Green synthesis of hybrid silver nano structures using *Cassia occidentalis* plant leaf broth and their characterization

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Abstract

In the present work, we report on green synthesis of hybrid silver nano structures using a solution of $AgNO_3$ and leaf broth of *Cassia occidentalis* plant as reducing agent. The incubation of $AgNO_3$ solution and leaf broth for 48 hrs under neutral pH and constant stirring at 150 rpm resulted in the formation of hybrid silver nanostructures comprised of silver nano particles (AgNPs) and silver nanorods (AgNRs). The bio reduction of Ag^+ ions to AgNPs and AgNRs is confirmed via appearance of surface plasmon resonance peaks at 420 and 370 nm in the UV visible spectrum. The synthesized nanostructures are purified and further characterized using XRD and FT-ATR. The morphology of nanostructures is examined by SEM studies which further revealed the formation of spherical shaped AgNPs and rod shaped AgNRs. The study therefore concludes that it is possible to synthesize the AgNRs and AgNPs effectively using silver nitrate ($AgNO_3$) solution and the leaf broth of *Cassia occidentalis.* However, further work is needed to establish the employability of these nanostructures in various applications.

Keywords: Silver nano hybrid, silver nano rods, silver nano particles, green synthesis, bio reduction.

Introduction

Silver is one of the most commercialized nano materials with 500 tons of silver nanoparticles produced every year and its production is estimated to increase next few years **[1]**. Silver has the highest thermal and electrical conductivity making it a good candidate as interconnects in electronic devices. Silver also show good inhibitory and bacterial effects along with antifungal, anti-inflammatory and anti-angiogenesis due to which it finds applications in the field of biomolecular detection and medicine **[2]**. Silver exists in different one-dimensional nano forms such as nanorods, nanowires, nanobelts, nanotubes and these materials are useful for applications requiring anisotropic properties such as directional conductivity **[3, 4, 5, 6].** Recently, much effort has been devoted to synthesis of AgNR. Until now, the most widely used synthetic methods involve either template or non-template based solution phase chemical approaches. Several templates based methods employing DNA **[7]**, carbon nanotube **[8]**, mesoporous silica **[9]** and polymer membranes **[10]** as templates have been reported on the synthesis of AgNRs. However, removal of these rigid templates requires complicated process, which consequently limit the scale of application of synthesised materials. Therefore, it is rational to develop the non-template based process for the synthesis of AgNR.

Green synthesis is an alternative technique that yield biocompatible nano materials at low cost **[11]**. Green synthesis provides advancement compared to other method as it is simple, eco-friendly, cost effective and reproducible **[12, 13]**. This technique is considered attractive as it uses naturally occurring reagents such as sugars, biodegradable polymers, plant extract as reducing and capping agents **[12]**. The green synthesis of AgNRs using plant extracts as reducing agent is not widely reported and there is need for more such studies. Silver nano particles strongly absorb and scatter light due to excitation of localized surface plasmon resonance (LSPR). The LSPR at resonance wave length depends on the nano particle size, shape and surrounding dielectric environment. The optical resonance enables silver nanoparticles to be used as ultra-bright non-bleaching nanolables and nano sensors **[14, 15].**

Hybrid nano materials are emerging category of materials with an extended range of properties and applications. These materials are widely useful as composites in biosensor matrices, optoelectronics and medical devices **[16, 17]**. Biocompatible hybrid materials are very useful in biomedical application. In this context, biosynthesis of silver nanohybrid of AgNPs and AgNRs is significant and it yield biocompatible nanomaterial which can be employed in various biomedical applications. The objective of the present work is to biosynthesize the nanohybrid of AgNPs and AgNRs. In the present work, we report the green synthesis of a hybrid nano mixture of AgNRs and AgNPs by a simple mixing of $AgNO_3$ solution with a leaf broth of *Cassia occidentalis* plant. This work is novel in the sense that it uses leaf broth as reducing agent to synthesis nano hybrid of AgNPs and AgNRs, and the entire reaction is carried out at normal temperature, pressure and under neutral pH conditions.

Materials

Cassia occidentalis plant leaf broth and $AgNO_3$ are used as the starting materials in synthesis process. *Cassia occidentalis* leaves collected from local garden are used in preparation of leaf broth. $AgNO_3$ (A.R grade 99.8% pure) and sodium hydroxide (A.R grade 98% pure) used in experiments are procured from Sigma Aldrich (Germany) and Fischer Scientific (Mumbai, India), and used without any further purification. Deionised water is used as solvent in all experiments.

Methods

Preparation of leaf broth

Fresh leaves of *Cassia occidentalis* plant are thoroughly washed in deionised water and shade dried. The dried leaves are crushed and 1 g of the dried leaves are added to 25 ml deionised water and boiled for 10 minutes leading to ruptures walls of leaf cell and release of intracellular materials into solution. After boiling, the solution is filtered and proper amount of deionized water is added to keep the volume of filtrate to 25 ml. The resulting broth solution is stored for further use.

Green synthesis of hybrid silver nano structures

For green synthesis, 10 ml of the above leaf broth is mixed with 25 ml of aqueous 3 mM $AgNO_3$ solution and neutral pH is maintained using 1N sodium hydroxide. Thereafter, the mixture is stirred at 200 rpm in the dark at room temperature for 48 hours. The formation of hybrid silver nano structures namely AgNPs and AgNRs are monitored and confirmed by UV-Visible spectroscopy. The formed hybrid silver nano structures are centrifuged at 10,000 rpm for 15 min and purified using methanol. The repeated purification is done by giving several washes in methanol solution to remove the plant residues. Hybrid silver nano structures are finally dried at room temperature for evaporating methanol.

Characterization of nanostructures

Characterization of nanostructures is performed using UV-visible, Fourier Transform Attenuated Total Reflection (FT-ATR) and X-ray diffraction spectroscopic (XRD) techniques. The morphological characteristics of nanostructures are studied using scanning electron microscopy (SEM) technique. The instruments used in characterization are UV-visible spectrophotometer (Shimadzu-1800, Singapore), FT-ATR spectrometer (Jasco 4110, Japan), X-ray diffractometer (AXRD Bench-top Powder Diffractometer, Proto Manufacturing Limited, Canada) and Scanning electron microscope (ZEISS EVO40EP, Germany).

For UV visible studies, an aliquot of reaction mixture is used and absorbance is measured using $AgNO_3$ solution as blank and for FT-ATR, XRD and SEM, the biosynthesised nanostructure samples are used after purification by repeated washing using methanol followed by drying at room temperature. In FT-ATR the solid sample is mounted on the sample holder and it is scanned in the wavelength range of 400 to 4000 cm^{-1} (resolution x8). For XRD, the dry solid samples were placed on the sample holder and the patterns are recorded in the scanning rate of 5^0 min^{-1} and 2θ value ranging from 10 to 90^0. The instrument used Cu Kα (λ = 1.5405 A^0) as X-ray source. For SEM studies, the dry nano hybrid powder is dispersed on the carbon tape pasted sample holder and image is captured.

Results and discussion

UV-visible analysis

An aliquot of the reaction mixture is diluted and it is used for the UV measurements using 3mM $AgNO_3$ as reference (blank). The formation of AgNPs and AgNRs in the reaction mixture is confirmed through UV-visible studies. The UV visible spectrum of reaction mixture shows the appearance of two strong bands in the spectrum at 370 nm and 420 nm. The band at 420 nm corresponds to AgNPs while the band at 370 nm may be attributed to surface plasmon resonance (SPR) of AgNRs **[11, 14, 15]**. The appearance of these two bands in the spectrum is a clear indication of simultaneous formation of AgNPs and AgNRs in the reaction mixture. The formation of nanohybrid is further confirmed by change in color of reaction mixture from pale green to dark brown. The UV-visible spectrum of reaction mixture is shown in **Fig. 1.**

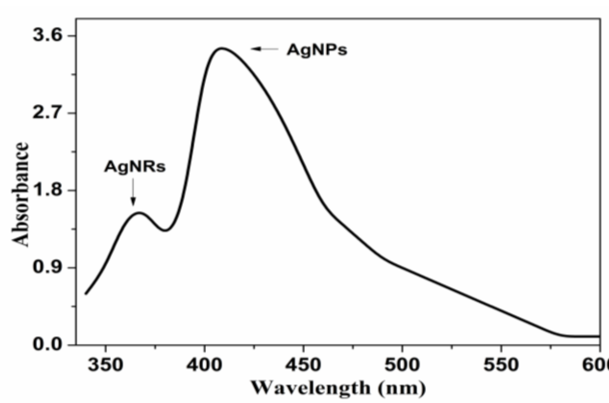

Fig. 1. UV visible spectra of reaction mixture indicating formation of Ag nanohybrids.

FT-ATR analysis of hybrid silver nanostructures

FT-ATR analysis is carried out to identify the possible bio-molecules responsible for the reduction of the Ag^+ ions and capping of the silver nanostructure. FT-IR spectra shows a number of vibration bands in the region of 1000-3500 cm^{-1} (**Fig. 2**). The absorption peak located at around 1107 cm^{-1} may be assigned as the absorption peak of –C-O- group in alcohols. The weak band located at 1280 cm^{-1} is due to C-H deformation vibrations. The strong peak located at around 1620 cm^{-1} corresponds to –C=C- stretching vibration. The peak located around 3450 cm^{-1} represent –O-H stretching vibration of hydroxyl group. This analysis shows polyhydroxy components like alkaloids, flavonoids and polysaccharose, present in plant extract are the capping ligands of the silver nanostructures.

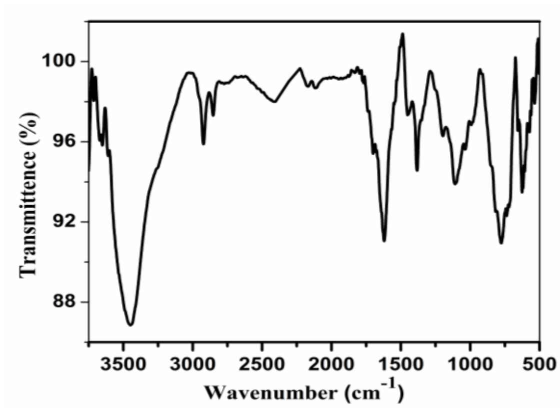

Fig. 2. FTIR spectra of Ag nanohybrids.

XRD studies

The crystalline nature of synthesized hybrid silver nano structures is studied by powder XRD technique. Powder XRD spectral pattern of hybrid silver nano structures is shown in **Fig 3**. The diffraction peaks located at 38.1, 44.4, 64.2 and 77.1 correspond respectively to lattice planes with miller indices (111), (200), (220) and (311) of hybrid silver nano structures. The other peaks in XRD spectrum are possibly contributed by impurities and residues in plant extract. The crystal domain size (D) is calculated from the width of XRD peaks using Scherrer's formula

$$D = \frac{0.94\lambda}{\beta Cos\theta}$$

where, D is the average crystal domain size perpendicular to reflecting planes, λ is wave length of X-rays used, θ is the diffraction angle and β is full width half maximum(FWHM). The calculated average crystal domain size from XRD data is about 21.9 nm **(Table 1).**

Table 1. XRD parameters of biosynthesized silver nano hybrids.

Sl. No	2θ (degree)	FWHM	Miller Indices (hkl)	Crystal domain size D (nm)	Average domain size (nm)
1	38.1	0.4352	111	20.15	
2	44.4	0.7897	200	11.32	21.9
3	64.2	0.3346	220	29.28	
4	77.1	0.3925	311	27.04	

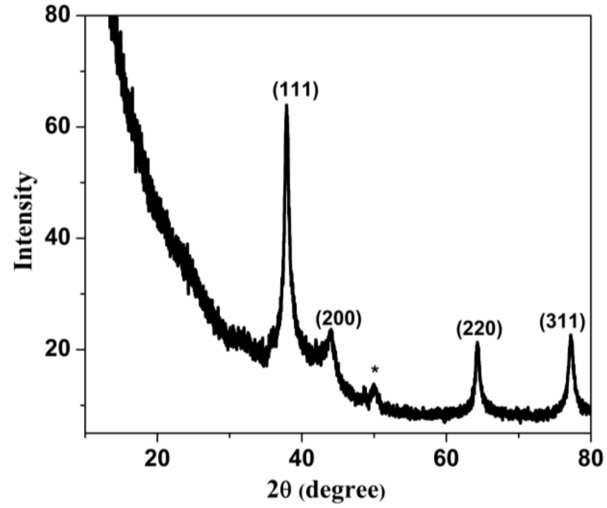

Fig. 3. XRD pattern of biosynthesized silver nano hybrids.

SEM analysis of silver nanostructures

The SEM study is carried out to understand the surface morphology of silver hybrid nanostructures. **(Fig. 4).** SEM image shows the presence of powdered nanostructures and also the rod-shaped structures. The powdered particles represent AgNPs while the rod shaped coiled structures embedded in the powder indicate AgNRs. These results are in agreement with the UV-vis, XRD data. The results clearly indicate that mixture of AgNPs and AgNRs can be effectively synthesised using a simple biosynthesis method by a simple mixing solution of $AgNO_3$ and plant extract of *Cassia occidentalis.* However, further study is essential to optimize the experimental conditions to effectively produce and separate AgNRs from AgNPs. By varying broth conditions, pH and temperature, it may be possible to achive a selective production of AgNRs or AgNPs. Authors conclude that the further study is essential in this direction.

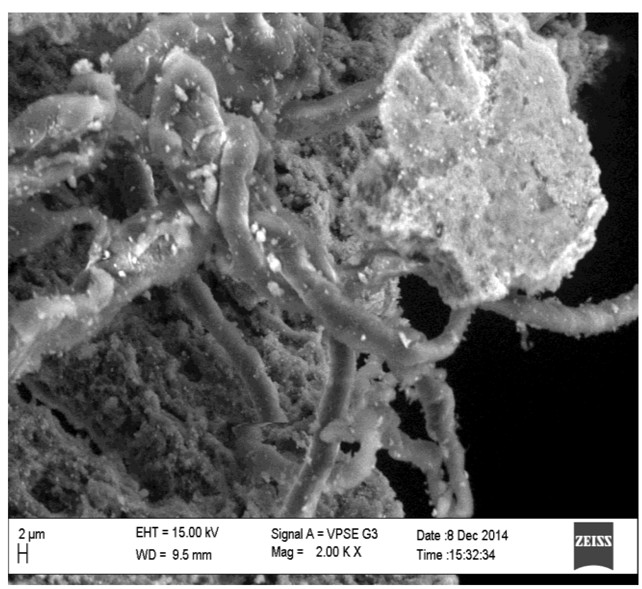

Fig. 4. SEM image revealing the surface morphology of Ag nanohybrids.

Conclusion

The results of present study suggest that it is possible to synthesize a hybrid of AgNPs and AgNR by simple mixing of $AgNO_3$ solution with leaf broth of *Cassia occidentalis* plant. This is a very simple, cost effective and environmentally friendly method. However, further study in the direction of optimizing the reaction conditions such as pH, temperature, broth conditions is needed to identify condition that selectively yield only AgNPs or AgNRs. The experimental probes to assess thermal stability, purity and catalytic properties of synthesised nanostructures needs to be carried out. Further, the employability of biosynthesized nanostructures in various applications such as biosensing, solar cells, nano electronics, imaging and water remediation need to be examined.

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