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Optical, Morphological and Structural Studies on Silver Nanoparticles Green Synthesized Using AzadirachtaIndica Leaves Extract

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ABSTRACT: The green processes in material science are becoming increasingly popular and are much needed as a result of worldwide problems associated with environmental concerns. In the present work, leaf extract of Azadirachtaindica, (commonly known as Neem) was used for bio-reduction of silver ions to silver nanoparticles. Neem extract and $AgNO_3$ solution in different concentrations were treated and it resulted in the reduction of Ag+ ions to Ag metal atoms, which further accumulated as Ag nanoparticles. The prepared nanoparticles were characterized by UV-vis spectroscopy, SEM, FT-IR spectroscopy and XRD analysis. The present study established that the shape and size of the silver nanoparticles can be effectively controlled and modulated using green synthesis technique.

KEYWORDS:green synthesis, silver nanoparticles, biosynthesis, azadirachtaindica extract

I. INTRODUCTION

Environment friendly processes in material synthesis are becoming more popular now a days and are considered to be solutions for problems associated with worldwide environmental concerns. Green synthesis of inorganic metal nanoparticles is an emerging field and has received increased attention due to the importance in developing congenial technologies in material synthesis [1, 2]. The biosynthesis of metal nanoparticles can be carried out using bio-reduction agent like bacteria, fungi and plant extracts. The advantages of biological generation of nanoparticles are three fold; the bio-species can act as a template, reducing and even as capping agent for nanoparticles [3]. Synthesis of metal nanoparticles in biological routes has accomplished increased interest due to their unusual chemical [4], optical [5], electronic [6] and photo-electrochemical [7] properties.

Practical applications of green synthesized metal nanoparticles spans from antimicrobial activity, biological sensing and imaging, conductive inks and catalysis. Guzman et al studied the applications of metal nanoparticles as an antimicrobial agent; it is applied in textiles, home water purification systems, medical devices, cosmetics, electronics, and household appliances [8]. ZainbJassim et al also investigated antibacterial activity of chemically synthesized silver nanoparticles [9]. Besides their antimicrobial features, silver nanoparticles exhibit strong optical features making the nanoparticles suitable for biological sensing and imaging [10, 11]. Due to their high conductivity, silver nanoparticles are applied in conductive inks, adhesives and pastes for a range of electronic devices [12]. Silver nanoparticles are also used as catalysts in several chemical reactions such as the oxidation of styrene [13]. Various strategies are employed for synthesis of silver nanoparticles including reduction in solutions [8], thermal decomposition of silver compounds [14], microwave assisted synthesis [15], laser mediated synthesis [16] and biological reduction method [17]. The latest is the most preferred way for the synthesis of nanoparticles as it offers one step, eco-friendly way of synthesis of nanoparticles.
A survey of earlier literature suggests that leaf extracts from various plants such as Azadirachtaindica [18], Aloe vera [19], Eclipta [20], Gliricidiasepium [21], Rosa rugosa [22], Chenopodiumalbum [23], Cycas, Acalyphaindica [24], Hibiscus rosasinensis [25], Ipomoea aquatica, Enhydrafluctuans, Ludwigiaadscendens [26], Psidiumguajava [27], Garciniamangostana [28], Cocosnucifera coir [29] etc. have been explored for the synthesis of silver and gold nanoparticles. The present work aims to use the leaf extract of Azadirachtaindica (commonly known as Neem), a member of the Meliaceae family and a medicinal plant, for the green synthesis of silver nanoparticles. This plant is commonly used for the treatment of bacterial, fungal, viral and many types of skin ailments since ancient times. The

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aqueous Neem extract is used in the synthesis of various nanoparticles such as gold, zinc oxide, silver, etc. [30]. Terpenoids and flavanones are the two important phytochemicals present in Neem which play a vital role in stabilizing the nanoparticle and also act as capping and reducing agent [31]. The effect of concentration of Azardirachtaindica leaf extract and temperature on the synthesis of AgNPs is studied by Asimuddin et al. and eco-friendly and cost effective synthesis of AgNPs having potential for biomedical applications is demonstrated [32,33]. Tripathy et al investigated the effect of process variables like concentrations, reaction pH, mixing ratio of the reactants and interaction time on the morphology and size of silver nanoparticles synthesized using aqueous extract of Azadirachtaindica (Neem) leaves [34]. The rate of reduction of metal ions using plants has been found to be much faster as compared to micro-organisms and stable formation of metal nanoparticles has been reported. The shape and size of the nanoparticles synthesized using plants can be controlled and modulated by changing the pH [35].Sonali et al synthesized silver nanoparticles using methanolic leaf extract of Azadirachtaindicaas well as Ocimum sanctum and the antimicrobial activity is screened against the bacteria Escherichia coli, Klebsiellapneumoniaeand Staphylococcus aureususing disc diffusion method [36]. In the present study, silver nanoparticles are produced at low concentration of leaf extract without using any additional harmful chemical/physical reagents. Optical absorption studies of the samples are conducted using UV visible spectroscopy. Structural and morphological investigations are conducted using GIXRD and SEM respectively. FTIR studies were also conducted. The work adds to the confirmation of previous reports on biosynthesis of nano-metals using plant leaf extracts.

II. MATERIAL AND METHODS

All glass wares, used in the present study were initially washed with dilute HNO_3 and distilled water, then dried in hot air oven. Deionized water was used throughout the reactions. 99.9 % pure silver nitrate ($AgNO_3$), obtained from Sigma–Aldrich chemicals is used. 0.01N aqueous $AgNO_3$ solution is prepared out of this for the present work. For this, 0.283×10^{-3}kg of $AgNO_3$ is taken in chemical balance, it is then dissolved in 0.20 L distilled water. The mixture is stirred for 10 minutes. Fresh leaves of Neem are collected and thoroughly cleaned with distilled water. 0.05 kg of the leaves are boiled in 0.25 L distilled water for 15 minutes. Then the extract is separated out by filtering. For the synthesis of silver nanoparticles, a certain volume of Neemleaf extract (0.5 to 20 ml) is mixed with silver nitrate solution in different volumes as given in table 1.

Table 1 Details of samples prepared

Sample no	$AgNO_3$ (ml)	Neam Extract(ml)	Colour of the sample
(1)	20	0.5	Light Golden color
(2)	20	1	Deep Golden color
(3)	20	2	Light Brown color
(4)	20	3.5	Brown
(5)	10	10	Deep Brown
(6)	2	20	Deep Brown
(7)	0.25	5	Light brown

The obtained liquid mixture is stirred for 20 minutes. Different colors are obtained for different mixtures and are presented in table 1. The UV-vis spectra is characterized using a JASCO V 550 UV-vis spectrophotometer, the spectrum was scanned from 200 to 900nm wavelengths. For studying the surface morphology of silver nanoparticles synthesized, a thin layer of the liquid mixture is dip coated on glass plates and get dried and subjected to Scanning Electron Microscopy (SEM) analysis. The SEM characterization was done by a Carl Zeiss EVO 18 Scanning mode and magnification: 5x to 300,000x. For understanding the involvement of different functional groups in the reduction process, FTIR spectroscopy is also conducted. Dry powders of Ag nanoparticles are subjected to Grazing Incidence X-ray Diffraction (GIXRD) analysis for confirmation about structural parameters.

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III. RESULT AND DISCUSSION

A. COLOUR CHANGE AND UV-VISIBLE SPECTROSCOPIC ANALYSIS

To study the effects of leaves extract concentrations on the formation of AgNPs, different experiments were performed with various amounts of leaves extract and keeping other variables constants. Fig. 1 illustrates the change in colour occurred in sample mixtures with different volumes of the reactants. Upon addition of leaves extract into the aqueous solution of $AgNO_3$, the colour of the mixture is gradually changed from light golden to deep golden, then to light brown and then to deep brown, depending upon the concentration of leaves extract. However, in the absence of leaves extract, no change in the colour of the reactants was observed even after long time. This clearly confirms the role of leaves extract as bio-reductant [33]. The reduction of Ag^+ ions to Ag^0 ions cause colour change of prepared solution. Ahmad et al. observed the appearance of brown colour which is attributed to the excitation of surface plasmon vibrations, typical of silver nanoparticles [3]. The localized plasmonic resonance are collective oscillations of the conduction electrons confined to silver nanoparticles. Excitation of the localized plasmons causes strong light scattering by an electric field at a wavelength where surface plasmon resonance (SPR) occurs. The optical absorption spectrum of metal nanoparticles is dominated by the SPR, which exhibits a shift towards the red end or blue end depending upon the particle parameters including size, shape, state of aggregation and the surrounding dielectric medium [37].

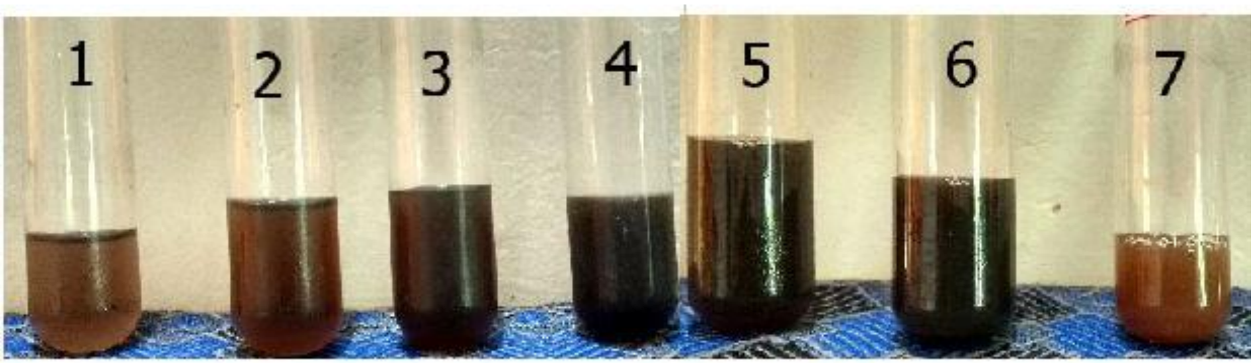

Fig. 1 Colour difference between samples (1), (2), (3), (4), (5), (6) and (7)

UV-visible absorption studies were conducted on all the samples. The obtained absorption spectra is shown in figure 2. Small and large plasmonic peaks within the range 300 to 600 nm indicated the presence of nanoparticles with different sizes and shapes. As the amount of leaf extract increases, from sample (1) to (3), the maximum optical absorption is observed around 445 nm with increasing intensity. Tripathy et al, reported s increase in intensity of absorption with concentration of plant extract [34]. In the wavelength range 350 to 600 nm, absorption peaks are observed to be Gaussian for these samples. Another small absorption peak around 300 nm are also seen. As the amount of the leaf extract further increases, for the sample (4), optical absorption with Landau peak around 445 nm is observed. Mixtures with highly increased amounts of the leaves extract resulted in broad absorption spectra. The plasmon peak is sensitive to the size and shape of the resultant NPs. While the sharp and lower wavelength absorption peak reflect the smaller size of AgNPs, whereas a broader peak at higher wavelength points towards the presence of larger size and aggregated AgNPs [38].

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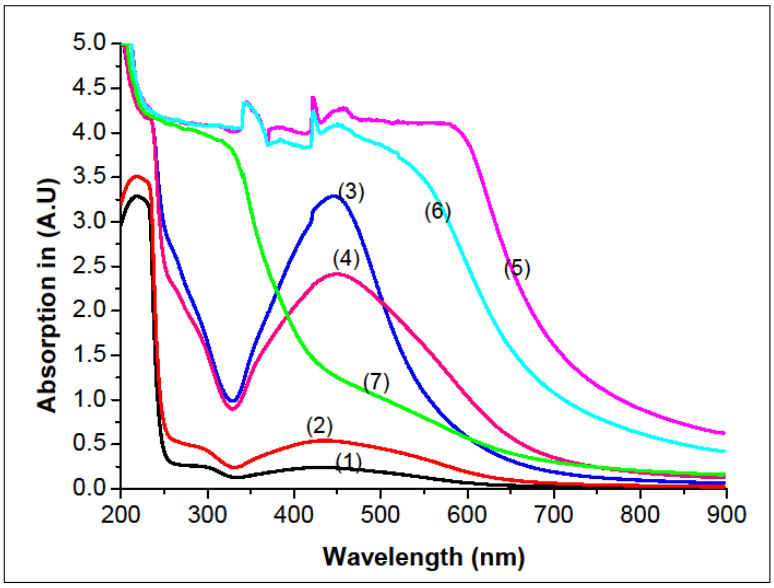

Fig. 2 UV-visible absorption spectrum of samples (1), (2), (3), (4), (5), (6) and (7)

B. SEM ANALYSIS

The SEM images of AgNPs in samples (3), (4), (5) and (7) are shown in figure 3. SEM Analysis of the sample (3) revealed aggregation of AgNPs formed with diameter range from 20 to 50 nm. Mono dispersive spherical nanoparticles of size ranging from 90 to 150 nm are observed in sample (4). In sample (5), the size of the nanoparticles are found to be increased to the order of 150 nm. Spherical nanoparticles are found to be in an agglomerated form. This change is attributed to increased concentration of the leaves extract. Further increase in the leaves extract resulted in the formation of more enlarged particles of spherical shape, mono dispersedly distributed. Similar observations were found in literature [33]. The size and shape formation of AgNPs may not stay constant and is dependent on the surrounding chemical and physical environment. In real aquatic systems with salinity or harsh pH values, AgNPs tend to aggregate to form large clusters and their physicochemical properties and mobility may change as well.

The raw images obtained from the study area have undergone several treatments visual improvement to enhance the expression of vegetation. The results of color compositions, neo channel NDVI and their optimization are shown in figure 2.

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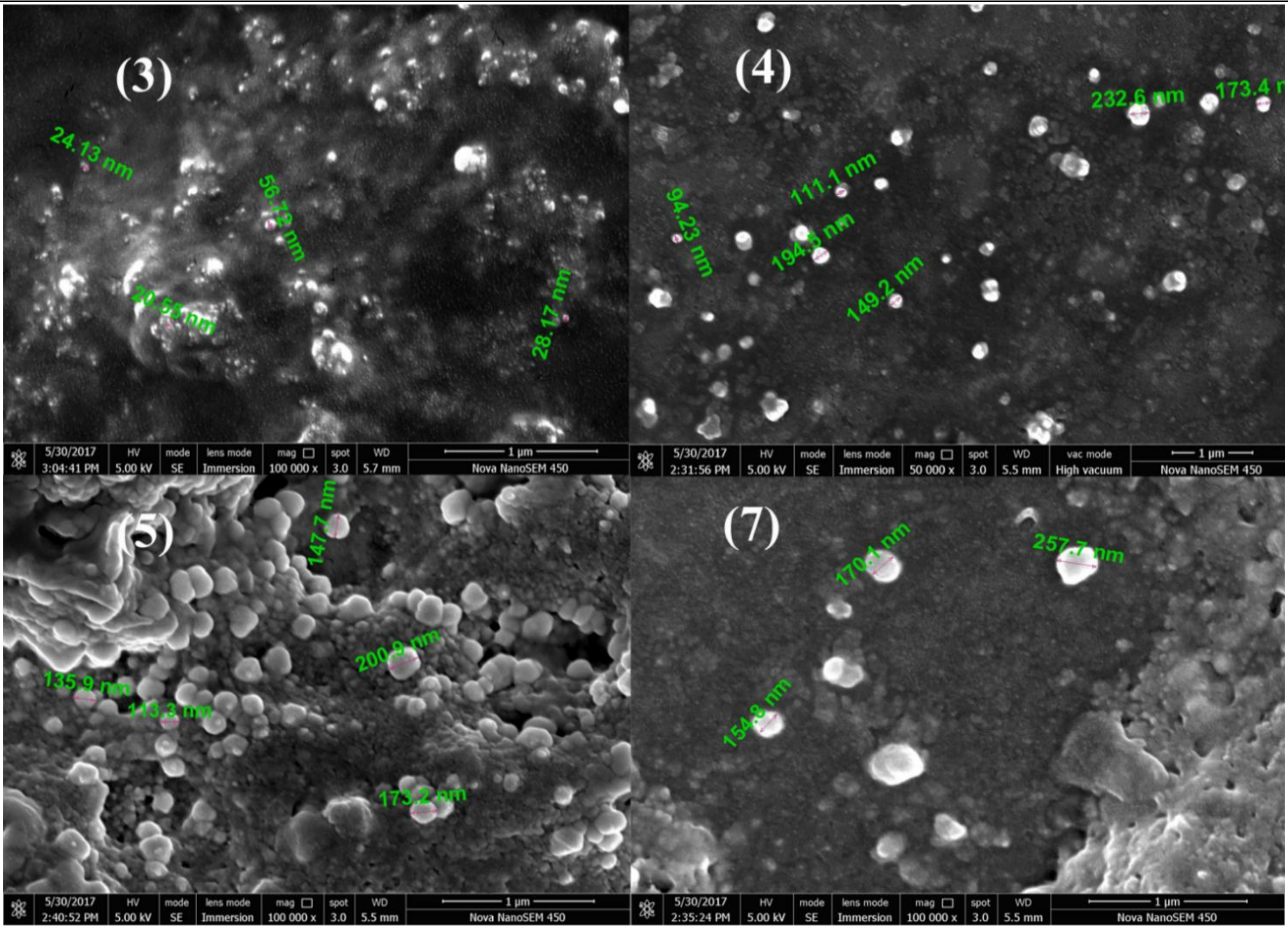

Fig. 3The SEM images of AgNPs in sample (3), (4), (5) and (7)

C. FTIR ANALYSIS

FTIR spectroscopy was used to confirm the presence of residual phytomolecules of leaves extract on the surface of AgNPs as stabilizing ligands. The FTIR spectra of Ag NPs (samples (3) and (4)) with absorption peaks at 3329, 2116, and 1644 were observed (Fig. 4). Similar absorption peaks were observed also for the pure plant extract with increased intensity (not shown here). The spectra obtained to characterize the interaction between $AgNO_3$ and leaves extract has strong peak at 3329 cm^{-1}. The highest absorption peak at 3329 cm^{-1} reflects that the OH group might be responsible for the reducing property of the extract. The absorbance band at 1644 cm^{-1} is associated with the stretching vibration of –C=C- or aromatic groups. However the exact procedures of bio-reduction is not fully comprehended. Also the precise direction in which the electrons are transported is a matter requiring investigation.

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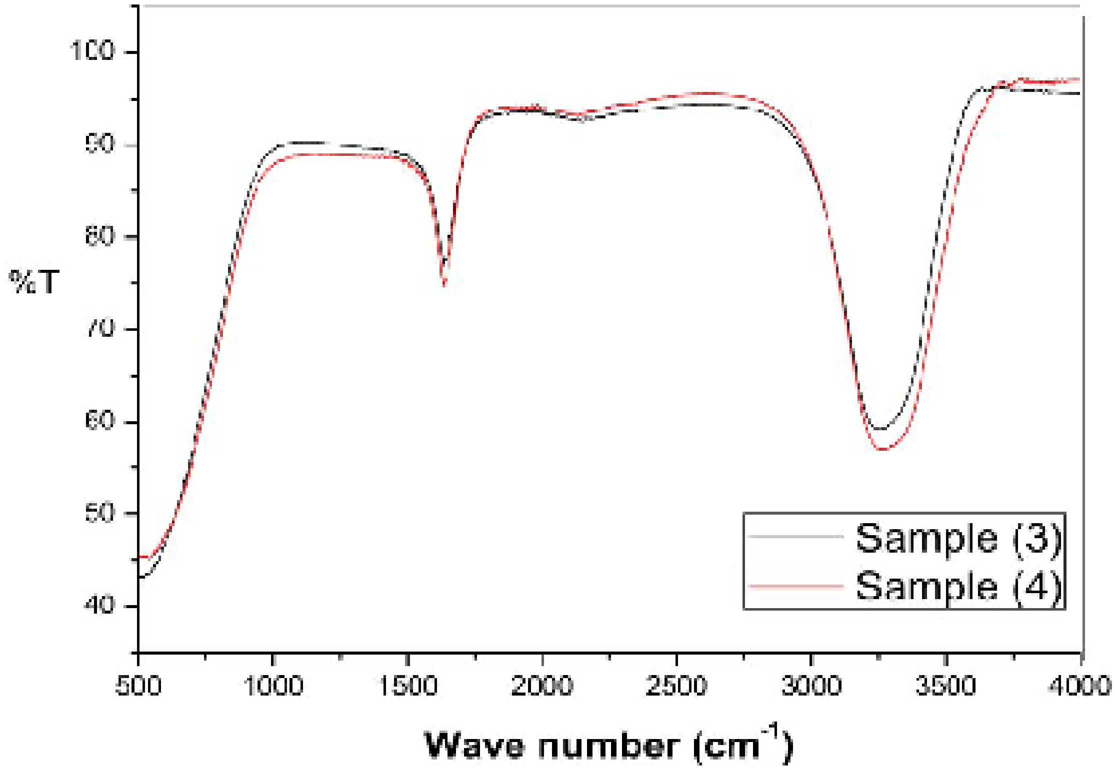

Fig. 4 FTIR Spectra of samples (3) and (4)

D. XRD ANALYSIS

The structure was confirmed by XRD analysis for the sample (3). The dry powders of the silver nanoparticles were used for XRD analysis. The diffracted intensities were recorded from 25º to 60º at 2θ angles. In the XRD analysis, it has been found that the observed diffraction peak at diffraction angle (2θ) of 38.10 matches with (111) plane of FCC silver with JCPDS Pattern number 00- 004-0783. Along with that, the presence of Silver Oxide (AgO) (JCPDS Pattern number 01-076-1489) at 2θ value of 32.08 with a d-spacing of 2.78 A^0 is also detected. AgO may be formed after formation of silver nanoparticles, which reacts with water in the solution since the nanoparticles are highly reactive due to their high surface to volume ratio [39]. The observed peak broadening and noise were probably related to the effect of nano-sized particles and the presence of various crystalline biological macromolecules in the plant extracts. The obtained results illustrate that silver ions had indeed been reduced to Ag^o by Aloe vera plant extract under reaction conditions. Peaks were also observed suggesting that the crystallization of bio-organic phase occurs on the surface of the silver nanoparticles [40]. Diffraction peaks at 2θ value of 26.39, 27.66 and 46.15 possibly due to organic impurities present in the sample. In order to get rid of the same, the sample can be further calcined.

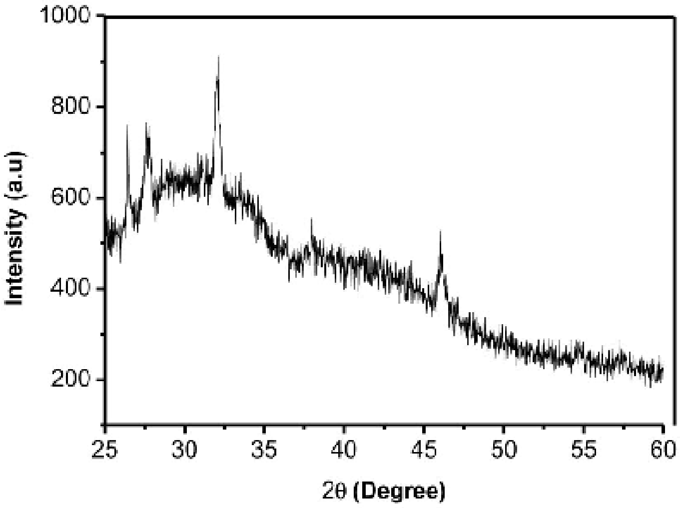

Fig. 5 GIXRD spectrum of sample (3)

IV. CONCLUSION

In the present study, the synthesis and characterization of AgNPs using bio-reduction is done. Neem extract and $AgNO_3$ solution in different concentrations were treated and it resulted in the reduction of Ag+ ions to Ag metal atoms, which further accumulated as Ag nano particles. The prepared nanoparticles were characterized by UV-Vis spectroscopy, SEM, FT-IR spectroscopy and XRD analysis. UV-Visible absorption gives absorption peaks between wavelengths 300 and 550nm. The result from SEM imaging reveals the size and shape of biosynthesized nanoparticles. The study established that the shape and size of the silver nanoparticles can be controlled and modulated using green synthesis technique.

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