Characterization of Novel Biodegradable Polymer Stabilized Nano Silver

S.Kavitha[a], D.Geetha[a*] and P.S.Ramesh[b]

Abstract

Biodegradable Polymer (Chitosan) stabilized Silver nanoparticles (AgNPs) were prepared by simple chemical reduction method. Silver nitrate ($AgNO_3$) used as a precursor in an aqueous solution of chitosan, which is behaving like stabilizing and reducing agent. Three different sample solutions were prepared viz., 0.4, 0.8 and 1.2% w/v chitosan at a constant temperature (80°C). The formation of nano silver was identified by the color change from white precipitate to pale brown color. Also Surface Plasmon Resonance band (SPR) at 400-432 nm range and the N-H band of the FT-IR spectrum. Stability of the maximum absorption wave lengths of the samples was monitored for 100 days by UV-visible Spectroscopy. The sample $AgNO_3$ in 1.2 % w/v chitosan was more stable than the other two samples. FT-IR spectroscopic analysis revealed a shifting of N-H stretching vibration band from 3367-3228 cm^{-1} with the formation of nanoparticles. X-Ray diffraction (XRD) pattern suggests small particle which was size consistent with cubic silver nanoparticles. Scanning Electron Microscopy (SEM) with EDS and Atomic Force Microscopy (AFM) of the prepared samples showed a size distribution with spherical morphology of silver nanoparticles. The average particle size of the stabilized samples ranged from ~10-20 nm. It was demonstrated that this convenient method is versatile to produce silver nanoparticles with controlled size and shape.

Keywords: Silver nanoparticles, Chitosan, Chemical reduction method.

[a]*Department of Physics,Annamalai University, Tamil Nadu-608002. Email:* geeramphyau@gmail.com

,[b]*Physics wing (DDE), AnnamalaiUniversity,Tamilnadu, India-608 002*

1. Introduction

Nanotechnology is emerging as a rapidly growing field with its application in science and technology for the purpose of manufacturing new materials at the nanoscale level [1]. It has various potential applications in photo catalysis, solar

energy, electronics, optics, sensor and so on [2]. Bio nanotechnology has emerged up as integration between biotechnology and nanotechnology for developing biosynthetic and environmental-friendly technology for synthesis of nanomaterials [3].

Research is investing time into modifying traditional materials to make them more user-friendly, and into designing novel polymer composites with good degradable property out of naturally occurring materials [4].

Many techniques of synthesizing silver nanoparticles, such as chemical reduction of silver ions in aqueous solutions with or without stabilizing agents[5], thermal decomposition in organic solvents, chemical reduction and photo reduction in reverse micelles[6] and radiation chemical reduction have been reported in the literature.

Chemical reduction is the most widely used method to prepare AgNPs colloidal dispersion using a suitable stabilizing agent; $AgNO_3$ is often used as the primary source of Ag^+ for AgNPs generation. Stabilizing agents are used to control the growth and dispersion of nanoparticles in the aqueous media [7].This method is commonly used to prepare silver nanoparticles in industrial applications because of its great advantages. However, in chemical methods, the chemical reduction using different reducing agents such as sodium borohydride, hydrazine etc., is the most frequently used process to reduce silver ion (Ag^+) to silver atom (Ag) [8]. Stabilizing agents, such as polymers are usually used to prepare the stabilized AgNPs during the reduction process [9].

Chitosan (Cts) is a non-toxic, inexpensive and biocompatible polymer, biodegradable by different hydrolytic enzymes. Chitosan has been widely used in the regeneration of different types of tissues, especially skin [10] and bones and in many other biomedical and pharmaceuticals applications.

In the study, we proposed a new method by reducing $AgNO_3$ with three different concentrations (0.4, 0.8 and 1.2 ml) at a moderate temperature (80°C) for the preparation of silver nanoparticles. The nanoparticles were characterized by Ultraviolet-Visible (UV-Vis) Spectroscopy, X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy with EDS and Atomic Force Microscopy (AFM).

2. Experimental Method

Material and Synthesis of Silver NPs

Silver nitrate ($AgNO_3$, 99.9%) was purchased from Sd-fine and used as a precursor in the formation of AgNPs. Chitosan were purchased from Sd-fine and used as both reducing and stabilizing agents. All chemicals were used without further purification. Demonized (DI) water was used as the solvent.

Preparation of Silver NPs was performed by the addition of an aqueous $AgNO_3$ solution to an aqueous Cts solution. In a typical procedure, 1g of chitosan was dissolved in 99g of DI water to

prepare a 1wt% solution. The aqueous chitosan solution was mixed with 0.05g of $AgNO_3$ dissolved in 20 ml of DI water in heated at 80°C

3. Result and discussion

It is well known that silver nanoparticles exhibit yellowish- brown color in aqueous solution due to excitation of surface plasmon vibration in silver nanoparticles [11]. Reduction of silver ions to silver nanoparticles could be followed by a color change and UV-Vis spectroscopy. The technique outlined above has proven to be very useful for the analysis of nanoparticles [12]. Therefore, the progress in conversion reaction of silver ions to silver nanoparticles was followed by a color change and spectroscopic techniques.

In this study chitosan were prepared at three different concentrations (0.8, 1.0 and 1.2% w/v) with water and this solution was mixed with $AgNO_3$ solution separately. And chitosan is reacted with the Ag^+ ion to form metalo polymer [Ag/Cts]. This polymer was aged at three different concentrations at moderate temperature 80°C to form Ag/Cts nanocomposite. From this process, Ag+ was successfully reduced to Ag nanoparticles.

3.1. UV-Vis Spectroscopy

The silver nanoparticles were characterized by UV-Vis spectroscopy, one of the most widely used techniques for structural characterizations of silver nanoparticles [13]. The absorption spectrum of the yellowish-brown silver nanoparticles solution prepared with the proposed showed a surface plasmon absorption band with a maximum of 432 nm, indicating the presence of spherical Ag nanoparticles.

In general it was known that silver nanoparticles have a strong absorption peak at about 400-450nm [14]. This UV absorption peak shows the confirmation of nano-sized silver particles, and its particle size, and the particle size distribution. The narrower the absorption peak gives better particle size and standard deviation respectively. Therefore, whether the formation of nano-sized silver particles with narrow size distribution is accomplished or not can be predicted by analysis of UV absorption peak [15].

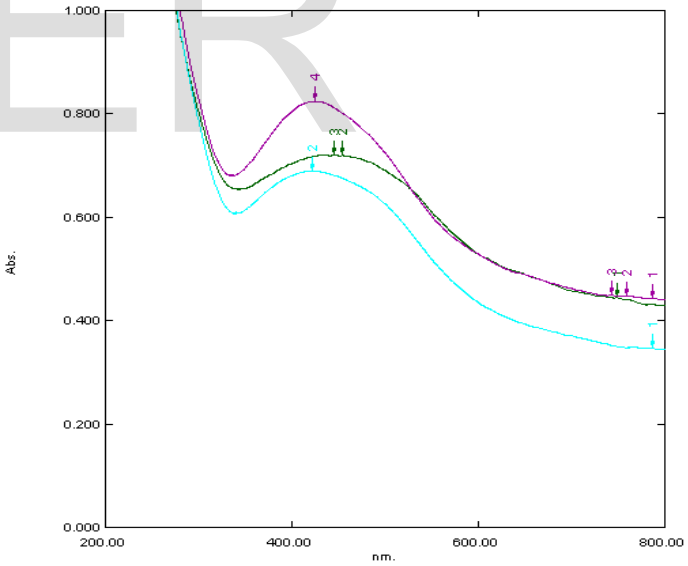

Fig 1. The UV-visible cures of silver nanoparticles produced under different concentrations of chitosan (0.4, 0.8, and 1.2 % w/v) at 80°C.

Fig (1). Shows the UV-Visible spectra of silver nanoparticles produced under different

concentration of chitosan (0.4, 0.8, and 1.2 % w/v). It can be seen that the higher the chitosan concentration (1.2 % w/v) the lower the maximum absorbance wavelength and therefore, the smaller the nanoparticles. The similar results have been reported by pal on his gold nanoparticle synthesis that increasing concentrations of PVP limited the particle size through the restriction of particle growth [16].

3.2. Fourier Transform Infrared Spectroscopy (FT-IR)

FTIR absorption spectra of Ag/Cts nanocomposites in three different concentrations are shown in Fig 2a, b and c respectively. Both the spectra the presence of bands due to O-H stretching (around – 4310 cm-1). The peaks are 3402, 3417 and 3410 cm-1(O-H stretch overlapped with N-H stretching vibration). FTIR spectrum of Ag/Cts (1.2% w/v) nanocomposites showed absorption band at 2164 cm^{-1} (C-N asymmetric band stretching), 1637 cm^{-1}, corresponding to the amide I of polypeptides and 1473 and 1400 cm^{-1} (asymmetric C-H bending of CH2 group) . Following reaction with 1.0 and 0.8 % w/v solution, the amide I band appeared at 1664 and 1643 cm^{-1}[17]. The intense band found in fig 2a, b, c at 1421 and 815 cm^{-1} corresponding to the C-H in plane deformation with aromatic ring stretching. Band at 1083, 1085 and 1070 cm^{-1} in the spectra indicated C-O stretching. The bands visible in between 500 and 749 cm-1 signified the presence of R-CH group. The above results show that there is a shift in N-H stretching vibration around 3410 cm^{-1}. It also conform that the synthesized compounds is silver nanoparticles

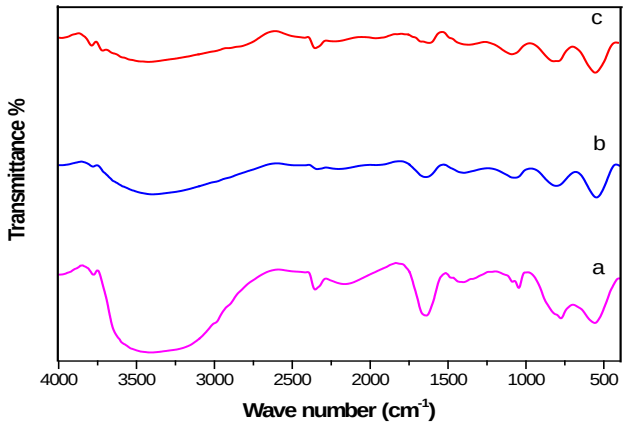

Fig 2. FT-IR Spectra of (a) 0.4, (b) 0.8 and (c) 1.2% w/v are different
concentration of Ag/Cts nanocomposite.

3.3. X-Ray Diffraction (XRD)

The XRD analysis of Ag/Cts nanocomposite is illustrated in fig 3.The wide peak at 2θ = 20 is a characteristic of chitosan, whereas the other one peak refers to the existence of zero-valent silver on the surface of the nanocomposite. The one peaks at 2θ can be attributed to the (111) planes of face-centered cubic (FCC) silver crystals, respectively. The crystal size of the particles calculated from the Scherer equation, $D=K\lambda/\beta \cos\theta$. Where D is the crystal size of the catalyst, λ the X-ray wavelength (1.54 A°), β- the full width at half maximum (FWHW) of the catalyst, K is a co-efficient (0.89) and θ- is the diffraction angle. Whereas the result showed that the crystal size decreasing with increasing the concentration. Where, 10nm (a), 9nm

(b) and 8nm (c) for Ag/Cts nanocomposites at constant temperature (80°C). Moreover, the sharp and intensive peak at 2θ= 38.3° (111) indicated a highly organized crystal structure of AgNPs.

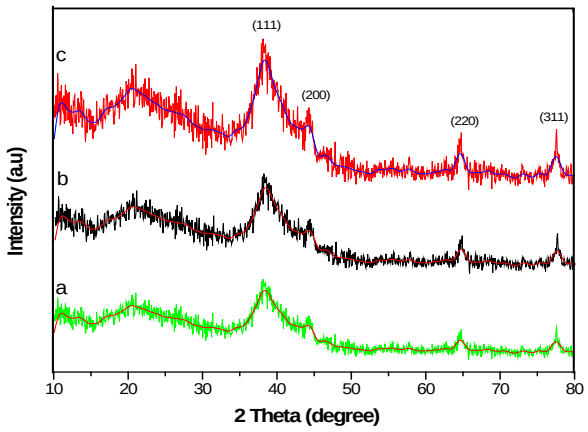

Fig 3. XRD spectra of Ag/Cts nanocomposite of (a) 0.4, (b) 0.8 and (c) 1.2% w/v at constant temperature (80°C)

3.4. Scanning Electron Microscopy (SEM) with EDS

Scanning electron microscopy was used to investigate the surface morphology of chitosan-Ag nanocomposite three concentrations of 0.4, 0.8 and 1.2% (w/v). The SEM with EDS pictures of Ag/Cts nanocomposite shown in fig 4. The particles of the material all have spherical or steroidal morphology and have the particles size range of 48nm (80°C).The Ag/Cts nanocomposite has aggregated particle structure (fig 4c); however, the micrographs of fig 3a and b are uniform. The particles in nanocomposite were also found (fig 4c) and the surface was somewhat rough. It is noteworthy that the particles are non- uniformly mixed in an Ag/Cts matrix. Energy dispersive X-ray analysis (EDS) of silver nanoparticles revealing strong signal in the silver region and thus confirms the formation of silver nanoparticles

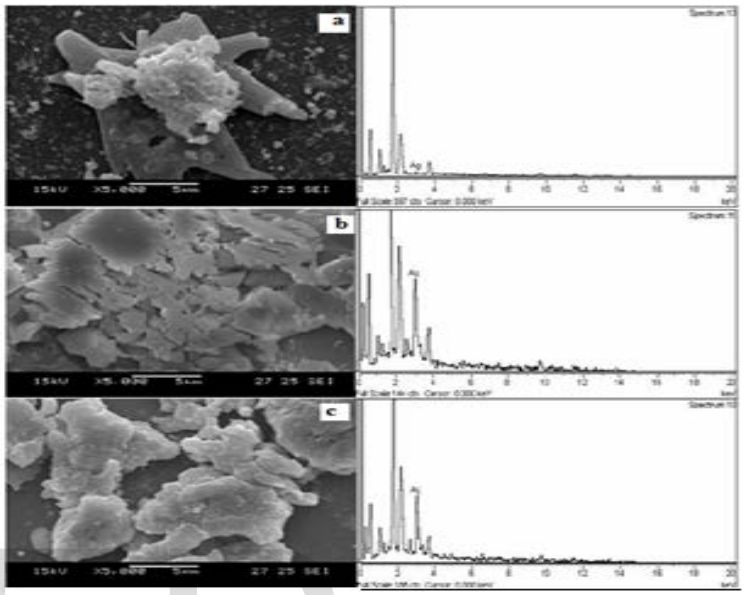

Fig 4. SEM image with EDX spectrum of (a) 0.4, (b) 0.8 and (c) 1.2% w/v are different concentration of Ag/Cts nanocomposite.

3.5. Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) has been implemented as a structural characterization technique for the examination of nano powders materials in contact mode. AFM offers the significant advantage of probing in high details the surface topography qualitatively (by surface images) and quantitatively due to its nanometer scale spatial resolution, both lateral and vertical. AFM has proved to be very helpful in the determination and verification of various morphological features and parameters. The formation of silver nanoparticles is confirmed by

AFM analysis. The AFM image clearly (Fig.5) shows the surface morphology of the well-dispersed silver nanoparticles. Fig .5 shows the 3D AFM photograph of synthesized silver nanoparticles. The AFM photograph of silver nanoparticles is formed under condition of Ag/PEG concentration of 1.2 % w/v. The tapping mode AFM image clearly shows the formation of nanoparticles with spherical or steroidal shape. Owing to agglomeration of particle only approximate sizes are reported. The size of the particle is 34.2 nm.

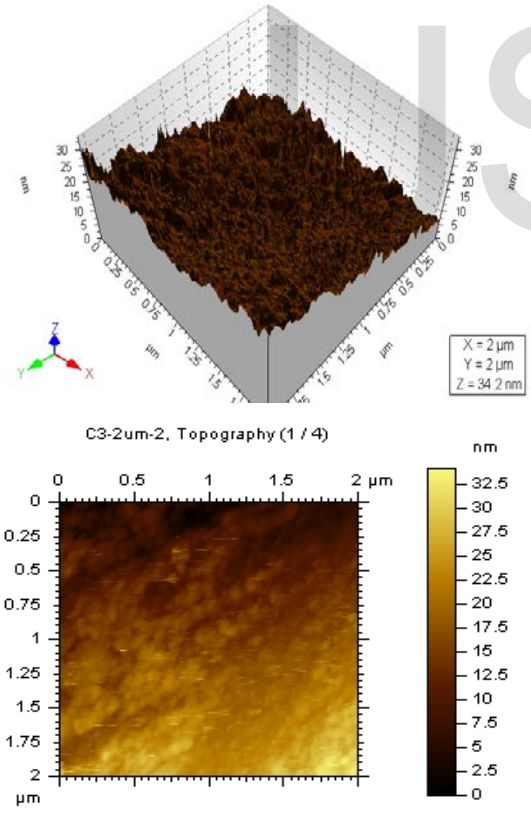

Fig 5. Surface topography of 3-Dimensional image and height of Ag/Cts nanocomposite of 1.2% w/v at constant temperature (80°C)

4. Conclusion

Nano silver chitosan solution can be interesting stabilizer. The chitosan silver nanocomposite was prepared via chemical reduction method and thereby reduction of silver ions in to Ag/NPs. The developed silver nanoparticles are well characterized using different techniques, to conform the formation of silver nanoparticles. The morphology of nanocomposite was examined by SEM with and AFM. FT-IR, XRD and UV-Visible spectra reveled the formation of silver nanoparticles.

References

1. Albrecht M.A, Evan C.W and Raston C.L. Green chem (2006) 8 417-32.
2. Jin J, Isoda S, Wang F and Adachi M. J.physics.chem (2006) 110, 2087-2092.
3. MahendraRai, AlkaYadav and Aniket Grade. Biotechology advances (2009) 27, 76-83.
4. Kolybaba M, Tabil L.G, Panigrahi W.J, Powell T and Wang B. (2003).
5. Liz-Marzan L.M, and Lado-Tourino I. Langmuir (1996)12, 3585-3589.
6. Pileni M.P. Langmuri (2000) 17, 2329-2333.
7. Sadeghi S and Moghbeli M.R. J.colloidds and surfaces A (2012) 409, 42-51.
8. Wang L, mWang F and Chen D. (2008) 62, 2153-2156.
9. Khanna P.K, Singh N, Charan AS, Subbarao V.V.V.S, Gokhale R, Mulik U.P. Mater chem., phys (2005) 93, 117-121.
10. Liu H, Mao J, Yao K, Yang G, Cui L and Cao Y. J.Biomater.sci (2004) 15, 25-40.
11. Jae Y.S, and Beom S.K. Bioprocess Biosyst.Eng (2009) 32, 79-84.
12. Sastry M, Patil V and Sainkar S.R. J.phys.chem.B (1998) 102, 1404-1410.

13. Sun Y.P, Atprmgitjawat P and Meziani M.J. Langmuir (2001) 17, 5707-5710.
14. Kapoor S. Langmuri (1998) 14, 1021-1029.
15. Ki Do Im, Dac Nam Han and Hee Jair Kim. (2004).
16. Mandal M, Ghosh S.K, Kundu S, Esumi K and Pal T. Langmuri (2002) 18, 7792.
17. Sathyavathi R, Krishna M.B, Rao S.V, Saritha R, Rao D.N. Adv sci Lett (2010) 3, 01-06.