

Optical study of *Desmodium elegan* mediated silver nanoparticles using Tauc's equation

Umeza Mishal¹, Muhammad Rahim^{2,1*}, Saif ud Din Jillani¹, Muhammad Ateeq³, Nasir Abbas^{2,5}, Muhammad Khalid¹, Perveen Fazil⁴, Muhammad Arif Hussain²

¹Department of Physics, University of Karachi, Pakistan ²Department of Basic Sciences, DHA Suffa University, Karachi, Pakistan ³Department of Chemistry, Abdul Wali Khan University Mardan, Pakistan ⁴Department of Chemistry, University of Karachi, Pakistan ⁵Department of Applied Physics, University of Karachi, Pakistan

Received 7 September 2022, Revised 6 February 2023, Accepted 7 February 2023

ABSTRACT

Green synthesis of metallic nanoparticles is more eco-friendly, simpler, and nontoxic as compared to chemical synthesis. Due to their thermal stability and good electrical conduction silver nanoparticles have significant importance these days. In the present work, the stable silver nanoparticles were prepared from the aqueous solution of $AgNO_3$ by green synthesis technique in which the Desmodium elegan plant extract was used as a reducing and capping agent to convert Ag^+ to Ag^0 . A UV-visible spectrometer is used in the range of 200 nm to 800 nm with a scanning speed of 200 nm per minute, the absorption band is found at a 450 nm peak that indicates the synthesis of silver nanoparticles. The particle size of the nanoparticles was in the range of 11 nm to 70 nm with an average of 45 nm and a spherical shape. Further confirmation of nano size, scanning electron microscopy (SEM) was also utilized for the size distribution and shape of the synthesized nanoparticles. The synthesized nanoparticles SEM studies show irregular spherical morphology with polydispersed trend and the average particle size was found at 45 nm. The absorption band for the synthesized sample was found at 450 nm peak. The bandgap energy was 2.84 eV estimated by Tauc's equation. This indicates that the synthesized nanoparticles electrically lie in the range of semiconductors and can be used as a biosensor. This synthesis technique is a nontoxic technique so these particles may be used for water treatment.

Keywords: Green synthesis, plant mediated nanoparticle, silver nanoparticle.

1. INTRODUCTION

Silver nanoparticles have gained the attention of researchers due to their unique physical and chemical properties. These properties include high thermal and electrical conductivity and chemical stability. Silver nanoparticles have also good antimicrobial and antibacterial activities. These nanoparticles have better physiochemical properties as compared to other noble metal nanoparticles. Chemical stability and an absorption band at a visible range increase their importance in practical applications. During surface-plasmon resonance, silver nanoparticles have a minimum loss that increases their efficiency [1-7]. Silver nanoparticles are also used as catalysts due to no toxicity as compared to other metal nanoparticles. It is also economically low cost as compared to other noble metallic particles like Gold and Platinum. Silver nanoparticles have also attracted the attention of many bio-medical researchers due to their use in a wide range as strong

^{*} Corresponding author: muhammad.rahim@dsu.edu.pk

antimicrobial and anti-bacterial agents. Due to these properties silver nanoparticles are used in the health sector and food industries. In recent days these have been used to successfully remove dirt and control the microbe in sports kits like socks. These are also used in wound dressing, boards, and surgical instruments, biomedical devices and masks. [8-13]. A product marketed by Samsung Company called Silver Nano used to remove dust and dirt from households, is also made of silver nanoparticles. Such application increases the demand for research in silver nanoparticles and their devices [14-18].

There are many methods for the synthesis of silver nanoparticles. Chemical reduction is one the most commonly used synthesis techniques in which silver ions are reduced by a reducing agent to form a stable independent unit as nanoparticles [19-23].

The size and other physical parameters of the silver nanoparticles are controlled by changing the concentration of the reducing agent and capping agents. [24-27]. Generally, in silver nanoparticles synthesis, sodium borohydride is used as a reducing agent in chemical synthesis. Chemical synthesis is not a good option for biological applications due to chemical hazards and toxicity. Therefore, biological methods are used for the synthesis of silver nanoparticles. In biological techniques, biological components like yeast, fungus, or bacteria are used as reducing and capping agents [28-33]. Out of all the biological techniques, green synthesis is considered to be the most eco-friendly. In this technique, plant extractions are used as capping and reducing agents [34-38]. Different literature survey indicates that various plant extracts are used for the synthesis of silver nanoparticles such as *Withania somnifera* and *Acalypha indica*. Earlier research has shown that *Acalypha indica, Helianthus annus, Mentha piperita, Oryza sativa,* and *Gliricidia sepium* can be extracted successfully through green synthesis, which eliminates particle toxicity compared to chemical routes. [39-42].



Figure 1. A pictorial illustration of green synthesis of Silver nanoparticles by using *Desmodium elegan* broth as reductant.

In the present work, the silver nanoparticles were synthesized using extraction of the plant *Desmodium elegan* (from the family Fabaceae) usually recognized as *elegant tick clover* and it is found in the Asian region. Due to the containing significant phytochemical compounds *Desmodium elegan* plays an essential role in the synthesis process. The compounds like flavonoids, sterols, and reducing sugar are used for the capping of silver nanoparticles and also as reduction agents [34, 43-46].

2. EXPERIMENTAL DETAILS

Initially, *Demodium elegen* leaves were sequentially washed through tap water and then distilled to properly clean and remove the impurities. The leaves were stored at room temperature until dried and cut down into small pieces. Then, 200 ml of distilled water was added to 20 g of the chopped

leaves and heated for about 1 hour at 60 °C. The Whatmann No. 1 filter paper was used to separate *the Demodium elegen* extract at room temperature.

In the present work, 0.1 mM aqueous solution of AgNO₃ was prepared to obtain Ag+ ions. 5 ml of *Demodium elegen* solution was mixed drop by drop with 50 ml of AgNO₃ solution and stirred for two hours at 2500 rpm at room temperature. The color of the solution changed after two hours of constant stirring at 2500 rpm at room temperature. First, the solution color changed from yellowish green to light brown and later became dark reddish. This color change was an indication of the formation of nanoparticles. The formation of nanostructure is further confirmed by the UV-visible spectroscopy technique. For this purpose, the Shimadzu-UV 1800 UV-Visible spectrophotometer was employed in the range of 200-800 nm wavelength with ±1 nm resolution.

The plant mediated silver nanoparticles were studied by the AFM characterization for revealing size and shape. For AFM studies the (Agilent 5500, USA AFM) model is used under normal atmospheric environment with taping mode. The SEM examination was done with the JEOL JSM 6480 LV SEM machine and was run at 20 kV for the determination of the size and morphology of silver nanoparticles synthesized with *Desmodium elegan* extract.



Figure 2. Visually inspection of colors of solutions before and after the final sample.

3. RESULTS AND DISCUSSION

3.1 Characterization

3.1.1 Study of UV-Visible Spectroscopy

The UV-visible spectroscopy was carried out for characterization and confirmation of silver nanoparticles. The absorption spectrum of the colloidal solution of silver nanoparticles was recorded and corrected by comparing it with reference spectra. A sharp absorption peak at 415 nm reveals the formation of silver nanoparticles. This displayed absorption peak is related to the Surface Plasmon Resonance band of silver nanoparticles. Figure 3 shows the broadening of the absorption peak which indicates that the silver nanoparticles were polydispersed.



Figure 3. UV-Visible absorption spectrum of the Desmodium elegan mediated silver nanoparticles

3.1.2 Study of Atomic Force Microscopy

The AFM was carried out for size determination of silver nanoparticles. A 100 μ l of solution sample thin layer was dried on a freshly cleaved mica slide for about five minutes at normal room temperature. The dried sample was scanned by a Silicon cantilever of length 125 micrometers with resonance frequency of 330 KHz. The force constant was 42 N/ m and the obtained micro images were studied with the Agilent's Pico view data processing software. As we can see the micro image depicted in Figure. 4 shows the polydispersed and the mostly spherical shape. The size of silver nanoparticles using *Desmodium elegan extract is found in* the range of 11-70 nm and the average size was measured at 45 nm from AFM measurements.



Figure 4. AFM analysis of *Desmodium elegan* mediated silver nanoparticles.

3.1.3 Scanning Electron Microscopy:

The SEM was also carried out for size determination of *Desmodium elegan* mediated silver nanoparticles. The SEM analysis showed the irregular spherical morphology with polydispersed as depicted in Figure 5. The sample was placed under the mercury lamp for 10 minutes to dry clearly before examination. A small amount of the sample was lyophilized by spreading on a SEM grid. In the SEM analysis particle size was found between 11-80 nm and the average size was 45 nm as same as observed in the AFM analysis. There is a slight difference found in the AFM and SEM data about particle sizes. AFM size is between 11 -70 nm while the SEM is between 11-80 nm and the average was the same in both analyzed sizes. The shape of SEM images are irregular spherical patterns with different sizes and in AFM are generally found in spherical form. These size and shape variations may be due to the difference in analysis processes of each characterization technique and their impacts.



Figure 5. Particle size distribution from AFM Desmodium elegan mediated silver nanoparticles



Figure 6. SEM analysis of Desmodium elegan mediated silver nanoparticles





3.2 Determination of Bandgap Energy

For the determination of the bandgap energy of *Desmodium elegan* mediated silver nanoparticles, Tauc's method is incorporated. For this purpose, data obtained from the UV-visible spectrometer is utilized and analyzed using Origin. Tauc's equation is as,

$$\alpha h \nu = A (h \nu - E_g)^n$$

where A and (n) are constant and the nature of optical transition respectively. The values of (n = 2) determined the direct bandgap materials and (n = 1/2) indirect bandgap materials. The above equation can be modified as,

$$\alpha h \nu = A (h \nu - E_a)^{1/2}$$

Here, the hv represents the energy of the incident photon for the silver nanoparticles and Eg is bandgap energy. In Tauc's method, the graph known as Tauc's plot is used to determine the bandgap energy by plotting between incident photon energy (hv) and $(\alpha hv)^2$. Finally, bandgap energy is extracted from the tangent drawn on the plot, then it is extrapolated to the value of $(\alpha hv)^2$ at 0 as illustrated in Figure 8. According to the above statement, Tauc's equation will be:

$$h\nu = E$$

The bandgap is found with the value 2.84 eV as we can see in Figure 8 the tangent line hit the X-axis at 2.84 eV energy value with direct transition.



Figure 8. Tauc's plot of Desmodium elegan mediated silver nanoparticles

4. CONCLUSIONS

The *Desmodium elegan* plant extract is successfully used in the green synthesis of Silver nanoparticles and the plant extract effectively plays the role of deducted agent to eliminate Ag⁺ ions as well as and capping agent for silver nanoparticles. The SEM and the AFM characterization revealed the morphology and particle size majority of particles were found in spherical shape while some were observed with irregular angular morphology. The average size of *Desmodium elegan* broth capping silver nanoparticles was found in the range of 45 nm and the overall size was measured 11 nm to 70 nm. The SEM and AFM characterizations revealed nearly the same size measurements. Tauc's analysis shows the bandgap energy of the *Desmodium elegan* broth capping silver nanoparticle is 2.84 eV and the UV-visible spectrum of absorption peak (SPR) accrued at 415 nm. It can be concluded the Desmodium elegan broth has a significant reducing capacity and capping capability for silver nanoparticles as compared to the chemical synthesis. The toxicity of nanomaterial also be eliminated by this technique. The prepared sample by the current synthesis

technique may be used in water treatment to remove the other harmful pollutants. The degradation of water by these particles will free from any harmfully toxic effect of the reductant particles as normally other chemically synthesized particles.

ACKNOWLEDGEMENTS

The corresponding author acknowledged the facilitation of the Department of Basic Sciences, DHA Suffa University, Karachi, Pakistan. One of the authors i.e., Perveen Fazil acknowledged the research funding of the Karachi University Research Program (KURP).

REFERENCES

- [1] S. Ahmadi, "The importance of silver nanoparticles in human life," Advances in Applied NanoBio-Technologies, vol. 1, no. 1, (2020) pp. 5-9.
- [2] J. Natsuki, T. Natsuki, and Y. Hashimoto, "A review of silver nanoparticles: synthesis methods, properties and applications," Int. J. Mater. Sci. Appl, vol. 4, no. 5, (2015) pp. 325-332.
- [3] S. Ali et al., "Synthesis and Photonics Applications of Afzelechin Conjugated Silver Nanoparticles," Coatings, vol. 11, no. 11, (2021) p. 1295.
- [4] I. Ali et al., "Sensing applications of triazole conjugated silver nanoparticles," Journal of Molecular Structure, vol. 1226, (2021) p. 129306.
- [5] A. Ullah et al., "A Novel Colorimetric Chemosensor Based on Ferene-S-Conjugated Silver Nanoparticles for Selective Recognition of Fe2+," Coatings, vol. 11, no. 11, (2021) p. 1293.
- [6] S. Ali et al., "Effect of nickel substitution on structural and dielectric properties of Mg-Zn based spinel ferrite nanoparticles," Physica Scripta, vol. 97, no. 6, (2022) p. 065802.
- [7] M. R. Shah and M. Ateeq, "Atomic Force Microscopy for Microbial Cell Surfaces," in Micro and Nanomanufacturing Volume II: Springer, (2018), pp. 203-224.
- [8] I. Ali et al., "Acridine-2, 4-Dinitrophenyl Hydrazone Conjugated Silver Nanoparticles as an Efficient Sensor for Quantification of Mercury in Tap Water," Journal of Chemistry, vol. 2022 (2022).
- [9] R. A. S. Siddiqui, N. Kabir, S. U. Simjee, M. Ateeq, R. Hafizur, and M. R. Shah, "Protective activity of cinnamic acid and its gold nanoparticles against rhabdomyolysis-induced acute kidney injury in mice," in Journal of Pharmacological and Toxicological Methods, vol. 93, (2018) pp. 139-139: ELSEVIER SCIENCE INC 360 PARK AVE SOUTH, NEW YORK, NY 10010-1710 USA.
- [10] N. Chouhan, "Silver nanoparticles: Synthesis, characterization and applications," 2018.
- [11] Z. Sadowski, "Biosynthesis and application of silver and gold nanoparticles," Silver nanoparticles, (2010) pp. 257-276.
- [12] X. Xu, Q. Yang, Y. Wang, H. Yu, X. Chen, and X. Jing, "Biodegradable electrospun poly (L-lactide) fibers containing antibacterial silver nanoparticles," European polymer journal, vol. 42, no. 9, (2006) pp. 2081-2087.
- [13] A. B. Lansdown, "Silver in health care: antimicrobial effects and safety in use," in Biofunctional textiles and the skin, vol. 33: Karger Publishers, (2006) pp. 17-34.
- [14] M. U. Rashid, M. K. H. Bhuiyan, and M. E. Quayum, "Synthesis of silver nano particles (Ag-NPs) and their uses for quantitative analysis of vitamin C tablets," Dhaka University Journal of Pharmaceutical Sciences, vol. 12, no. 1, (2013) pp. 29-33.
- [15] S. Rajawat and M. Malik, "Silver Nanoparticles: Properties, Synthesis Techniques, Characterizations, Antibacterial and Anticancer Studies," ed: Springer, 2019.
- [16] A. Ullah et al., "Highly selective colorimetric naked-eye Cu2+ detection using new bispyrazolone silver nanoparticle-based chemosensor," International Journal of Environmental Analytical Chemistry, vol. 98, no. 10, (2018) pp. 977-985.

- [17] A. Ali et al., "Seasonal dynamics, record of ticks infesting humans, wild and domestic animals and molecular phylogeny of Rhipicephalus microplus in Khyber Pakhtunkhwa Pakistan," vol. 10, (2019) p. 793.
- [18] A. Zada et al., "Suitable energy platform significantly improves charge separation of g-C3N4 for CO2 reduction and pollutant oxidation under visible-light," vol. 29, no. 2, (2019) pp. 138-144.
- [19] C. Kinnear, T. L. Moore, L. Rodriguez-Lorenzo, B. Rothen-Rutishauser, and A. Petri-Fink, "Form follows function: nanoparticle shape and its implications for nanomedicine," Chemical reviews, vol. 117, no. 17, (2017) pp. 11476-11521.
- [20] N. Channa et al., "Fabrication of Cobalt Ferrite Nanoparticles with a Facile Approach: Variations in Structural, Dielectric and Morphological Properties by Influence of Annealing Temperature," International Journal of Nanoelectronics & Materials, vol. 15, no. 1, (2022).
- [21] M. Ateeq, M. R. Shah, H. Ali, N. Kabir, A. Khan, and S. J. N. J. o. C. Nadeem, "Hepatoprotective and urease inhibitory activities of garlic conjugated gold nanoparticles," vol. 39, no. 6, (2015) pp. 5003-5007.
- [22] R. A. Siddiqui et al., "N-(2-hydroxyphenyl) acetamide and its gold nanoparticle conjugation prevent glycerol-induced acute kidney injury by attenuating inflammation and oxidative injury in mice," vol. 450, (2019) pp. 43-52.
- [23] A. Zada et al., "Surface plasmon resonance excited electron induction greatly extends H2 evolution and pollutant degradation activity of g-C3N4 under visible light irradiation," vol. 67, no. 6, (2020) pp. 983-989.
- [24] S. H. Lee and B.-H. Jun, "Silver nanoparticles: synthesis and application for nanomedicine," International journal of molecular sciences, vol. 20, no. 4, (2019) p. 865.
- [25] M. Xu, M. S. Khan, P. Fazil, and M. Ateeq, "Effect of Calcination Temperature on the Photocatalytic H2 Evolution of Bronze Phase Monoclinic TiO2 (B) Nanosheets," Journal of the Chemical Society of Pakistan, vol. 44, no. 3, (2022).
- [26] N. Kabir, H. Ali, M. Ateeq, M. F. Bertino, M. R. Shah, and L. J. R. A. Franzel, "Silymarin coated gold nanoparticles ameliorates CCI 4-induced hepatic injury and cirrhosis through down regulation of hepatic stellate cells and attenuation of Kupffer cells," vol. 4, no. 18, (2014) pp. 9012-9020.
- [27] A. Ullah et al., "A Novel Colorimetric Chemosensor Based on Ferene-S-Conjugated Silver Nanoparticles for Selective Recognition of Fe2+," vol. 11, no. 11, (2021) p. 1293.
- [28] S. Ali et al., "Synthesis and Photonics Applications of Afzelechin Conjugated Silver Nanoparticles," vol. 11, no. 11, (2021) p. 1295.
- [29] G. Rukh et al., "Conjugation of Antimicrobial Peptide to Zinc Phthalocyanine for an Efficient Photodynamic Antimicrobial Chemotherapy," vol. 12, no. 2, p. 200, 2022.
- [30] I. Ali et al., "Sensing applications of triazole conjugated silver nanoparticles," vol. 1226, (2021) p. 129306.
- [31] N. Ullah, F. Shah, R. A. Khan, M. Ateeq, H. Muhammad, and A. R. J. I. J. o. E. A. C. Khan, "Restricted access-activated carbon clothes-based lead extraction from human serum: skipping the sample preparation step for biological media," vol. 96, no. 11, (2016) pp. 1048-1058.
- [32] T. U. Rehman et al., "Fabrication of stable superabsorbent hydrogels for successful removal of crystal violet from waste water," vol. 9, no. 68, (2019) pp. 40051-40061.
- [33] S. Mirza, M. S. Ahmad, M. I. A. Shah, and M. Ateeq, "Magnetic nanoparticles: drug delivery and bioimaging applications," in Metal nanoparticles for drug delivery and diagnostic applications: Elsevier, (2020) pp. 189-213.
- [34] M. Ateeq et al., "Green synthesis and molecular recognition ability of patuletin coated gold nanoparticles," Biosensors and Bioelectronics, vol. 63, (2015) pp. 499-505.

- [35] R. A. Siddiqui, S. U. Simjee, M. Ateeq, and M. R. Shah, "N-(2-Hydoxyphenyl Acetamide) and its Gold Nanoparticles Prevent Rhabdomyolysis-Induced Acute Kidney Injury In Vivo," Journal of Pharmacological and Toxicological Methods, vol. 88, (2017) pp. 209-210.
- [36] N. Ullah, F. Shah, R. A. Khan, M. Ateeq, H. Muhammad, and A. R. Khan, "Restricted accessactivated carbon clothes-based lead extraction from human serum: skipping the sample preparation step for biological media," International Journal of Environmental Analytical Chemistry, vol. 96, no. 11, (2016) pp. 1048-1058.
- [37] S. Dawadi et al., "Current research on silver nanoparticles: Synthesis, characterization, and applications," Journal of Nanomaterials, vol. 2021, (2021).
- [38] A. Roy, O. Bulut, S. Some, A. K. Mandal, and M. D. Yilmaz, "Green synthesis of silver nanoparticles: biomolecule-nanoparticle organizations targeting antimicrobial activity," RSC advances, vol. 9, no. 5, (2019) pp. 2673-2702.
- [39] S. Ahmad et al., "Green nanotechnology: A review on green synthesis of silver nanoparticles— An ecofriendly approach," International journal of nanomedicine, vol. 14, (2019) p. 5087.
- [40] S. K. Chandraker, M. K. Ghosh, M. Lal, and R. Shukla, "A review on plant-mediated synthesis of silver nanoparticles, their characterization and applications," Nano Express, vol. 2, no. 2, (2021) p. 022008.
- [41] M. R. Shah et al., "Morphological analysis of the antimicrobial action of silver and gold nanoparticles stabilized with ceftriaxone on Escherichia coli using atomic force microscopy," New Journal of Chemistry, vol. 38, no. 11, (2014) pp. 5633-5640.
- [42] N. Kabir, H. Ali, M. Ateeq, M. F. Bertino, M. R. Shah, and L. Franzel, "Silymarin coated gold nanoparticles ameliorates CCI 4-induced hepatic injury and cirrhosis through down regulation of hepatic stellate cells and attenuation of Kupffer cells," RSC Advances, vol. 4, no. 18, (2014) pp. 9012-9020.
- [43] A. Khan et al., "In vitro biological screening of the stem of Desmodium elegans," Asian Pacific journal of tropical biomedicine, vol. 3, no. 9, (2013) pp. 711-715.
- [44] N. Ahmad, S. Sharma, V. Singh, S. Shamsi, A. Fatma, and B. Mehta, "Biosynthesis of silver nanoparticles from Desmodium triflorum: a novel approach towards weed utilization," Biotechnology research international, vol. 2011, (2011).
- [45] V. Bhatt and V. K. Purohit, "Floristic structure and phytodiversity along an elevational gradient in Peepalkoti-Joshimath area of Garhwal Himalaya, India," Nature and Science, vol. 7, no. 9, (2009) pp. 63-74.
- [46] I. Javed et al., "Synthesis, characterization and evaluation of lecithin-based nanocarriers for the enhanced pharmacological and oral pharmacokinetic profile of amphotericin B,": Journal of materials chemistry B, vol. 3, no. 42, (2015) pp. 8359-8365.