GREEN SYNTHESIS OF PLASMON SILVER NANO PARTICLES FOR FABRICATION OF BIO/CHEMICAL SENSOR

DR.ENAKSHI DAS

Abstract: The main aim of the work presented in this paper is to develop Nano Structure Plasmon Silver Particles for a bio sensors or chemical sensors by using non-toxic & eco-friendly method of novel synthesis route. Leaf extract is used in this method as reducing and capping agent for the synthesis of silver nanoparticles. The bio fabrication of pure metallic silver nanoparticles are carried out by reduction of Ag^{+1} to Ag^{o} with the aqueous extract of lemon grass (*cymbopogon flexuosus*) and their characterization was studied in detail. Ag NPs were characterized by UV–vis spectrophotometer, X-Ray Diffractometer (XRD), Atomic Force Microscopy (AFM) and Fourier transform Infra-Red (FTIR) spectroscopy. Optical properties of developed nanoparticles also depend upon the refractive index near the nanoparticle surface. The nanoparticle extinction spectrum experiences red shifting as the refractive index near the nanoparticle surface increases. The formation and stability of the reduced silver nanoparticles in the colloidal solution were monitored by UV–vis spectrophotometer analysis. The mean particle diameter of silver nanoparticles was calculated from the XRD pattern using Scherer's equation. Silver nanoparticle absorption and scattering properties can be tuned by controlling the particle size, shape, and the local refractive index near the particle surface. Under the UV-Visible wavelength nano particles shown quiet good Surface Plasmon Resonance behaviour. The reported results have potential for developing nanosensors based on small nanoparticles. These results are useful indications for in situ characterization and monitoring of AgNPs synthesis and for the engineering of AgNPs with new plasmonic properties. Most importantly, this paper outlines an approach for realizing optimal plasmonic material properties for specific frequencies and applications. Using the Raman Spectroscopy the shift of surface Plasmon resonance peak can be monitored while silver nanoparticles are exposed to variable concentration of poisonous gases like ozone, CO etc. Potentially, this system can be useful as a Gas Sensor or Bio Sensor that identifies the presence of gases or bio molecules at low part-per-billion concentrations in gaseous media and biomaterials.

Keywords: Nanostructure Plasmon; Surface Plasmon Resonance; Nano sensors; Raman Spectroscopy.

Introduction: When dealing with the object of dimension between 1 and 100 nm (nano material) the ratio between interface and inner atoms becomes significant. These strongly influence physical and chemical behaviour of the nano materials. The spread of nanotechnology is strictly due to the improvement of characterization and synthesis techniques on nano meter scale [1]. Nano-sized clusters of noble metals (especially Au, Ag) exhibit unique optical properties which are not present in the spectrum of the bulk metal. Absorption and scattering of incident light, occurring when the photon frequency is resonant with collective oscillations of conduction electrons, results in strong UV–Vis bands. This effect is known as non-propagating or Localized Surface Plasmon Resonance (LSPR)[1] – [2]. A rigorous mathematical description of this phenomenon was achieved by Mie [2]. In his formulation, the extinction (scattering + absorption) $E(\lambda)$ of a spheroid metal nanoparticle is related to the properties of the system by the equation

$$E(\lambda) \propto \left[\frac{\varepsilon_i(\lambda)}{(\varepsilon_r(\lambda) + \chi\varepsilon_{\text{med}})^2 + \varepsilon_i(\lambda)^2} \right]$$

Where ε_{med} is the dielectric constant of the medium surrounding the NP, χ is a factor related to the geometry (for a sphere, $\chi = 2$)), ε_i and ε_r are the imaginary and real part of the dielectric function of the NP. There is a favourable combination of physical-chemical properties and advances in chemical synthesis. The surface plasma absorption (SPA) is the main characteristics of AgNP. Silver nanoparticles absorb and scatter light with extraordinary efficiency. Their strong interaction with light occurs because the conduction electrons on the metal surface undergo a collective oscillation when they are excited by light at specific wavelengths. This oscillation is known as a surface Plasmon resonance (SPR). Frequency of silver SPA can also be tuned from visible to near infrared depending on shape, size or nano particle assembly. They have high chemical stability and photo stability, especially AgNP are non-toxic for living organism. Because of their physicochemical stability, bright colour and biocompatibility, recent years have faced sensible progress in AgNP synthesis with tailored shape and size. This with engineered properties opens the access of nanotechnology to manifold applications. When light interacts with metal-dielectric materials, surface Plasmon are produced. Plasmon materials are meta materials that exploit these surface Plasmon. When the incident light couples with the surface

Plasmon it creates propagating electromagnetic waves known as Surface Plasmon Polaritons (SPPs) which ripple along the metal-dielectric interface. Compared with the incident light the SPPs are found to be much shorter in wavelength [3]. It is understood from literature that surface Plasmon resonance at the surfaces of gold nanostructures has created great interest in fabrication of gold nanoparticles. The study of nano optical branches such as nano plasmonics is of much interest to material engineers, physicists, chemists and biologists. Generation of nano-particles using plant extracts are amongst the most researched topics in nanotechnology. The various advantages of using plant extracts for nano-particles synthesis are:

1. It eliminates the tedious and time consuming process of maintaining cell cultures[4]-[5]
2. The process is simple and eco-friendly[6]
3. It eliminates absorption of toxic chemical on the surface that may have adverse effect in the medical applications.
4. Provides advancement over chemical and physical method as it is environment friendly, easily scaled up for large scale synthesis and in this method there is no need to use toxic chemicals.

Silver and gold nanoparticles are reported to be nontoxic to human and most effective against bacteria, viruses, and other eukaryotic micro-organisms at very low concentration and without any known side effects [7].This is their advantages over other nano materials. In the recent years, much advancement is brought to the technology for synthesis and characterization of nanoparticles. It is an important necessity to produce nanoparticles in an eco-friendly manner. Biological organisms such as plant extract or plant biomass could be an alternative to chemical and physical methods for the production of nanoparticles in an eco-friendly manner [8]-[11]. Another study was carried out by Masurkar et al [12], who reported rapid biosynthesis of silver nanoparticles using *Cymbopogan citrates*.

The present paper provides our initial research work on synthesis of Plasmon silver nano particles from lemon grass extract and their characterisation. The main aim of this work is to develop Nano structured Plasmon materials for a bio/chemical sensors by using non-toxic & eco-friendly method of novel synthesis route.

Experimental:

Materials and Methods: The bio fabrication of pure metallic silver nanoparticles are carried out by reduction of Ag^{1+} to Ag^{o} with the aqueous extract of lemon grass and their characterization. Deionised water was used throughout the reactions. All glass wares were washed with dilute nitric acid HNO_3 and distilled water, then dried in hot air oven. For the synthesis of silver nanoparticles, lemon grass extract is used as reducing and capping agent. Silver nitrate ($AgNO_3$) and lemon grass are used as Materials for the synthesis of silver nano particles. Both materials are commercially available. The silver nitrate was purchased from Sigma Aldrich and the lemon grass from specialized shop.100 gram of *Lemon grass* leaves were thoroughly washed and then finely cut and mixed in 100 ml of distilled water. The mixture was then boiled and decanted. Thus grass extract was prepared. A stock solution of $AgNO_3$ 2×10^{-2} M was prepared by dissolving 0.34 g/100 ml de-ionized water.

Green Synthesis of Silver Nanoparticles: For the synthesis of the silver nanoparticles, a certain volume of the lemon grass extract was added to the $AgNO_3$ solution and the volume was adjusted to 10 ml with de-ionized water. The solution was stirred for few minutes. The reduction process Ag^{+} to Ag^{o} nanoparticles was followed by the colour change of the solution from yellow to brownish-yellow to deep brown depending on parameters studied such as the extract concentration, temperature and pHs. The nanoparticles were prepared at different pH values, the pH of the solutions was adjusted using 0.1 N H_3PO_4 or 0.1 N NaOH solutions. Silver nano particles are sputter coated on to a transparent substrate.

Characterisation:

UV-Vis Spectra analysis: The absorption spectra of the synthesized silver nanoparticles were recorded against water, which shows the formation and stability of silver nanoparticles Fig.1 shows the UV–visible spectra of silver nanoparticle formation using constant $AgNO_3$ concentration (2×10^{-3} M) with different extract concentrations at room temperature after 24 h.

X-Ray Diffraction (XRD): XRD is a non-destructive analytical method which identifies and determines various crystalline forms of materials. The solution of nanoparticles obtained was purified by repeated centrifugation at 10,000 rpm followed by re-dispersion of nanoparticles into distilled water. After freeze drying of the purified particles, the structure and composition of nano particles were analyzed by XRD [13-16].As waves interact with a regular structure the diffraction occurs. To check phase formation and purity, XRD patterns were recorded using powder X-ray Diffractometer. In the present research work XRD was carried out for synthesised silver nano materials using instrument with Cu$K\alpha$ radiation

Fourier Transform-Infra Red (FT-IR) spectroscopy: Dry powders of the nanoparticles were prepared for Fourier transform infrared (FTIR) spectroscopy measurements. After 24 h of reaction of the salt solutions with the lemon grass extract synthesized Ag nanoparticles were centrifuged at 10,000 rpm for 30 min and then the pellet was redispersed in sterile distilled water to ensure better

separation of the uncoordinated biological molecules from nanoparticles. The purified pellets were then dried and the powders subjected to FTIR spectroscopy measurement. GX Perkin Elmer Fourier transform infrared spectrometer used to carry out the experiment.

Scanning Electron Microscopy: Scanning electron microscopy provided further insight into the morphology and size details of the silver nanoparticles.

Results and Discussion: The colour of the solutions changed from pale yellow to yellowish brown to deep brown depending on the extract concentration indicating silver nanoparticle formation as the colour change observed is due to excitation of surface Plasmon vibration in the silver nanoparticles. It can be seen from UV-Vis spectra that the Surface Plasmon Resonance (SPR) of AgNPs is observed at 445–463 nm. The SPR of silver nanoparticles produced a peak centred near 450 nm, indicating the reduction of silver nitrate into silver nanoparticles. UV-Vis absorbance of the reaction mixture was taken around 5 minutes, indicating rapid green synthesis of silver nanoparticles.

Optical properties are observed to be dependent on the refractive index near the nanoparticle surface. As the refractive index of the nanoparticle surface increases, the nanoparticle extinction spectrum shifts to longer wavelengths (known as red-shifting). In other words the nanoparticle extinction peak location will shift to shorter wavelengths (blue-shift) if the refractive index of local nanoparticle surface decreases. The fig.2 shows the extinction spectrum of a silver nanosphere as the near surface refractive index is increased.

X-ray diffraction results (Fig.3) clearly show that the silver nanoparticles formed by the reduction of Ag+ ions by the lemon grass extract are crystalline in nature. The average size of the silver nano particle was found to be approximately 20 nm. The average particle size of biosynthesized silver nanoparticles was calculated using the Debye-Scherer equation [17]-[18]

$D = K\lambda / (\beta \cos\theta)$. Where, D is the crystalline size of Silver nano particles, λ is the wavelength of the X-ray source (0.1541 nm) used in XRD, β is the band width of diffraction peak, K is the Scherer constant with a value from 0.9 to 1, and θ is the Bragg angle.

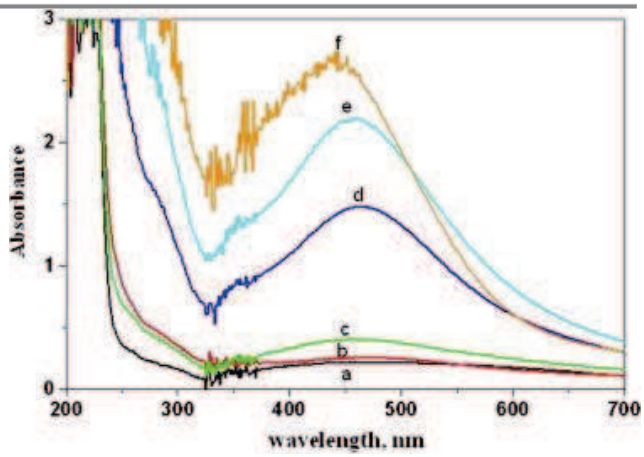

Fig.1: UV–Vis spectra of silver nanoparticles at different concentrations of lemon grass extract (a, b, c, d, e and f refer to 0.1, 0.3, 0.6, 2, 5 and 7 ml, respectively).

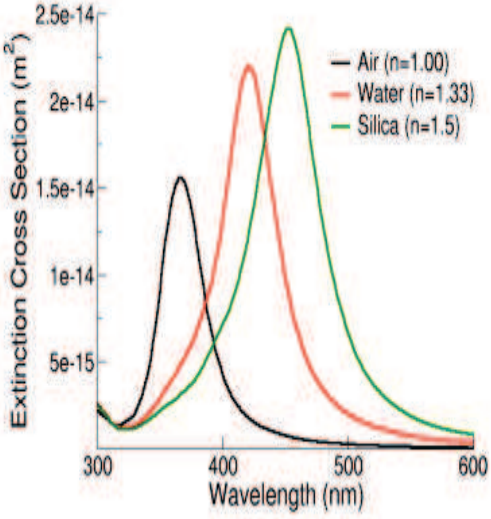

Fig.2: As the refractive index of the medium increases, the nanoparticle spectrum shifts to longer wavelength

FTIR spectrum of the lemon grass and AgNp synthesized using lemon grass extracts was shown in Fig.4. FTIR measurements were carried out to identify the possible biomolecules responsible for capping and efficient stabilization of the green synthesised metal nanoparticles.

Fig.5 shows the scanning electron micrograph of the lemon grass treated with 3 mM silver nitrate solution for 24 h. SEM determination of the brown colour stable samples showed the formation of silver nanoparticles and well dispersed nanoparticles could be seen in the samples treated with silver nitrate.

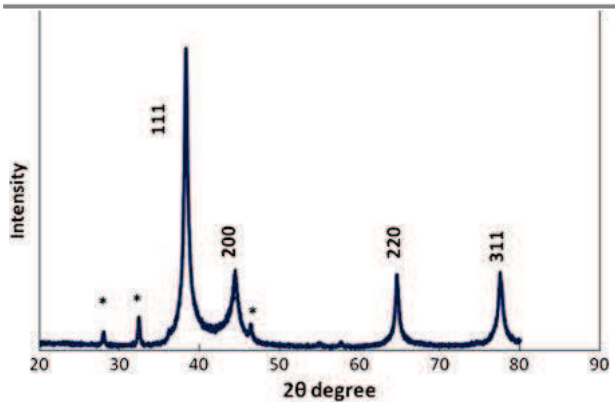

Fig.3: XRD pattern of silver nanoparticles green synthesized by lemon grass extract.

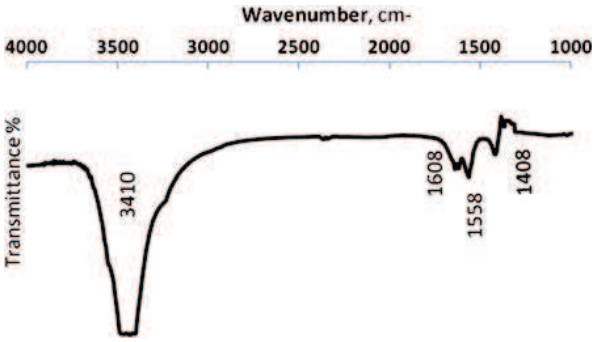

Fig.4: FTIR of silver nanoparticles biosynthesized by lemon grass extract

Conclusion: In the UV-Visible wavelength nano particles have shown quiet good surface Plasmon resonance behaviour. UV–vis spectrophotometer, FTIR, XRD and SEM techniques have confirmed the reduction of silver nitrate to silver nanoparticles. Nanoparticles synthesized in present research work could find applications in the field of nano optics as optical sensors specially as Bio/Chemical sensors. Green synthesis of metallic nanoparticles is a successive alternative to chemical synthesis. Present work is certainly based on furthering fundamental knowledge on nano sensors and devices. Using the Raman Spectroscopy the shift of surface Plasmon

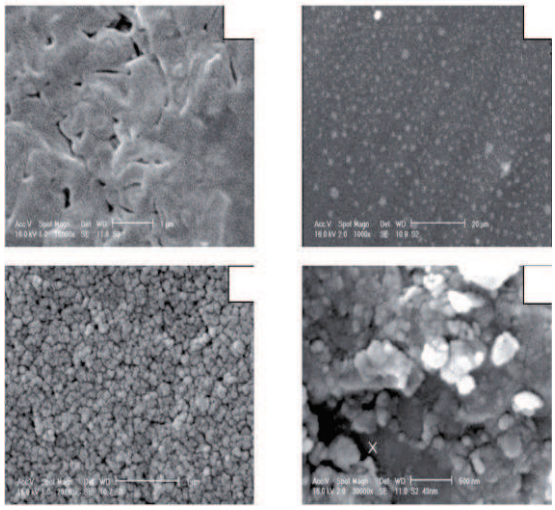

Fig.5: Scanning electron micrograph of the lemon grass incubated with deionised water (first fig.) & SEM of silver nanoparticles obtained with lemon grass extract incubated with 0.003 M silver nitrate solution (fourth fig.)

resonance peak can be monitored while silver nanoparticles are exposed to variable concentration of poisonous gases like ozone, CO etc. Potentially, this system can be useful as a Gas Sensor or Bio Sensor that identifies the presence of gases or bio molecules at low part-per-billion concentrations in gaseous media and biomaterials. Testing the Plasmon materials as sensor by Raman scattering experiments using Raman Spectrometers will be carried out in future.

References:

1. Huldah Samuel, V. Rajkumar Dare, Generalized Parikh Vectors and Partial Line Languages; Mathematical Sciences international Research Journal ISSN 2278 – 8697 Vol 3 Issue 2 (2014), Pg 558-560
2. Das Enakshi, 'Development of Nano structure Plasmon Gold by Green Synthesis for Fabrication of Bio/Chemical Sensor', *Res. J. Recent. Sci.* Vol. 3(ISC-2013),(2014), 1-8
3. A. Szabo, L. Stolz, R. Granzow, 'Curr. Opin. Struct.' Biol., 5 pp. (1995),699- 705
4. Kuttge, M.; Vesseur, E.; Koenderink, A.; Lezec, H.; Atwater, H.; Garcia De Abajo, F.; Polman, A. Local cathodoluminescence, *Physical Review B.* (2009)79 (11)
5. ChelladuraiMalarkodi, ShanmugamRajeshkumar, MahendranVanaja, KanniahPaulkumar, GnanadhasGnanajobitha, GurusamyAnnadurai, ' Eco-friendly synthesis and characterization of gold nanoparticles using Klebsiellapneumoniae'Journal Of Nanostructure in Chemistry; 3 2013),30
6. *Bonthu Kotaiah, T. Arundhathi, Pathan Mehra Jahan,* Comparative Analysis of Machine Learning Techniques For Software Reliability Prediction; Mathematical Sciences international Research Journal ISSN 2278 – 8697 Vol 3 Spl Issue (2014), Pg 977-992
7. Sumit.S.Lal, P.L.Nayak' International Journal of Science Innovations and Discoveries', 2 (2012), 325-350

8. S. Vijayabalaji, Multi Decision Making in Generalized Soft-Rough; Mathematical Sciences International Research Journal ISSN 2278 – 8697 Vol 3 Issue 1 (2014), Pg 19-24
9. Ratul Kumar Das, NayanmoniGogoi, PunuriJayasekharBabu, Pragya Sharma, ChandanMahanta at al., 'The Synthesis of Gold Nanoparticles Using Amaranthusspinosus Leaf Extract and Study of Their Optical Properties' , 'Advances in Materials Physics and Chemistry', 2(1): (2012)275-28
10. Jeong SH, Yeo SY, Yi SC, ' The effect of filler particle size on the antibacterial properties of compounded polymer/silver fibres', *J Materials Sci*, 40. (2005)5407-5411
11. L.Hari Krishna, M.Veera Krishna ,M.C.Raju, Hall Current Effects on Unsteady MHD Flow In A Rotating Parallel Plate Channel Bounded By Porous Bed on the Lower Half – Darcy Lapwood Model; Mathematical Sciences International Research Journal ISSN 2278 – 8697 Vol 4 Spl Issue (2015), Pg 29-40
12. Sastry M, Ahmad A, Khan MI and Kumar R, ' Microbial nanoparticle production *Nan biotechnology*, ed. by Niemeyer CM and Mir kin CA'. Wiley-VCH, Weinheim, (2004) 126–135
13. Bhattacharya D and Rajinder G, 'Nanotechnology and potential of microorganisms', *Crit Rev Biotechnology* 25. (2005)199–204
14. Mohanpuria P, Rana NK and Yadav SK, ' Biosynthesis of nanoparticles: technological concepts and future applications' *J Nanopart Res* 10, (2008)507–517
15. N.Vithya, Dr. P. Thangavelu, on Generalised B#-Closed Sets; Mathematical Sciences international Research Journal ISSN 2278 – 8697 Vol 3 Issue 2 (2014), Pg 561-563
16. Pillai Raji K., Sareen Sarah John., Toms Joseph C., Chandramohanakumar N., Balagopalan M, Vermifugal Activity of Bio fabricated Silver Nanoparticles, *Research Journal of Recent Sciences* Vol. 1.(ISC-2011), (2012)47-51
17. Ruchi Sandilya, Sarvesh Kumar, Discontinuous Finite Volume Methods for Parabolic Optimal Control Problems; Mathematical Sciences international Research Journal : ISSN 2278-8697 Volume 4 Issue 2 (2015), Pg 15-22
18. Masurkar SA, Chaudhari PR, Shidore VB, Kamble SP,' Rapid biosynthesis of silver nanoparticles using Cymbopogan citrates and its antimicrobial activity', *Nano-micro letters*(2011)
19. Linga Rao M, Savithramma N, Biological synthesis of silver nanoparticles using Svensonia hyderabadensis leaf extract and evaluation of their antimicrobial efficacy, *J Pharm Sci Res*, **3**, (2011) 1117-1121
20. Priya M,M. Selvi BK, John Paul JA, 'Green synthesis of silver nanoparticles from the leaf extracts of Euphorbia hirta and Nerium indicum', *Digest J Nanomaterials Bio structures*, **6**. (2011)869-877
21. Rajinder Kashyap Anil Thakur, D. K. Sharma, Spectrophometric Determination of Methyisothiocyanate in Its Commercial formulation and Four Indian Soils; Mathematical Sciences international Research Journal ISSN 2278 – 8697 Vol 4 Issue 1 (2015), Pg 77-81
22. Mallikarjuna K, Narasimha G, Dillip GR, Praveen B, Shreedhar B, Shree Lakshmi C, Reddy BVS, Deva Prasada Raju B, 'Green synthesis of silver nanoparticles using Ocimum leaf extract and their characterization', *Digest J Nanomaterials Biostructures,***6**. (2011)181-186
23. Prashanth S, Menaka I, Muthezhilan R, Sharma NK, 'Synthesis of plant-mediated silver nanoparticles using medicinal plant extract and evaluation of its antimicrobial activities', *Int J Eng Sci Tech,***3**. (2011)6235-6250
24. Ahmad N, Sharma S, Alam MK, Singh VN, Shamsi SF, Mehta BR, Fatma A,' Rapid synthesis of silver nanoparticles using dried medicinal plant of basil' Colloids Surf B Biointerfaces 81(1): (2010)81–86
25. Vidhu VK, Aromal A, Philip D, 'Green synthesis of silver nanoparticles using Macrotyloma uniflorum'. Spectrochim Acta A Mol Biomol Spectros', 83: (2011),392–397.
26. Dr. D. Madhusudhanarao,V. Syam Julius Rajendra, M.Sajanilavanya, M. Vasantha, Concepts on Strongly Γ-Cancellative Regular Γ-Semigroups; Mathematical Sciences international Research Journal : ISSN 2278-8697 Volume 4 Issue 2 (2015), Pg 58-60.

***

Dr. Enakshi Das/ Professor/ Department of Physics/
Saveetha Engineering College/ Chennai/ India/