

Scientific paper

A Novel Green Chemical Route for Synthesis of Silver Nanoparticles Using *Camellia Sinensis*

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Abstract

The thrust to develop environmental friendly procedures for production of Nanoparticles arises from the very fact that current nanotechnology research uses a lot of chemicals, which are potential threat to both environment and public health. Tea (*Camellia Sinensis*) with its rich source of polyphenolic compounds has been exploited for the reduction and capping of silver nanoparticles (Ag-NPs), making it a complete green chemical route. The reduction of Ag⁺ to Ag⁰ was observed by the color change from pale yellow to dark yellow. The reaction was followed with the help of UV-Visible spectrometer. Crystal structure was obtained by carrying out X-ray diffraction studies and it showed face centered cubic (fcc) structure. The particle size and morphology were obtained from transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS) studies. An average particle size of 25 nm silver particles could be obtained using this method and the TEM and SAXS data corroborate with each other.

Keywords: Silver nanoparticles, Green synthesis, Tea polyphenols, Small Angle X-ray Scattering (SAXS).

1. Introduction

Synthesis of silver nanoparticles (Ag NPs) have gained considerable interest due to their unique properties such as excellent electrical and thermal conductivity, chemical stability, catalytical activity, non linear optical behavior, anti microbial and anti bacterial effects.¹⁻⁵ They also show a very peculiar nature of collective oscillation and absorption of light by surface electrons termed as surface plasmon resonance (SPR) in the UV-Vis region,⁶ which makes them potential biomaterials. As both size and shape of Ag NPs affect the optical and electronic properties, a number of methods have been reported for the preparation of Ag NPs with varying sizes and shapes.^{7, 8} Most of the methods generally involve chemical reduction of metal salt with different external reducing agents.^{9, 10} To control the size and shape, various capping agents were employed such as alkanethiols, alkylamines or polymers such as PVP.¹¹

One of the major setbacks of chemically synthesized Ag NPs is that as synthesized nanoparticles are covered

by capping agents. This not only reduces their activity in the semiconductor nanoparticles but also some of the organic layers cannot be used for bio applications as they hinder the biocompatibility of the nanoparticles. Therefore pretreatment such as washing of the surfactant or stabilizer becomes a prime requisite. Though various chemical routes are available for the synthesis of Ag NPs, synthesis and design of nanomaterials through biological routes (use of natural products) have attracted significant interest because of the eco-friendly products, biocompatibility, easy scale up operations and also their economic viability in the long run. Hence developing of reliable biosynthesis protocols has gained importance and also the clubbing of nanotechnology to green chemistry has become the new facet in the area of nanoscience.¹²

Among various biosynthetic routes use of microorganisms has been well studied, the use of extracellular precipitation by both unicellular and multicellular organisms has been dealt in with detail.^{13, 14} Even their use as nanofactories i.e. intracellular production of nanoparticles is also being explored.¹⁵ Though the use of microorga-

nisms is well studied its counter part, the plant kingdom and its use for the synthesis of nanoparticles is relatively less explored. Some work has been carried out for the production of Ag NPs using either the whole plant or plant parts extracts.^{16–21} Usage of plants or plant products give a distinctive edge over the microorganism routes since one need not undergo the cumbersome process of maintaining cultures. In this work we report an effective room temperature synthetic procedure for the reduction of Ag¹ to Ag⁰ using *Camellia Sinensis* leaf extract, commonly known as tea.

2. Experimental

Silver nitrate (AgNO₃, 99.9% pure) was obtained from Alfa Aesar Laboratories, India. Commercially available tea powder, Tata Tea Limited, India, was used for preparation of tea extract and ultra high pure water with a resistivity of 18.2 MΩcm was used as medium to dissolve the silver salt and for making the tea extracts. 0.5 g of tea grains were weighed and transferred into a 50 ml volumetric flask and was filled up to the mark with water. The contents of the flask were thoroughly agitated for 1 hour in a shaking water bath at 30 °C and then allowed to stay over night. The reddish brown color solution was decanted and then centrifuged at 500 rpm to remove any un-dissolved sediments. The aliquot was recovered by filtering the solution through a filter paper and used for further experiments. A dilute solution of silver (0.5 M) was prepared by dissolving suitable amount of AgNO₃ in water.

To carry out the Ag⁺ → Ag⁰ reaction, 5ml each of 0.5 M AgNO₃ solutions were pipetted out into four identical transparent plastic vials marked as experiments 1, 2, 3 and 4, to which selective volumes of 1, 2, 3 and 5 ml of tea aliquot was added respectively. All the four vials were made up to 10 ml by adding suitable amount of water as shown in Table 1. The vials were capped to prevent external contamination and evaporation of solvent. The solutions were left to react for three hours. The above-obtained emulsions were characterized using UV-Vis spectrometer (Perkin Elmer Lambda 25). Fourier transform infrared spectroscopy (FTIR) was used to study the interactions between the tea extract and Ag NPs for which, a (Perkin Elmer Spectrum GX) FTIR spectrometer was used to record the spectra. Ag NPs were separated from the mother solution by centrifugation at very high rate of 20000 rpm, and the powders thus obtained were placed on Si substrate to obtain the crystal structure using X-ray diffractometer (XRD-Philips-PW3020). To obtain the particle size and shape the powders were redispersed in water using a rod ultrasonicator and small angle X-ray scattering (SAXS- Anton Paar-PW3830) was carried out on these solutions. A drop of the redispersed solution was dropped onto a carbon coated copper grid to carry out transmission electron microscopy (TEM- Philips, TECHNAI FE 12) studies.

Table 1. Experimental conditions for synthesis of Ag-NPs along with their λ_{\max} and SAXS values.

| | Volume (ml) | | H ₂ O | UV-Absorption | Particle Size |
|--------------|---------------------------|-------------------|------------------|-----------------------|---------------|
| | AgNO ₃ (0.5 M) | Camellia-sinensis | | λ_{\max} (nm) | SAXS (nm) |
| Experiment 1 | 5 | 1 | 4 | 445 | 24 |
| Experiment 2 | 5 | 2 | 3 | 446 | 25 |
| Experiment 3 | 5 | 3 | 2 | 445 | 25 |
| Experiment 4 | 5 | 5 | Nil | 444 | 26.5 |

3. Results and Discussion

On standing for three hours the pale yellow colored solutions turned to dark yellow color indicating the reduction of Ag (I) to Ag (0). The color change shows that the tea extract is acting, as a mild reducing agent as evidenced by a very slow process. The choice of tea (*Camellia Sinensis*) as reducing agent is based on its rich content of polyphenolic compounds whose prime constituents are theaflavins and thearubigins.^{22,23} These polyphenols not only act as reducing agents but also perform the role of stabilizing or capping agents due to their bulky and steric nature. The formation of Ag NPs was confirmed by the appearance of characteristic surface plasmon band around 445 nm in the UV-Vis region. Fig. 1 shows the UV-Vis spectra of the solutions and it can be observed that the λ_{\max} is centered at around 445 nm, which corresponds to the transverse plasmon band of Ag NPs. No shift was observed in the λ_{\max} values from experiment 1 to 4, which indicates that the particle size and shape remained similar even with the increase in reducing agent. Increase in the absorption maxima of the peaks with increase in tea con-

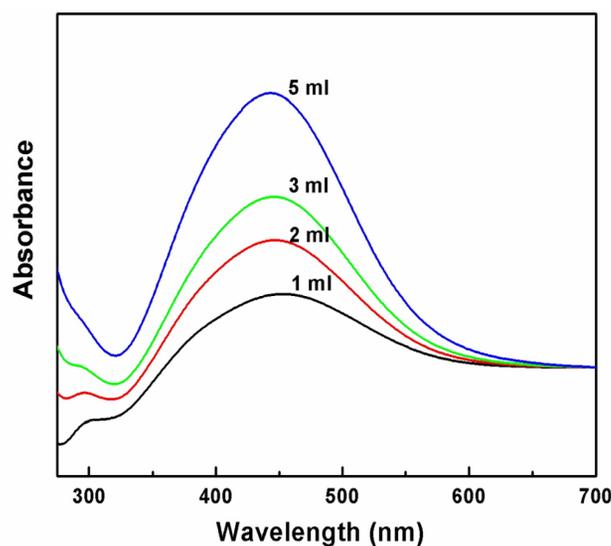


Figure 1: UV-Vis spectra of Ag (0.5 M) solutions after reaction with varying volumes of *Camellia Sinensis* extract.

tent indicate that more number of optical centers have formed which could be due to the complete reduction with increase in reducing agent. The complete reduction of Ag (I) ions is evidenced by the decrease in intensity of the small hump around 300 nm that corresponds to Ag (I) ion from experiment 1 to 4.

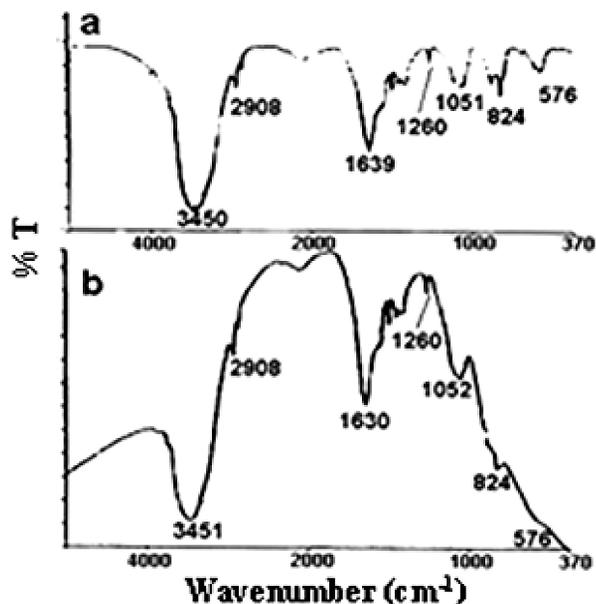


Figure 2: FTIR spectra of a) tea leaf extract and b) colloidal solution of Ag NPs after reaction for 3 hrs.

The nature of interaction between the tea extract and Ag NPs was studied with the help of FTIR spectra. Fig. 2 shows the FTIR spectra of a) un-reacted tea extract and b) colloidal solution of Ag NPs obtained after the reaction. From fig 2a it could be observed that the un-reacted tea extract consists of a broad peak at 3450 cm^{-1} , which corresponds to the O–H stretch and the peaks at 2908 cm^{-1} and 1051 cm^{-1} could be attributed to the stretching and bending modes of $\text{sp}^2\text{ C–H}$ bonds. Peak at 1638 cm^{-1} could be attributed to the C=O stretch of the acid groups present in thearubigins, whereas the peak at 1260 cm^{-1} can be assigned to C–O stretch and small peaks present at 824 cm^{-1} and 576 cm^{-1} confirms the presence of aromatic substituted rings. Except for a slight shift in the C=O stretch from 1638 cm^{-1} to 1630 cm^{-1} rest of the peaks remain unchanged in the spectra obtained from that of Ag NPs after the reaction with tea extract as shown in Fig 2b. The slight red shift in the carbonyl frequency by 8 cm^{-1} indicates a weak coordination between the carbonyl group and Ag NPs and thus proves that the Ag NPs are protected by the natural compound (thearubigin) present in tea.

Fig. 3 shows the XRD patterns of the Ag nanopowders obtained from various experiments (1–4). A typical XRD pattern was obtained for all the powders and the pattern consists of five distinct peaks at corresponding 2θ values of 38.40, 44.52, 65.71, 77.64 and 81.75. These values

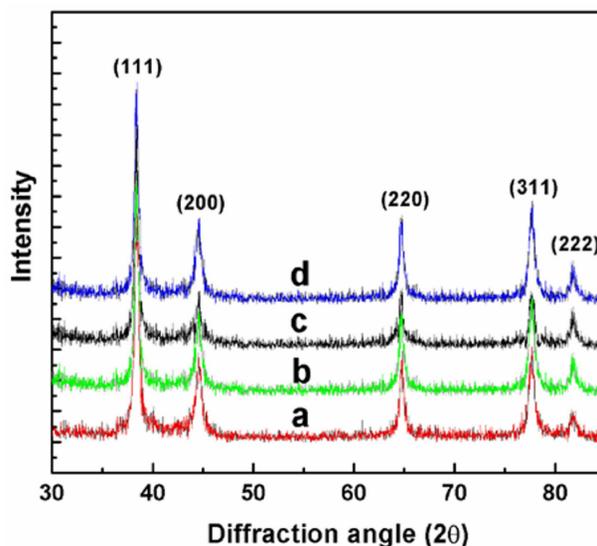


Figure 3: XRD pattern of the Ag nanopowders obtained from a) experiment 1 b) experiment 2, c) experiment 3, d) experiment 4.

reveal that it is a face centered cubic (fcc) structure. The discernible peaks can be indexed to (111), (200), (220), (311) and (222) planes of a cubic unit cell, which corresponds to the cubic structure of silver (JCPDS card No. 89-3722). Crystallite size calculations were carried out from the peak broadening using Debye-Scherrer formula that resulted in crystallite sizes ranging between 3–4 nm.

To obtain the particle size and shape SAXS and TEM studies were carried out. Fig. 4 shows the SAXS results. To obtain the small angle X-ray scattering, the sample was introduced into the sample holder using a syringe and the scattered pattern was obtained after 30 minutes. The pair distance distribution function $[P(r)]$ plot shows a single symmetric peak, which indicates that the particles

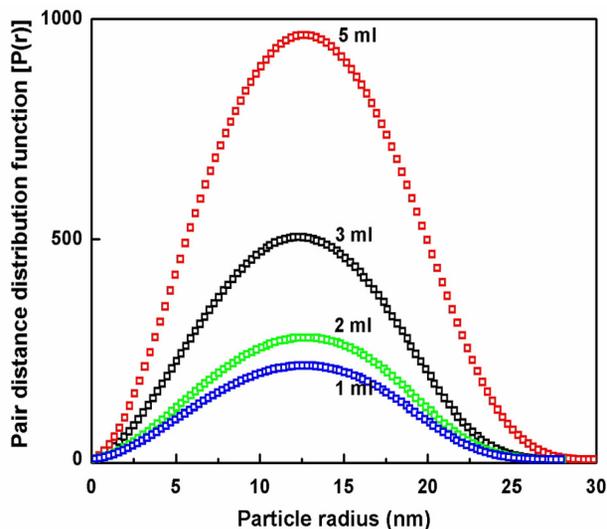


Figure 4: SAXS profiles of Ag-NPs obtained after reaction with varying volumes of *Camellia Sinensis* extract.

obtained are homogeneous in nature and nearly spherical in shape. The plot also reveals that the particle size remained more or less the same in all the experiments with an average particle size of 25 nm, except for a slight increase to 27 nm in case of experiment 4. The intensity of $[P(r)]$ increases with the increase in tea content, clearly showing that more number of particles have formed as also evidenced from UV-Vis spectra where there is no change in the λ_{\max} but increase in absorption maxima and also the XRD data where the crystallite size remained more or less the same.

TEM studies were carried out only for the powders obtained from experiment 4 as both UV-Vis and SAXS data pointed to a uniform particle size and shape. Fig. 5a shows the TEM micrograph obtained from experiment 4 and 5b the selected area electron diffraction (SAED) pattern of Ag NPs and 5c their particle size distribution.

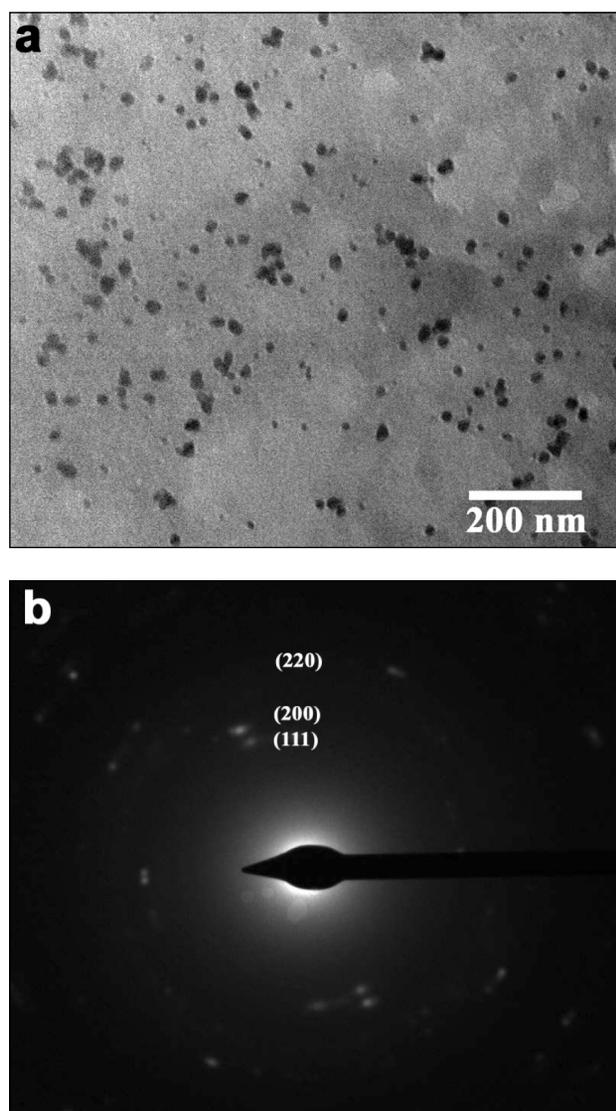


Figure 5: TEM images showing Ag-NPs (a) 25 nm obtained from experiment 4, (b) SAED pattern, and (c) the pictogram showing particle size distribution.

From Fig 5a it is evident that the nanoparticles are spherical in shape with an average particle size of 25 nm having a standard deviation of 5 nm, which is in corroboration with the values obtained from SAXS. The SAED pattern shown in fig 5b consists of three concentric rings with distinctive spots on the rings. These patterns are obtained from the lattice reflections of (111), (200) and (220) with the same inter-planar spacing as those obtained from XRD pattern in Fig. 3.

To ascertain the rate of reaction with respect to time absorption spectra of experiment 4 was recorded at an interval of 30 min for 210 min and the corresponding spectra are shown in Fig. 6. From Fig. 6a it could be observed

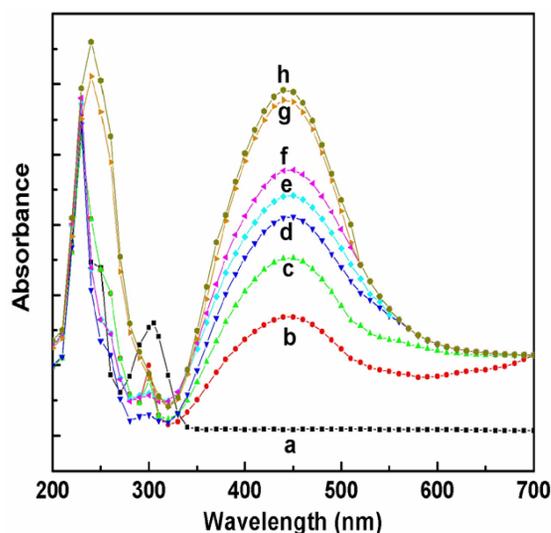
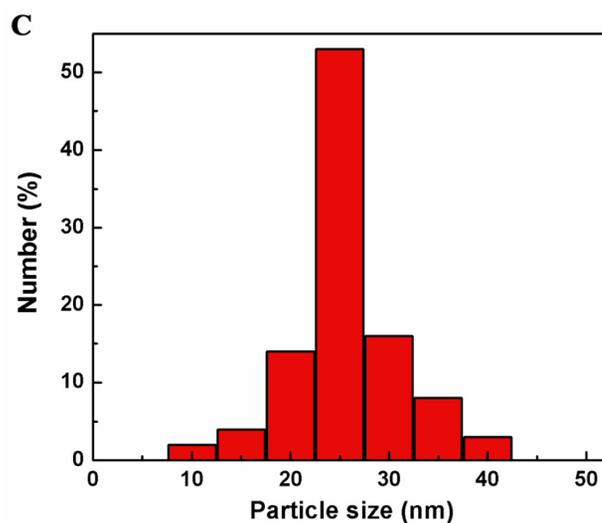


Figure 6: UV-Vis Absorption spectra of a) AgNO_3 solution (0.5 M) and b–h on reaction with 5 ml of *Camellia Sinensis* extract for varying time intervals, b) 30, c) 60 min, d) 90 min, e) 120 min, f) 150 min, g) 180 min and h) 210 min.



that for AgNO₃ solution only a single peak at 300 nm is observed, whereas the same solution on reaction with 5 ml of tea extract for various time intervals of 30, 60, 90, 120, 150, 180 and 210 min shows a decrease in the intensity of Ag⁺ ion peak at 300 nm and the appearance of surface plasmon resonance (SPR) band around 445 nm that arises due to the collective oscillations of surface electrons on interaction with the incident light. A gradual increase in the intensity of SPR band with increasing reaction time from b to h indicates the slow progression of Ag⁺ to Ag⁰ reaction. No significant change in the intensity from g to h also suggests that the reaction completes in 3 hrs.

4. Conclusions

An environmental friendly and green chemical approach is reported for the synthesis of Ag NPs. With the given conditions a narrowly dispersed Ag NPs in the range of 25 nm can be obtained. It could also be concluded that 5 ml of tea extract is sufficient for effective reduction and control of particle size and the reaction takes 3 hrs for completion. The tea extract has a consortium effect of reducing the silver salt solution and also hindering the particle growth. Thereby the choice of *Camellia Sinensis* (tea) as reducing agent is well justified.

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Povzetek

Potreba po okolju prijaznih postopkih priprave nanodelcev je posledica dejstva, da v obstoječih nanotehnologijah pogosto uporabljamo kemikalije, ki so lahko škodljive tako okolju kot zdravju ljudi. Čaj (*Camellia Sinensis*) z bogato zalogo polifenolnih spojin smo uporabili kot reducent in stabilizator nanodelcev srebra. Redukcijo Ag⁺ v Ag⁰ smo zaznali kot spremembo barve od svetlo do temno rumene. Reakcijo smo spremljali z UV–V spektrometrom. Kristalno strukturo smo analizirali z rentgensko praškovo analizo. Velikost in morfologijo delcev smo spremljali s presevno elektronsko mikroskopijo in z metodo ozkokotnega rentgenskega sipanja. Povprečna velikost delcev je 25 nm.

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