sodium citrate (reducing agent) was added drop by drop to the above solution and then 2 ml PVA (1%) is added to the above solution which acts as surfactant. Then after, the solution was kept sealed under continuous stirring (i.e. 3 hrs) by maintaining constant temperature of 75°C. By simply varying the silver precursor concentration of the reaction solution, we can tune the size of the nanoparticles. After the completion of the reaction, products were collected and thoroughly washed for several times with ethanol and finally subjected to vacuum dry at 80°C for 3 hrs. The above procedure is reiterated by varying the silver concentration of 0.02 M and 0.03 M.

The X-ray diffraction patterns of the samples were collected on a Rigaku D X-ray diffractometer with the Cu K α radiation ($\lambda=0.154$ nm). Elemental composition for the prepared samples was examined through energy dispersive X-ray analysis using Oxford Inca Penta FET x3 EDAX instrument attached to Carl Zeiss EVO MA 15 scanning electron microscopy. The FESEM images were obtained using a ZEISS, SUPRA55 field emission scanning electron microscopy. Photoluminescence measurements were obtained using JobinYvon Fluorolog-3 spectrophotometer with a xenon lamp as an excitation source and the excitation wavelength set at 390 nm.

Results and Discussion

Compositional studies: The prepared nanopowder was examined through energy dispersive X-ray analysis (EDAX) for compositional analysis. The EDAX spectrum of silver nanoparticles is depicted in figure-1. The EDAX profile showed the presence of elemental silver peak along with small carbon peak due to the adhesion of carbon tape on to the aluminium stud. Identification lines for the major emission energies for silver in the range 2.5 - 4 keV are displayed and these resemble with peaks in the spectrum, thus conforming that silver has been correctly identified¹³⁻¹⁴. Thus reduction of silver into elemental silver and absence of other impurities has been confirmed from EDAX studies.

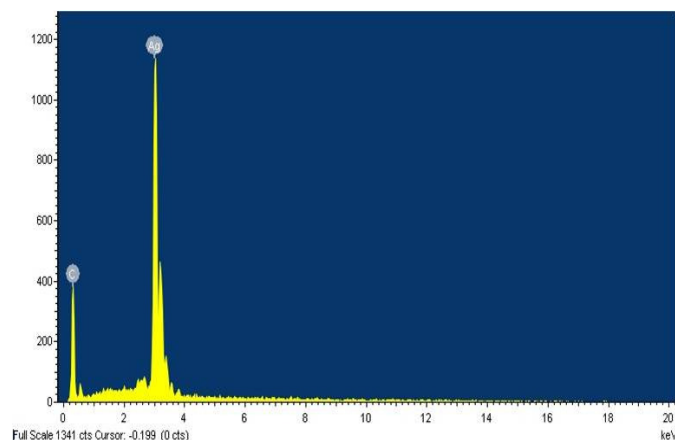


Figure-1

Typical EDAX spectrum of prepared Ag NPs at 0.01 M silver precursor

X-ray diffraction studies: Figure-2 shows the X-ray diffraction patterns of synthesized silver nanoparticles with varying silver concentration. XRD analysis shows the four diffraction peaks of (111), (200), (220) and (311) orientations with a face centred cubic structure and which is in consistent with the JCPDS (No. 04-0783) data. According to Debye-Scherrer's using (111) intense peak, the mean particle size of nanoparticles has shown increment from 24 to 45 nm with increase of silver precursor concentration¹⁵. The increase of average particle size with increase of silver nitrate concentration is evident with earlier literature¹⁶.

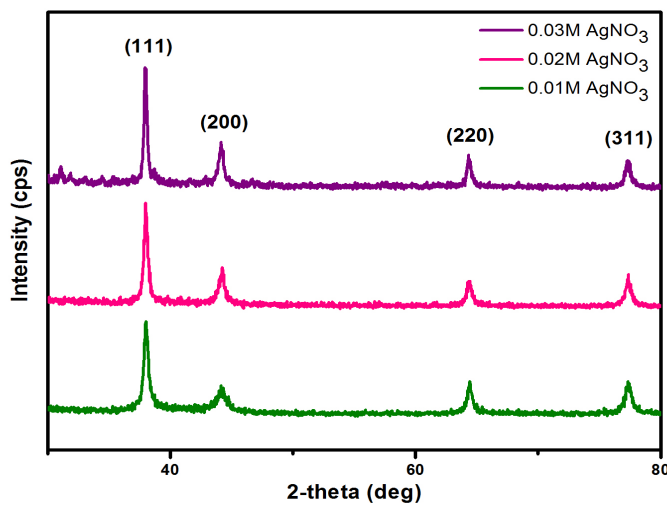


Figure-2

Representative XRD patterns of synthesized silver nanoparticles

Morphological studies: Field emission scanning electron microscopy images of prepared silver nanoparticles at different silver precursor concentrations are depicted in figure-3. FESEM studies revealed that surface morphology of the nanoparticles is spherical and the average sizes of the particles are found to be increased from 23 to 44 nm with increase of precursor concentration of 0.01 M – 0.03 M. FESEM images enumerates that the nanoparticles are homogeneous without any substantial agglomeration. Sileikaite et al. reported an average size of 100 nm Ag NPs using tri-sodiumcitrate as reducing agent and water as solvent¹². As silver nitrate concentration is increased, results in increase of average particle sizes were in accordance with Zielinska et al.¹⁶.

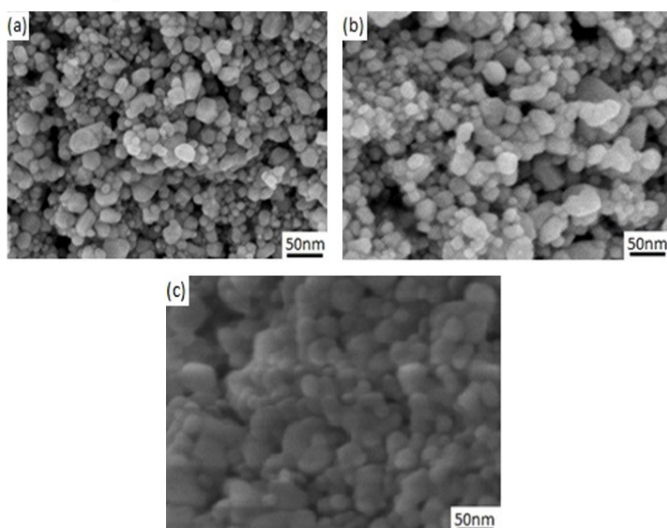


Figure-3

FESEM images of Ag NPs at different concentrations of silver precursor (a) 0.01 M, (b) 0.02 M and (c) 0.03 M

Photoluminescence studies: The synthesized silver nanoparticles were found to be photo luminescent at room temperature. Blue emission was noticed from the samples under excitation wave length of 390 nm. The intensity of photo luminescence peak is decreased with increase of silver precursor concentration from 0.01 M to 0.03 M insisting decrease of particle size as shown in figure-4. It was observed that the photoemission wavelength is independent of the particle size while the intensity increases sharply with decrease of particle size. This visible luminescence of nanoparticles was due to excitation of electrons from occupied *d* bands into states above the Fermi level¹⁷. Photo luminescent radiative recombination of an unoccupied *sp* band electron with the hole is due to electron-phonon and hole-phonon scattering process¹⁷⁻²⁰.

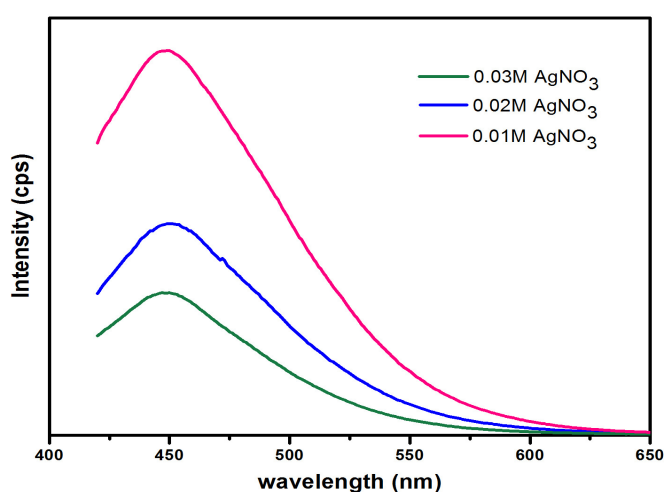


Figure-4
PL spectra of silver nanoparticles with different silver precursor concentrations

Conclusion

Silver nanoparticles have emerged as an important class of nanomaterials for a wide range of industrial and medical applications. Silver nanoparticles have been synthesized successfully using soft chemical route. Effect of silver precursor concentration on particle sizes has been investigated. XRD and FESEM analysis enunciate the increase of particle sizes with increase of silver precursor concentration. PL studies showed detraction of intensity with increase of silver concentration due to increase of particle size which is inconsistent with XRD and FESEM results. The nature and concentration of both reducing and capping agents played a major role in size distribution and shape of nanoparticles which greatly determines the nanoparticles functional properties.

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