Gamma Assisted Synthesis and Characterization of Colloidal SF-AgNPs

R. Madhukumar[1,a)], K. S. Harisha[2], S. Asha[2], Youjiang Wang[3] and Sangappa[2, e)]

1Department of Physics, R.T.E.S. Degree College, Ranebennur-581115 Karnataka, India.
2Department of Physics, Mangalore University, Mangalagangotri, Mangalore –574 199, Karnataka, India.
3School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA-30332, USA.

e)Corresponding author:syhalabhvi@yahoo.co.in
a)nwwton@gmail.com

Abstract. In this study describes the synthesis and characterization of silver nanoparticles and nanocomposite materials using aqueous silk fibroin (SF) solution obtained from *Bombyxmori* silk. The resultant products have been confirmed to be Ag-NPs was carried out based on UV-Vis spectroscopy (427 nm). The UV-visible spectra showed that the characteristic surface plasmon resonance (SPR) band at around 424 nm and high resolution transmission electron microscopic (HR-TEM) measurements. From this study, it was found that the increasing the radiation dose increases the rate of reduction and decreases the particle size. The size of the AgNPs can be tuned by controlling the radiation dose.

INTRODUCTION

The metal nanoparticles research has gained lot of importance over the last two decades. Recently, noble metal nanoparticles synthesis has much attention of many researchers. The development of clean synthetic procedures for the synthesis of metal nanoparticles have been the area focused researchers due to their interesting their unique properties and potential applications in different fields. Mainly in biosensor, catalytic, cosmetic, optical, electrical, magnetic and particularly antibacterial applications [1]. The metal nanoparticles, therefore, have potential uses in technological applications. Silver is a nontoxic inorganic material well known for possessing an inhibiting effects towards 650 types of microbe's growth [2]. Most of the physical and chemical methods used for the nanoparticles synthesis involves the usage of environmentally toxic or biologically hazards chemicals as reducing agent. Therefore, for environmental sustenance, the development of clean eco-friendly, green route approach for synthesis of silver nanoparticles is very much needed. More recently many researchers were well documented/demonstrated the bio or green route (Irradiation with high energy radiations) synthesis of silver nanoparticles [3-4]. In present work we introduce a simple, effective and environmentally friendly method for in situ preparation of silver nanoparticles using silk fibroin as a reducing agent at room temperature under gamma radiation environment. Since the silk fibroin extracted from *Bombyxmori* silk, a protein polymer, which is naturally abundant, nontoxic and biocompatible material, are introduced for AgNPs synthesized silver nanoparticles were characterized by UV-visible spectroscopy, TEM, and DLS.

EXPERIMENTAL TECHNIQUES

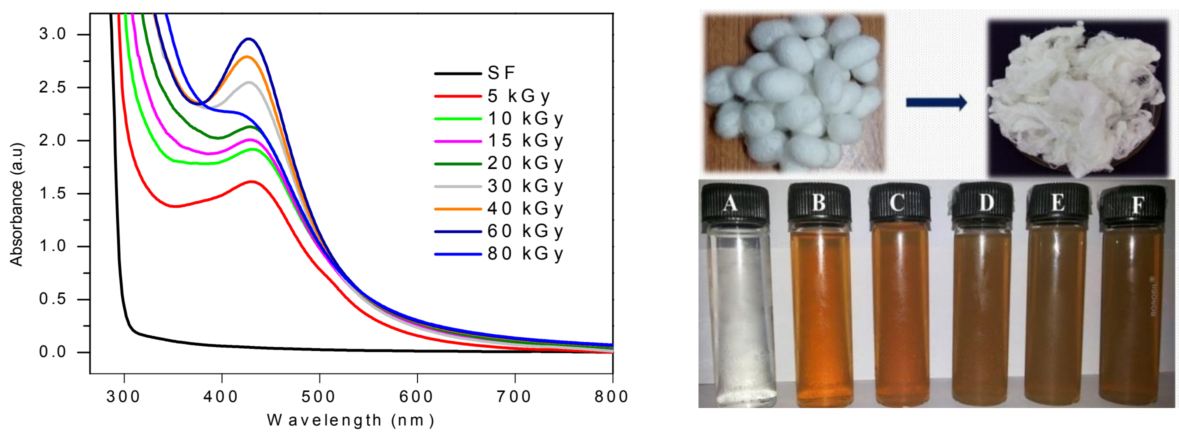
Preparation of silk fibroin (SF) solution: Pure Mysore silk (PMS) cocoons were cut into small pieces and then treated twice with boiling aqueous solution of 0.02M Na_2CO_3, for 30 min to remove the glue like sericin protein and washed with distilled water, and allowed to dry in air at room temperature [5]. The degummed silk were dissolved in 9.3 M LiBr salt solution at 70 $^{\circ}$C for 4 h, and then silk fibroin LiBr solution was dialyzed against deionized water for

72 h at room temperature using a dialysis cassette (MWCO:3500) in order to remove salt. Finally, the obtained optically clear solution was centrifuged at 4000 r/min for about 15 min to remove small amount of silk aggregates formed during the process. Then, the clear solution of SF was stored at 4 °C for further use. The concentration of SF was about 5 wt% and was diluted to 1 wt% by adding deionized water.

Preparation of SF-AgNPs solution and gamma irradiation: 10 mg of $AgNO_3$ powders were added into 10 mL of 1 wt% SF solution to form a transparent SF-$AgNO_3$ mixture solution. And then mixture solution was exposed to gamma radiation. The samples were irradiated in the dose ranging from 0-80 kGy in step of 10 kGy at CARRT center, Mangalore University, India. The synthesized silver nanoparticles were confirmed by UV-vis absorption, TEM.The UV-visible absorption spectra of SF-AgNPs solution have been recorded using UV-visible spectrophotometer (Shimadzu UV-1800, Japan) in the wavelength range 190–800 nm.The morphology of the silver nanoparticles was studied using transmission electron microscope (TEM), which was performed at 200 keV using JEOL JEM2010.

RESULTS AND DISCUSSIONS

UV-visible spectroscopy is one of the commonly used tools for the analysis of silver nanoparticles. The UV-visible absorption spectra of SF and SF-AgNPs sample are presented in Fig.1, in the wavelength range 180-800 nm. The recorded spectra of SF sample display absorption at λ=275 nm (not shown), which was attributed to the presence of the Tyr, Phe and Try residues in the silk fibroin (SF) chain [6].

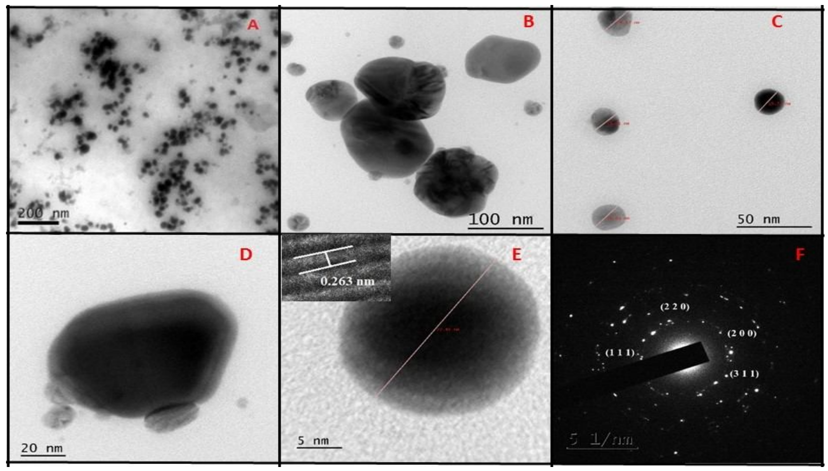


(a) (b)

FIGURE 1. (a) UV-Vis absorption spectra of Silk fibroin and SF-AgNPs. (b) (i) Photograph of silk cocoons, (ii) Silk fibroin solution; A – unirradiated, B – 10 kGy, C - 20 kGy, D – 40 kGy, E – 60 kGy, F – 80 kGy.

Fig. 2. Shows the TEM images of silver nanoparticles formed in the SF solution. Most of the silver nanoparticles were roughly spherical in shape with smooth edges. The structures were identical to those of the silver nanoparticles produced from the green route method [7].The HRTEM images (Fig 2b, c) further illustrated the nature of silver nanoparticles. The overall morphology of the silver nanoparticles produced by reduction of Ag^+ to Ag^0 with 0.1mg/mL, 60 kGy irradiated sample is composed of almost uniform nanoparticles.

Dynamic Light Scattering.To examine the average size and the potential stability of the silver nanoparticles formed in the SF solution dynamic light scattering (DLS) have been used. The DLS measurements of the selected samples are illustrated in Fig. 3. From Fig. 3(a) it is observed that at lower concentration (5 mg/mL) bigger particles (~40 nm) are formed.



(a)

FIGURE 2. (A) TEM images of AgNPs biosynthesized using the Silk fibroin, showing that particles are well dispersed (scale bar: 200 nm), (B) Typical high resolution TEM image of as biosynthesized AgNPs (scale bar: 20 nm), (C) High resolution TEM image of a single AgNP (scale bar: 10 nm), (D) Typical selected area electron diffraction of AgNPs biosynthesized using Silk fibroin (scale bar: 5 1/nm).

As the $AgNO_3$ concentration increased the size of the particles decreased (Fig. 3(b)) and it is ~20 nm at 15 mg/mL. Thus from this study it is evident that the average size of the nanoparticle decreased as the concentration increased. This was also supported by UV-visible study. Silver nanoparticles generally carry a negative charge[8-11].All silver nanoparticles synthesized from silk fibroin showed negative charge and were stable at room temperature.

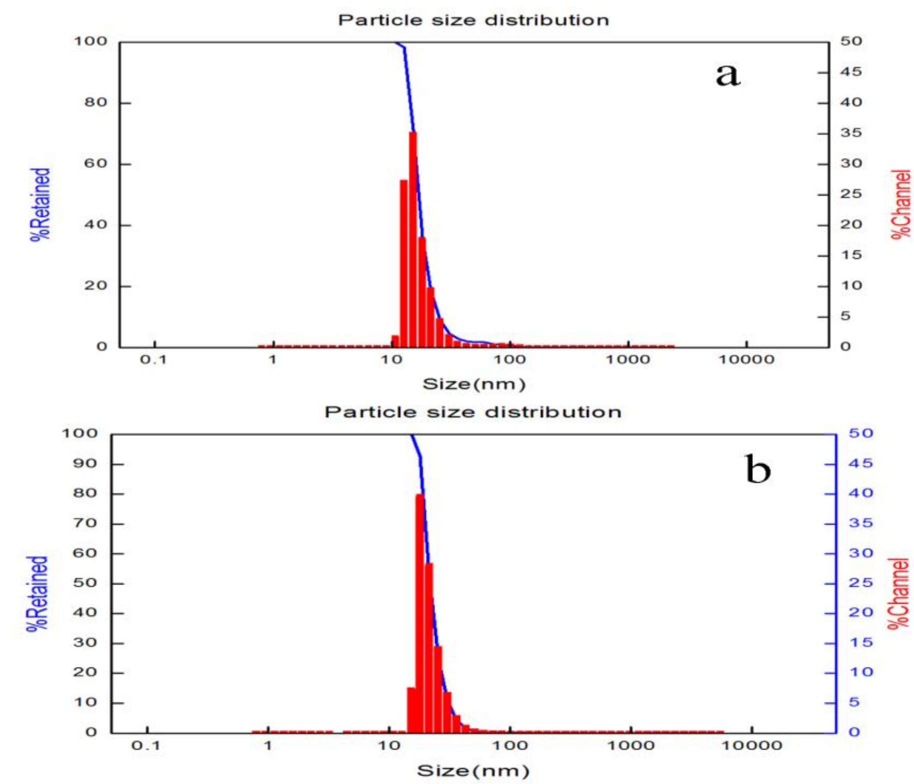


FIGURE 3. Dynamic light scattering experiment for particle size distribution analysis.

CONCLUSION

In this study, silver nanoparticles were synthesized by an eco-friendly bio based green route method. *Bombyxmori* silk fibroin can be used as both reducing and stabilizing agent for the synthesis of silver nitrate into silver nanoparticles under gamma radiation environment. Synthesized silver nanoparticles were confirmed by colour change which was observed by UV-visible spectra at 424 nm. The synthesized Ag nanoparticles were spherical in shape and their morphology was confirmed by TEM images. From this investigation, it was found that the increasing the radiation dose increasing the rate of reduction and decreases the particle size, and thus the size of the Ag nanoparticles can be tuned by controlling the radiation dose.

REFERENCE

1. P. Aramwit, N. Bang, J. Ratanvaraporn and S. Ekgasit, *Nanoscale Res Lett*. **9,** 79 (2014).
2. M. Sing, S. Sing, S. Prasad and I.S. Gambhir, *Dig. J. Nanomater. Bois*. **3,** 115 (2008).
3. R. Mariselvam, A.J.A. Ranjitsingh, A.U.R. Nanthini, K. Kalirajan, C. Padmalatha, and P.M. Selvakumar, *Spectrochimi. Act. A.***129(14)***,* 537 (2014).
4. R. Madhukumar, B. Lakshmeesha Rao, S. Asha, B. Narayana, K. Byrappa, Youjiang Wang, Donggang Yao and Sangappa, *Adv. Mater.Lett.***6(12)**, 1088-1093 (2015).
5. S. Asha, Sangappa, N. Prashantha, C.K. Sharath and S.Ganesh, *AIP Conf. Proc.***219**, 1591 (2014).
6. L.G. Hui, Y.L. De, D.Y. Xiao and H.X. Xing, *Sensors and Actuators B.***139(2),** 598 (2009).
7. M. Nilanjal, B. Jayashree, V.P. Dhagaye, G.S. Lodha and S. Sabharwal, *Adv. Mat. Lett.***4(6),** 458 (2013).
8. Y. Gou, R. Zhou, X. Ye, S. Gao, and X. Li, *Sci. Technol. Adv. Mater.*, **16**, 015004 (2015).
9. C.S. Shivananda, R. Madhukumar, B. Narayana, K. Byrappa, P. Renu, Youjiang Wang and Y. Sangappa, *Mat. Res. Inno.* **21**, 210-214, (2016).
10. Y. Sangappa, S. Latha, S. Asha, P. Sindhu,P. Parushuram, M. Shilpa, K. Byrappa, B. Narayana, *Mater. Res Innovations*. **3,** 1-7, (2017).
11. C. S. Shivananda, S. Asha, R. Madhukumar, S. Satish, B. Narayana, K. Byrappa, Youjiang Wang and Y. Sangappa, *Macromol. Res.***15,** 1-7 (2016).