Structural Studies of Silver Nanoparticles Obtained Through Single-Step Green Synthesis

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Abstract: Green synthesis of silver Nanoparticles (AGNP’s) has been the most prominent among the metallic nanoparticles for research for over a decade and half now due to both the simplicity of preparation and the applicability of biological species with extensive applications in medicine and biotechnology to reduce and trap the particles. The current article uses Eclipta Prostrata leaf extract as the biological species to cap the AGNP’s through a single step process. The characterization data obtained was used for the analysis of the sample structure. The article emphasizes the disquisition of their shape and size of the lattice parameters and proposes a general scheme and a mathematical model for the analysis of their dependence. The data of the synthesized AGNP’s has been used to advantage through the introduction of a structural shape factor for the crystalline nanoparticles. The properties of the structure of the AGNP’s proposed and evaluated through a theoretical model was undeviating with the experimental consequences. This modus operandi gives scope for the structural studies of ultrafine particles prepared using biological methods.

1. Introduction

Bio-convivial green synthesis of nanoparticles (NPs) in general and Silver Nanoparticles (AGNPs) in particular have been in vogue for a long time now with pronounced applications in Physics, Chemistry, and Medical research. Ethno-botanical species for mitigating and surmounting the NPs are being pursued as a large scale substitute to overcome many complex problems that humans have been facing while organizing themselves in a non-chaotic way, withal due to the achievability of desired dimensions and distribution without loss of morphology[1-7]. The species of plant in the family Asteraceae viz., Eclipta prostrata (syn. Eclipta prostrata) has been used for the synthesis of AGNPs[21-22, 28]. Due to the sui generis electrical, optical, conductivity, and thermal properties of AGNPs they possess unbound appositeness in different territories of sciences [8-19]. The extrapolation of the complex structural characteristics needs further insights and studies on its distinction from the bulk characteristics, though extensively in the literature[1-16].

The current study emphasizes the dovetailing of the size, shape, surface, and aggregation state of the AGNPs mathematically adopting basic principles of the properties of matter to study of the relative changes of the lattice parameters of the NPs relating the elastic energy to the surface energy of the NPs per unit area[20].

2. Experimental Method

Aqueous solution of silver nitrate (1mM) and the extract of Eclipta Prostrata used as the reaction medium have been mixed in the proportion of 1:9 and the contents were maintained at room temperature for about two hours until the reduction and capping of the AGNPs was distinctly visible through the change in the color of the solution to brown, which was the initial confirmation test of the
formation of AGNPs. Later the sample was repeatedly centrifuged and a colloid of AGNPs has been separated and stored for characterization.[28]

The process of characterization of the sample has been carried out using SEM, XRD, FTIR, UV-Visible spectrophotometer, which have been reported in detail elsewhere by the same authors[28]. The results have been compendiously summed up to sustain continuity of the analysis of the structural studies of the AGNPs.

The structural features of the synthesized silver nanoparticles using Eclipta prostrata leaf extract were characterized using SEM analysis (PHILIPS-XL-30SEM ) machine. It depicted high density nanoparticles synthesized by the Eclipta prostrata leaf extract and are relatively spherical in shape. X-ray diffraction has been a convenient method for determining the mean size of single-crystal nanoparticles.

After repeated centrifugation followed by re-dispersion of the pellet of silver nanoparticles into 10 ml of sterile distilled water and freeze drying the purified silver nanoparticles, the structure of the synthesized silver nanoparticles have been investigated with an XRD (RIGAKU-D Machine). Indexing process has been done and Miller Indices (h k l) to each peak have been assigned during the first step. The XRD results therefore suggest that the crystallization of the bioorganic phase occurs on the surface of the silver nanoparticles [29]. The particles have size ranging between 11 to 60 nm. From this study, considering the peak at degrees, average particle size has been estimated by using Debye-Scherrer formula [40,41]. And the average size of AGNPs thus synthesized was 34 nm

3. Results and Discussion

The chemical interaction between the phytochemicals present in Eclipta Prostrata leaf extract and AgNPs and how it has led to stabilization of AgNPs has been briefly presented here and has been reported by the same authors elsewhere[28].

The FTIR spectrum of Ag nanoparticles is shown in Fig 6. The spectrum of Ag nanoparticles show stretching at (units: wavenumber cm⁻¹) 3106 , 2962, 2885, 2791 , 2601 corresponds to O-H stretching for Carboxylic acids stretching, 2274 corresponds to N-H bond stretching of amines, 2169 corresponds to C-N stretching of the aromatic amino group and C-O stretching of alcohols and ethers respectively, 1126 corresponds to C–O stretch alcohols, 1392, 1436, 1497 corresponds to CH2 bend alkenes, 609, 685 and 890 corresponds to C–H bend alkenes. These stretching values indicate that the carbonyl group formed amino acid residues and that these residues “capped” the silver nanoparticles to prevent agglomeration, thereby stabilizing the medium. When the metal nanoparticles form in solution, they must be stabilized against the van der Waals forces of attraction which may otherwise cause coagulation. Physisorbed surfactant and polymers may cause steric or electrostatic barriers or purely electrostatic barriers around the particle surface and may thereby provide stabilization. FTIR peaks that were corresponding to aromatic rings, geminal methyls, and ether linkages indicate the presence of flavones and terpenoids responsible for the stabilization of the AgNPs synthesized by the Sesuvium portulacastrum leaf extract. The FTIR spectrum of Ag nanoparticles suggested that Ag nanoparticles were surrounded by different organic molecules such as terpenoids, alcohols, ketones, aldehydes and carboxylic acids.

3.1 Structural studies using UV-visible Spectra

The brown colour in the aqueous solution has been due to the surface Plasmon vibrations[29]. The polyol compounds, proteins, metabolites present in the plant system, the electrons released during glycolysis and the water soluble heterocyclic compounds were mainly responsible for the reduction of the silver ions and the stabilization of the nanoparticles respectively[30-33]. The UV-Vis spectral studies used to examine size and shape controlled nanoparticles in aqueous suspensions revealed an absorption peak at 416 nm and the broadening of the peak indicated that the particles are poly-dispersed[33, 38-39].
The much heavier ionic core of these particles induce polarization of the electrons from an incoming wave of the electric field[39] that would result in a restoring force which creates an in phase dipolar oscillation.

![Figure 1. UV-Visible spectra of Ag nanoparticles](image)

And the origin of the observed colour has been due to a strong absorption owing to the resonance between the frequency of the EM field and coherent electron motion. The difference in the energies of the conduction and valency bands in the case of AG is very low permitting free movement of electrons thus, leading to the oscillation of free electrons of AGNPs in resonance with the light wave ultimately resulting in SPR [37, 40-42]. Furthermore, UV-Vis a paramount tool of analysis of the metastable solution of single particles [43, 45]. Beyond this metastable state the dominant Van der Waal’s forces sequel the cluster formation [45-46]. The flattened spectrum indicated the saturated state of the reaction and reduction of AGNPs for this concentration of the Eclipta Prostrata leaf extract. [47-48]. The framework of Mie scattering theory to analyze optical spectra has been applied for the determination of the particle size of the AGNPs present in the stable suspension [34-52]. The full width at half maximum (FWHM) of the peak ω has been obtained from the spectral graph Fig.1 as follows.

\[
ω = \frac{(ε_0 + 2n^2)c m u_F}{2 N c e^2 D}
\]

where, and , the frequency independent part of complex form of the particle are, ε₀ - dielectric constant = 49, n - refractive index = 0.15016, c - velocity of light, m - mass of the electron, u_F - electron velocity at the Fermi Energy, N - Number of electrons per unit volume, e - charge of the electron, and D - Diameter of the particle. The particle diameter has been determined. It was found to be ~ 27 nm. The UV-vis spectra are fitted using log-normal function \( P(D) dD = \frac{1}{\sqrt{2πσD}} e^{-\left(\frac{\ln^2(D)}{2σ^2}\right)} \) to obtain the standard deviation (σ) as the system of the poly dispersed nanoparticles obeys log-normal size distribution function. Using σ and the mean particle size obtained particle size distribution curve has been generated as in Fig.3.

4. Model to study the variation of the lattice parameters
The synthesized AGNPs have been observed to be of a varying size and shape, the direct repercussion of which would be on the lattice parameters (LP). There would be an abstraction of the LPs as an inverse function with the particle size.
Recently a general mathematical model has been developed and employed [20, 55-59] to account for size effect on the LPs of the AGNPs. According to this method initially a particle from the bulk has been isolated assuming no loss of the structural properties. The surface tension of such an isolated particle would contract its size elastically, and finally aid its formation in an equilibrium state tending to attain a shape that possesses minimum energy.

Fig. 2. The Log-Normal Distribution

A shape factor $\alpha$ [55] has been introduced to include non-spherical NPs. By minimizing the sum of the increased surface energy and the elastic energy, a formula has been obtained in the generation of the lattice parameters. These lattice parameters have been compared with the corresponding experimental values. For an ideal crystal lattice, the lattice parameter contraction is proportional to the diameter of nanoparticle

$$\frac{\Delta a}{a} = \frac{(a_p - a)}{a} = \frac{(1 - \epsilon)R - R}{R}$$

where $a_p$ and $a$ are the lattice parameters of the nanoparticle and the corresponding bulk material.

Inserting Equation $\epsilon = \frac{1}{1 + \left(\frac{2\sigma}{\gamma}\right)R \cdot \alpha^2}$ From eqn. (10) in reference [20] the study of the variation of the LPs of the AGNPs has been possible.

| $\sigma$ Shear module (298 K) [60] | $3.03 \times 10^{10}$ (N/m$^2$) |
|---------------------------------|---------------------------------|
| $\gamma_0$ Surface energy (0 K) [61] | $1.250$ (J/m$^2$) |
| $\gamma$ Surface energy (298 K) (From Eqn.(3)) | $1.205$ (J/m$^2$) |

| Value of $\alpha$ | Value of D in (nm) |
|------------------|--------------------|
|                  | 27                 | 28 | 48 | 55.2 |
| 1.00             | -0.170             | -0.1639 | -0.095 | -0.0832 |
| 1.15             | -0.158             | -0.152 | -0.089 | -0.0776 |
| 1.18             | -0.156             | -0.1509 | -0.0881 | -0.0766 |
| 1.24             | -0.1527            | -0.1472 | -0.0859 | -0.0747 |
| 1.49             | -0.139             | -0.134 | -0.0784 | -0.0682 |
| 1.5              | -0.138             | -0.133 | -0.0781 | -0.0679 |

Table 1: The input physical parameters for the Silver Nanoparticles

Table 2: Lattice parameter variation
\[ \frac{\Delta a}{a} = \frac{1}{1 + KD} \]  

Equation (2) is the basic relation for the size and shape dependent lattice parameters of metallic nanoparticles,

where \( D (= 2R) \) is the diameter of the nanoparticle, and \( K = \frac{1}{\gamma} \).

Generally, both of the shear modulus and the surface energy are positive; therefore, the lattice parameter of the metallic nanoparticles will decrease with decrease in particle size. The shape dependent lattice parameters of nanoparticles in specific size have been simulated using MATLAB program and the results have been presented below.

There was a decrease in the variation of the lattice parameter with increased shape factor, which in turn depended on the particle dimensions and has been stronger in the case of smaller particle sizes contributing about 10-15% to the lattice parameter variation as depicted in Fig.3. As the model has been successful in bringing out a definitive relation to the experimental results to that of the theory with which many new characteristics of the nanostructures can be understood, it stands out as a ‘continuous media model’ and can be used to predict the lattice parameter variation of metallic nanoparticles.

5. Conclusions:

The UV-Visible spectra confirmed the reduction of silver ions at 416 nm. The dispersions of silver nanoparticles displayed intense colours due to the plasmon resonance absorption inveigled by the size, shape, inter-particle interactions, free electron density and surrounding medium. The dependence of bandwidth upon particle size \( \omega \sim 1/D \), results from the changing mean free path of electron[38] and shows that the bandwidth increases with the decrease of the cluster size. The normalized absorption coefficient which matches with the experiment within the experimental error has been presented in Fig.4. The mathematical model employed was successful in accounting for the size and shape dependent lattice parameters of metallic nanoparticles. And the results were consistent with the experiment. It has also been observed that about 10-15% variation of the LPs has been due to the particle shape. The model uses physical constants of the bulk material and is a continuous media model applicable for particles size up to about 90nm, beyond which the results deter.
This model has been successful for the LP variation studies and it is being explored further to investigate theoretically complex structural characteristics of NPs and to study the variation of dielectric and elastic properties and their influence in the controlled synthesis of nanoparticles.

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