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Green synthesis of silver oxide nanoparticles using *Trigonella foenum-graecum* leaf extract and their characterization

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Abstract. The unique physical and chemical properties of silver nanoparticles (Ag NPs) of different sizes and shapes made their synthesis expedient. The most important method of NPs synthesis is the chemical process. However, the disadvantages of this method are the need for specific conditions such as high temperatures, to ensure formation and stability of NPs, as well as use of heavy aromatic solvents. Biosynthesis of NPs is considered advantageous over the traditional chemical approach. In this paper, the first report of the synthesis of silver oxide (AgO) NPs using *Trigonella foenum-graecum* leaf extract as a reducing agent is presented. The NPs were characterized by X-ray diffraction (XRD), thermogravimetric analysis/differential thermal analysis (TA/DTA), UV, photoluminescence, SEM, EDX and high resolution transmission electron microscopy (HRTEM). The XRD confirmed the formation of high-purity AgO fine crystals. The average crystal size ranged from 27 to 32 nm as was revealed by HRTEM. From the Tauc plot, the optical band gap of the AgO crystals of 3.3 eV was determined. Thermal analysis provided the optimum temperature for calcination of the AgO NPs to be 400 °C.

Keywords: biosynthesis, bandgap, crystallite, structural, optical properties.

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1. Introduction

Today, nanotechnology has become an important research area, which penetrates in all the fields of science and technology, including chemical industry. The size, orientation and physical properties of NPs can modify the properties of any material. Various methods of NPs synthesis are being investigated and implemented. Among them, there is green synthesis of NPs, which is easy, efficient and environmentally friendly as compared to chemical synthesis that involves toxic solvents and use of high pressures and temperatures [1]. Moreover, products that have a connection with microorganisms cannot be good due to test environments. Therefore, green synthesis of NPs may be considered as the best choice.

Metal oxide NPs, in particular AgO ones, are interesting in view of their high technological potential. Silver is a very valuable material and reacts with oxygen to form various compounds such as Ag_2O, AgO, Ag_3O_4, and Ag_2O_3. Previously, silver NPs were synthesized using *Callistemon lanceolatus* [2], *Moringa oleifera* [3], and *Millingtonia hortensis* [4]. Although these methods use bio extracts, they also require a lot of chemicals as stabilizing or reducing agents [5]. Hence, in the present work, we synthesized silver oxide NPs by using the *Trigonella foenum-graecum* leaf extract [6], which acted as a reducing agent. Fenugreek (*Trigonella foenum-graecum*) is a medicinal plant found in nature. It belongs to the legumes family growing in India and Pakistan. It is known for its hypoglycemic, anti-helmintic, anti-bacterial, anti-inflammatory, anti-pyretic and anti-bacterial properties. This plant contains minerals, iron, phosphate, para-aminobenzoic acid (PABA), A and D vitamins, lecithin and choline, which help to dissolve cholesterol and fat. It also contains health-promoting neuroproteins, biotin and trimethylamine, which have a positive effect on the nervous system. The main ingredients are saponin, coumarin and fenugreekine, which reduce metal ions [7].

2. Experimental

2.1. Synthesis of silver oxide NPs

Silver nitrate is the most common precursor to silver compounds [8]. Analytical grade $AgNO_3$ (silver nitrate, ≥99.9%) was used as purchased without any further purification. Fresh leaves of *Trigonella foenum-graecum* (Fig. 1) were purchased in a local market in the Tirunelveli district. To prepare the leaf extract, the leaves were washed several times under running water to remove bacteria and then rinsed with distilled water. They were further blended with a mixer grinder and filtered to use in the synthesis process.

0.1 M of a silver nitrate standard solution was prepared using double distilled water. The leaf extract was added to this solution until a precipitate formed. Then the mixture was stirred for approximately four hours. At this, the color of the solution changed from transparent to dark brown (Fig. 2). The solution was filtered with a Whatman filter paper. The precipitate was washed twice with double distilled water and dried in an oven at 100 °C for 24 hours to obtain dry powder with AgO NPs.

Fig. 1. *Trigonella foenum-graecum* leaves.

2.1. Characterization techniques

The powder XRD spectra of the AgO NPs were measured by an Analytical EXPERT-PRO diffractometer using a CuK_α monochromatic radiation source (1.5406 Å). The 2θ value ranged from 0° to 80°. The measurements took place at the Manonmaniam Sundaranar University, Tirunelveli, Tamilnadu, India. The NPs were characterized at room temperature using Analytical Record. The UV-Vis spectra of the NPs were measured in the range of 200 to 900 nm using a Jasco UV650 UV-Vis spectrophotometer. The photoluminescence spectra were recorded on a spectrofluorometer. The SEM analysis was performed using a JEOL, JSM6390 scanning electron microscope, and the EDAX analysis was carried out using an Oxford Instruments INCApentaFETx3 energy dispersive X-ray spectrometer. The photoluminescence spectra were analyzed using a G9800 AA Cary Eclipse fluorescence spectrophotometer at the Standard Fireworks Rajaratnam College for Women, Sivakasi, TamilNadu, India. The TGA/DTA analyses were performed using an STA-600 (Perkin Elmer). The HRTEM images were recorded using a JEOL JEM 2100 high resolution transmission electron microscope.

3. Results and discussion

3.1. Structural analysis

The XRD spectra of the AgO NPs are shown in Fig. 3. The observed peaks match the JCPDS card no. 84-1108 data [8], which indicates the tetragonal crystal structure of the NPs. Presence of all the (*hkl*) peaks confirms that the NPs are polycrystalline. The 2θ peaks located at 26°, 32°, 39°, 46°, 55°, 57°, 67°, and 76° correspond to the Miller indices (112), (202), (004), (132), (224), (402), (206) and (136) of the AgO nanoparticles. No other

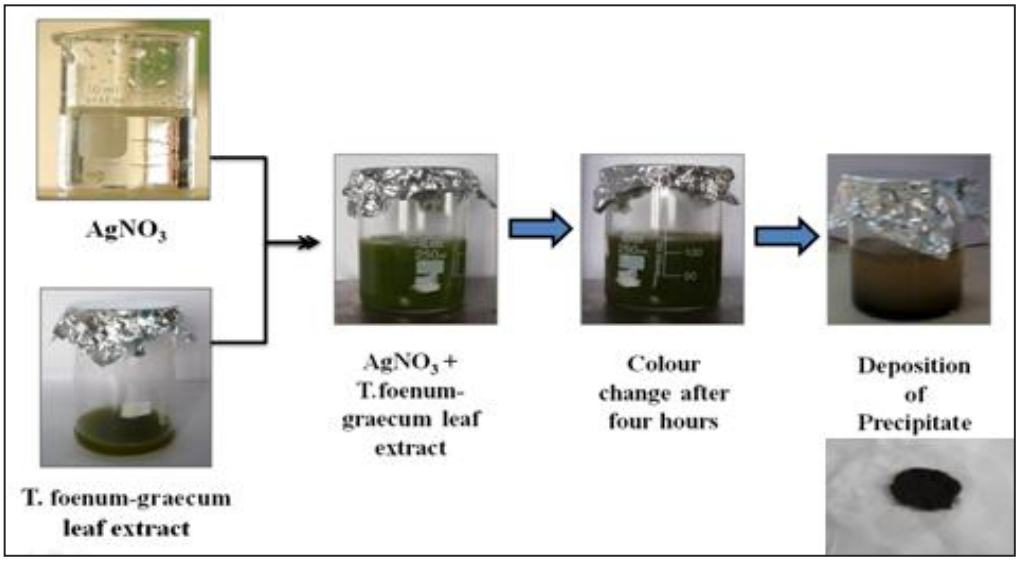

Fig. 2. Synthesis process using *Trigonella foenum-graecum* and the obtained AgO NPs.

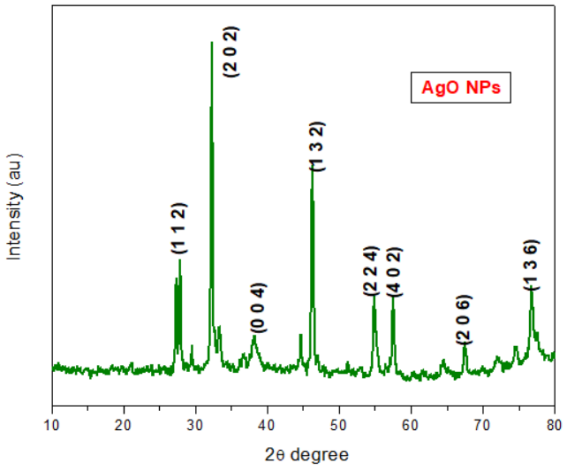

Fig. 3. X-ray diffraction pattern of AgO NPs.

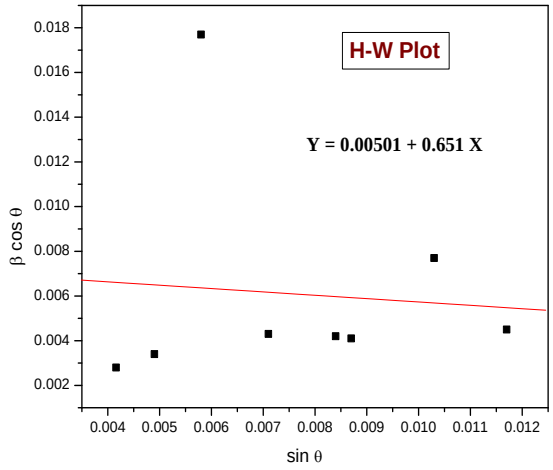

Fig. 4. Williamson–Hall plot.

distinct peaks related to impurities are observed indicating the NPs high purity. The average crystallite size D (in nm) is estimated using the Scherrer formula, $D = k\lambda/\beta \cos(\theta)$ [9, 10], where λ is the wavelength of the incident X-ray radiation (1.5406 Å), β is the half-width of the diffraction maximum (in radians), θ is the Bragg diffraction angle, and k is the Scherrer constant, respectively. The XRD results also confirm the tetragonal crystal structure of the NPs. The *hkl* plane is well indexed to the tetragonal phase with the lattice parameters $a = b = 6.7902$Å and $c = 9.3659$ Å. The average size of the NPs crystallites is around 32 nm. The effects of X-ray broadening, crystallite size and lattice stress on the peak width were investigated using the Williamson–Hall (W–H) analysis and mass-strain diagram [11]. The ($E\cos\theta$) *versus* ($4\sin\theta$) dependence

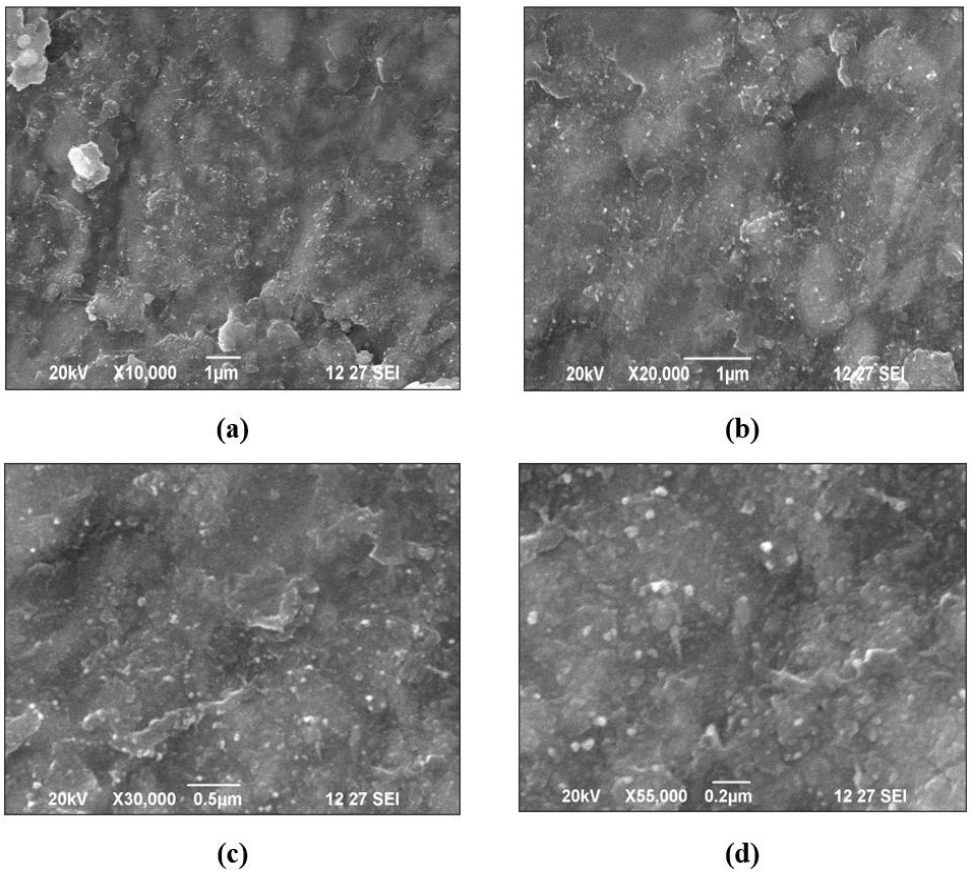

Fig. 5. SEM micrographs at different magnifications (a) ×10,000, (b) ×20,000, (c) ×30,000, and (d) ×55,000.

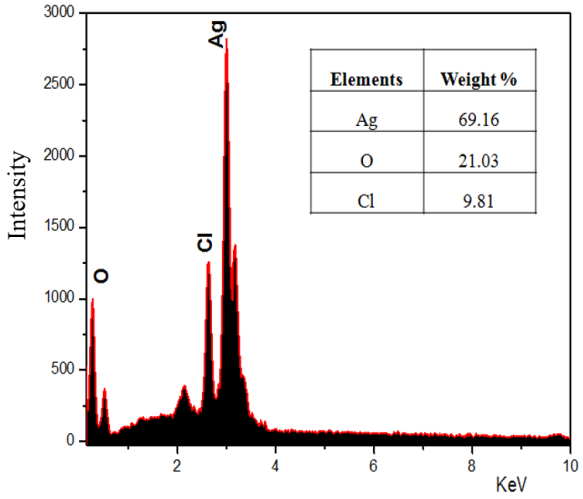

Fig. 6. EDX spectrum of AgO NPs.

was plotted to obtain the best expected values for the tetragonal phase of the AgO NPs. The slope of the inserted line and the *y*-intercept represent strain and crystallite size, respectively. The crystallite size and the value of micro-strain in the NPs were estimated to be 27 nm and $1.5218 \cdot 10^{-3}$, respectively. Fig. 4 represents the W–H plot for the synthesized NPs.

3.2. Morphological and elemental analysis

Scanning electron microscopy was used to study the morphology of the NPs. EDX was used to confirm the presence of metal traces. Fig. 5 shows the surface morphology of the silver oxide NPs at different magnifications. It is evident from the SEM images that the particles have a high density and swad together. The boundaries of individual particles are difficult to identify because of the clustering effect.

Fig. 6 shows the EDX spectrum of the biosynthesized AgO NPs. The high-intensity peak at 3 keV corresponding to silver and the peaks at 0.3 and 2.6 keV corresponding to oxygen and chlorine, respectively, are clearly visible. Metallic silver NPs show an optical peak of about 3 keV due to surface plasmon resonance [12]. Similar results in the 2-4 keV range were also reported for silver NPs produced using *Artemisia nilagirica* leaves and *Artocarpus heterophyllus* seed extracts [13].

3.3. Optical analysis

3.3.1. UV and visible-range spectroscopy

Reduction of Ag^+ ions to AgO from the removed leaves was monitored by recording the changes over time using a UV-Vis spectrophotometer as shown in Fig. 7. The plasmonic field resonance band is visible at 300 nm. The maximum absorbance corresponds to the band edge absorption. Beyond this band, the absorbance decreases due to the relatively lower number of absorption states. The transparency of metal nanoparticles is usually determined by SPR, which red- or blue-shifts depending on the size, shape, aggregate state of NPs and surrounding dielectric medium [14]. The optical band gap (OBG) of the metal nanoparticles is given by the Tauc equation, $\alpha h\nu = A(h\nu - E_a)n$, where α is the absorption coefficient, A is a constant and $h\nu$ is the force, respectively. Layers in the event correspond to the n directory implicit change permission. It can be seen from the inset in Fig. 7 that OBG is equal to 3.3 eV.

3.3.2. Photoluminescence analysis

PL of the biosynthesized AgO NPs was studied to understand their fluorescence properties. The PL spectra were measured at the excitation wavelengths in the range of 200 to 900 nm as shown in Fig. 8. The high-intensity peak around 380 nm (3.3 eV) corresponds to the silver NPs. It has a good agreement with the peak obtained in the UV analysis. The lower-intensity peaks at 520 and 790 nm are due to oxygen vacancies and surface defects, respectively. It can be seen from the HRTEM image that the sample contains particles of multiple sizes which give rise to the PL peaks. It should be noticed as well that the PL peak observed in the present work has pretty good agreement with the previously published results [15–18].

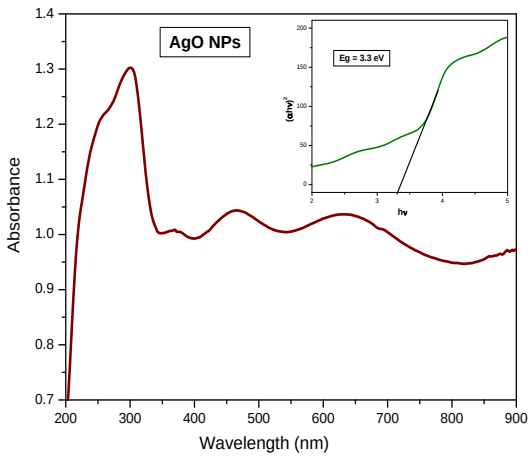

Fig. 7. UV absorbance spectrum and Tauc plot of AgO NPs.

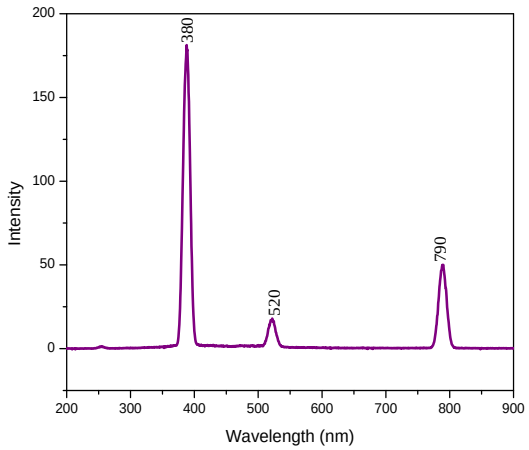

Fig. 8. Photoluminescence spectrum of AgO NPs.

Table. Percentage of weight loss at different temperatures.

Temperature	Percentage of weight loss
80 – 170 °C	2.27%
170 – 400 °C	29.72%
400 – 700 °C	17.98%

3.4. Thermal analysis

Thermogravimetric and differential thermal analysis enable determination of the calcination temperature of the synthesized NPs. The TGA/DTA curves for the synthesized AgO NPs are shown in Fig. 9. The TGA analysis was carried out in the temperature range of 80 °C to 900 °C to determine the decomposition temperature and rate [19]. The thermal weight decreases as the temperature increases (Fig. 10). Table represents the percentage of weight loss at different temperatures determined from the thermogravimetric analysis.

The initial weight loss of 2.27% is due to the desorption of water molecules present in the sample. Second weight loss of 29.72% is attributed to impurities or adsorbents. Finally, the weight loss of 17.98% is caused by thermal dehydration/decomposition during formation of crystalline AgO NPs. This process is accompanied by respective DTA transitions. Since no exothermic or endothermic reactions seem to take place above 400 °C, this temperature is considered to be the optimum one for calcination.

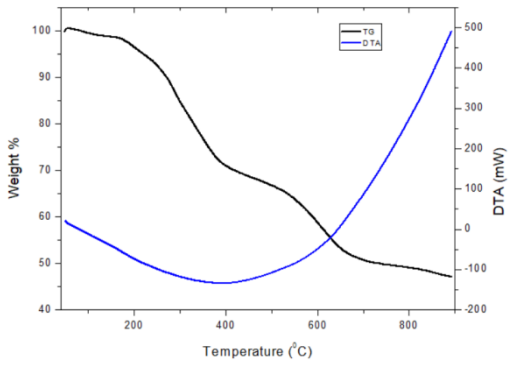

Fig. 9. TGA/DTA graph of AgO NPs.

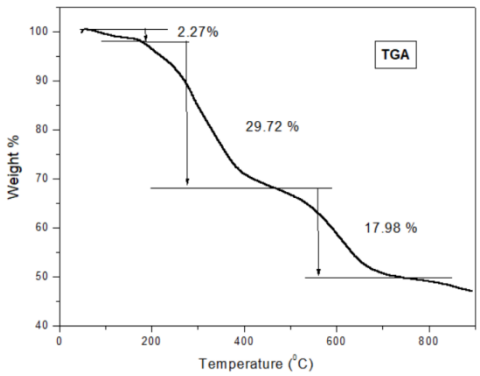

Fig. 10. Percentage of weight loss *versus* temperature.

3.5. HRTEM analysis

The morphology and the structure of the synthesized NPs were studied using HRTEM. Figs 11a to 11d represent the HRTEM images of the AgO NPs at different magnifications. It can be seen from these figures that the particles are spherical and agglomerated forming a porous structure. The NPs agglomerate to reduce the high surface energy caused by the high surface to volume ratios [20]. It can be seen from the images that the particles have different sizes ranged from about 20 to 35 nm, The selected area electron diffraction (SAED) pattern of a AgO NP is shown in Figs 12a to 12d, which agrees well with the value of about 29 nm determined by

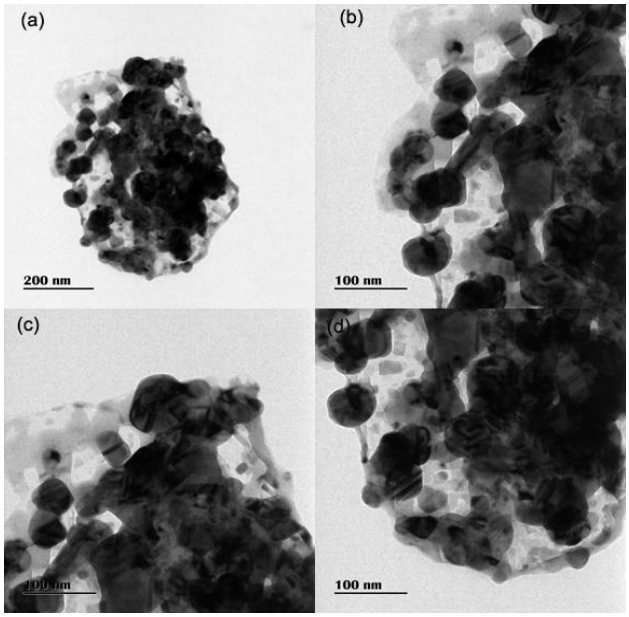

Fig. 11. HRTEM images of AgO NPs.

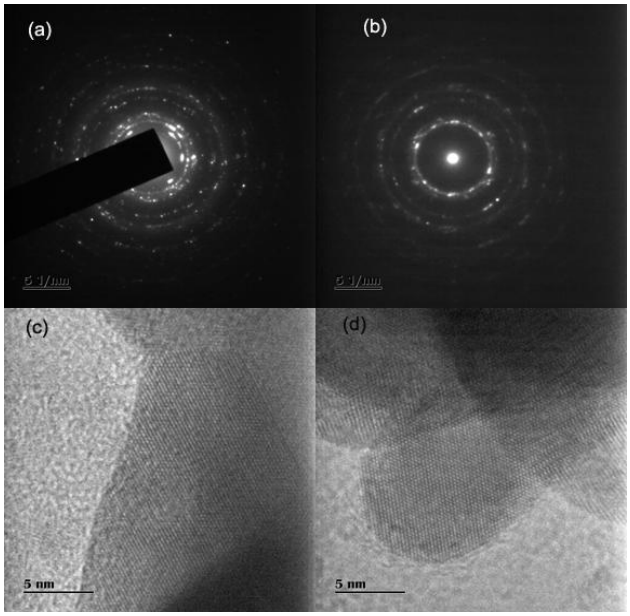

Fig. 12. SAED patterns of AgO NPs.

powder XRD. The lattice planes of the NPs are shown in Figs 12c and 12d. It can be seen from these figures that atoms are arranged in three-dimensional lattices.

4. Conclusions

An environment-friendly method was employed to synthesize silver oxide NPs. Ag NPs prepared in this process were quite stable and remain intact if it protected under light proof conditions. The synthesized NPs were about 29 nm in size as determined by the XRD and confirmed by HRTEM, and had tetragonal crystal structure. The NPs band gap of 3.3 eV was determined by the UV and PL analysis. The SEM investigations revealed the high density of the AgO NPs. A high-intensity peak at about 3 keV in the EDX spectrum is due to the presence of metallic silver in the synthesized NPs.

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Authors' contributions

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Roshan M.M.: project administration and supervision, writing – review & editing.
SaiGowri R.: writing – review & editing.
Vella Durai S.C.: formal analysis, visualization, conceptualization, methodology, writing – review & editing.

Зелений синтез наночастинок оксиду срібла з використанням екстракту листя *Trigonella foenum-graecum* та їх характеризація

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Анотація. Унікальні фізико-хімічні властивості наночастинок срібла (Ag НЧ) різних розмірів та форм зробили доцільним їх синтез. Найважливішим методом синтезу НЧ є хімічний процес. Недоліками цього методу є специфічні вимоги до умов синтезу, такі як високі температури, для забезпечення можливості утворення та стабільності НЧ, а також використання високоароматичних розчинників. Вважають, що біосинтез НЧ має переваги перед традиційним хімічним підходом. У цій роботі вперше повідомляється про синтез НЧ оксиду срібла (AgO) з використанням екстракту листя *Trigonella foenum-graecum* як відновника. НЧ були охарактеризовані з використанням дифракції рентгенівських променів, термогравіметричного аналізу/диференціального термічного аналізу, УФ, фотолюмінесценції, SEM та EDX аналізу, а також вискороздільної просвічуючої електронної мікроскопії. З використанням дифракції рентгенівських променів було підтверджено утворення дрібних кристалів AgO високої чистоти. Середні розміри кристалів становили від 27 до 32 нм, що було виявлено високороздільною просвічуючою електронною мікроскопією. Оптична заборонена зона кристалів AgO, визначена з графіка Таука, дорівнювала 3,3 еВ. Термічний аналіз показав, що оптимальна температура для прожарювання AgO НЧ становила 400 °C.

Ключові слова: біосинтез, заборонена зона, кристаліт, структурні, оптичні властивості.