Valorization of Vigna Unguiculata (Cowpea) Husk for Green Synthesis of Silver Nanoparticles and Evaluation of Its Free Radical Scavenging Potentials Towards Indoor Enironmental Application

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Abstract

The escalating challenge representing free radicals like Reactive Oxygen Species (ROS) and Reactive Nitrogen Species (RNS) necessitates innovative solutions within the confines of green nanotechnology. This research focuses on the free radical scavenging activities and the green synthesis of silver nanoparticles (AgNPs) from Vigna unguiculata (cowpea) husk aqueous extract for valuable possible indoor environmental uses. For the green synthesis of the silver nanoparticles, photo-activation was used, as Vigna unguiculata husk extract was employed as both a reducing and capping agent along with silver nitrate as the precursor. AgNPs synthesis, and subsequent characterizations were carried out utilizing UV-Vis spectra, Fourier Transform Infrared (FTIR) spectra, Energy Dispersive X-Ray (EDX) and Transmission Electronics Microscopy (TEM). The UV-Vis spectra exhibited a maximum absorbance of 448.0 nm, demonstrating the presence of the silver nanoparticles, and the surface plasmon resonance both FTIR and EDX demonstrated the presence of Ag. FTIR shows the functional groups at 3430.171017.61 cm^{-1}, and silver at nm, which was attributed to the silver nanoparticles surface with the reducing and capping agents being phenolic compounds and proteins. TEM demonstrated silver spherical nanoparticles and EDX demonstrated the silver. 3 nm. The synthesized AgNPs scavenged free radicals quite efficiently, with activity percentages of 56.49 ± 0.2, 52.55 ± 0.2, and 48.09 ± 0.3 at 50, 100, and 150 μg/ml respectively. The assessed total phenolic content for these volumes were 59.46 ± 0.2, 50.15 ± 0.2, and 43.18 ± 0.3 μg/ml respectively for 50, 100, and 150 μg/ml.

The biocompatible properties of the plant waste-mediated nanoparticles, combined with their free radical scavenging activities, present a promising green approach for mitigating oxidative stress in indoor environments. These research findings suggest potential applications in building materials, air filtration systems, and surface coatings to create oxidant-free indoor spaces while supporting sustainable development goals. This research contributes to the growing field of green nanotechnology through the biosynthesis of plant waste-mediated silver nanoparticles for free radical scavenging applications.

Introduction

As the world grows more integrated into the fourth industrial revolution, humanity faces increasing challenges in virtually all areas that innovation has touched. This era tackles more challenges than innovative solutions. Throughout the world, technological advancement has made our air unsafe through indiscriminate release of poisonous fumes, traffic-related air pollution (TRAP) and environmental tobacco smoke (ETS) issues to mention a few that results to oxidants which man breathe in as well as consumes daily [1, 2]. Through the incessant emission of oxidants from human activities, these free radicals compromise the integrity of indoor environments and consequently affect human health. The quality of the air indoors is a unique public health problem, along with the potential to cause oxidative stress. A heightened amount of reactive oxygen and nitrogen species (ROS and RNS) along with other organic compounds compounds with sulfur, that result in causing alkyl sulfonyl radicals (RS) are the result of the growing imbalance of the antioxidants and oxidants. There are oxidative species generating contaminants and pollutants, and transition metal ions in indoor dust, building materials, and airborne particulates which are indoor environment prooxidants that invoke the formation of ROS or RNS by reacting with hydrogen peroxide or with molecular oxygen.

While the human body naturally produces approximately 5grams of ROS per day under normal circumstances, maintaining a dynamic balance with oxygen forms essential for life, poor indoor air quality significantly disrupts this delicate equilibrium by introducing additional oxidative stress through chemical pollutants from building materials, cleaning products, outdoor air infiltration, physical factors such as particulate matter and electromagnetic radiation from radiating building materials, and biological contaminants including mold spores and bacterial endotoxins [2, 4].

The damage alluded to is biological and consists of the oxidation of unsaturated lipids, the inactivation of proteins, the modifications of enzymes, the alteration of DNA via ring cleavage & breaks, the withering of chains and the ultimate demise of cells, which may contribute to Alzheimer's, atherosclerosis, cardiovascular diseases, cancers, ADHD, and schizophrenia, as well as other psychological disorders [4, 5, 6]. In response to these ever-increasing oxidant menace on humans and their indoor environments, green nanotechnology emerges as a promising lasting solution for mitigating free radical challenges within indoor environments. Indeed, nanoparticles have attracted increasing attention for their ability to modulate oxidative processes and scavenge free radicals. Plant-mediated synthesis of nanoparticles offers a sustainable and environmentally friendly route that integrates biological reducing agents with nanotechnology. Beyond their physicochemical advantages, nanoparticles have also shown to alleviate oxidative stress in living systems where [7] researched on foliar application of nanoceria as improvement tolerance of *Abelmoschus esculenta* to cadmium stress by enhancing antioxidant enzyme activity and reducing associated damage. This evidence showcases broader potential of nanoparticles as free radical modulators, thus, aligns with the study on *Vigna unguiculata* husk-mediated silver nanoparticles as a novel strategy for environmental applications.

The proliferation of ROS/RNS and other oxidants in enclosed spaces poses significant threats to both human health and the structural integrity of buildings. Green synthesized metallic nanoparticles offer eco-friendly approaches to neutralize these harmful oxidants through the development of antioxidant nanoparticles that can effectively scavenge free radicals while maintaining ecological balance [2]. This innovative field represents a paradigm shift from conventional remediation methods, providing cleaner, more efficient, and sustainable solutions to indoor air quality challenges without introducing additional environmental burdens. This work provides a valid approach to deal with the problems posed by oxidative free radicals from the green synthesis of silver nanoparticles using the aqueous extract of Vigna unguiculata husks.

Methodology

Sample Collection and Preparation of Sample

Dried *Vigna unguiculata* husks were collected from agricultural waste section of *Wazo* Market (Cowpea processing section) within Ogbomoso Metropolis (8.1457o N, 4.2507oE), Oyo State, Nigeria(permissions were not required to get the cowpea husk). The samples were packed in a sterile polythene bag and later further dried in the laboratory for 72 hours at room temperature. After air drying, the Vigna unguiculata husks samples were pulverized aseptically. 1 gram (1g) of the pulverized sample was suspended in 100 ml distilled water and heated in a water bath at 60°C for 1 hour. The extract was filtered using Whatman No. 1 filter paper and centrifuged at 4000 rpm for 15 minutes to separate the extract supernatant from the pellet which was discarded.

Preparation and Synthesis of Green Synthesized Nanoparticles

Preparation of Silver Nitrate ($AgNO_3$) Solution and Synthesis of Silver Nanoparticles

Preparation of the silver nitrate solution involved dissolving 1mM of silver nitrate salt in 1000ml distilled water and storing the solution in an amber bottle, wrapped with foil, and kept in a dark cupboard at ambient temperature. Two milliliters (2 ml) of each sample supernatant was drawn using a sterile hypodermal syringe into a slant bottle and was labelled. After which 20ml of silver nitrate ($AgNO_3$) was added into the bottle containing 2 ml of the supernatants in ratio 2:20 and was re-labelled. To promote the synthesis of silver nanoparticles, the salt solution (AgNO3) and the sample supernatant were photo-activated by placing them in direct sunlight. For the control, only the aqueous solution was taken. The formation of silver nanoparticles (AgNps) was monitored by visually inspecting the colour change [8].

Characterization of the Synthesized Silver Nanoparticle

UV-Vis spectrum analysis

A quartz cuvette containing 2 milliliters of synthesized silver nanoparticles was placed in the spectrophotometer and readings were collected at wavelengths of 180–500 nm and a bandwidth of 2.0 nm.

Fourier Transform Infra-red (FTIR) Spectroscopy

The functional groups of the silver nanoparticles were measured using an FT-IR spectrophotometer. The sample solution was centrifuged for 10 minutes at 7000 rpm. The resultant pellets were washed in double distilled water and then freeze-dried. A few crystals were mixed and ground with KBr (Merck for spectroscopy) and the mixture was packed in an agate mortar and pestle to get a homogeneous sample from which a pellet was made under a pressure of 7 tons. For each sample, IR spectrums were collected in the 4000 – 400 cm-1 range using a Perkin Elmer 3000 MX spectrometer with 32 scans. The spectrometric IR analysis was done using the Win-IR Pro spectrometric software where the IR spectrums were analyzed and a peak sensitivity of 2 cm-1 was employed.

Energy Dispersive X-ray (EDX) Analysis

To understand the composition of the nanoparticle, I employed the Espirit 1.8.5 software. Conducting this analysis made it possible to find the most abundant element contained within the nanoparticle. For this analysis, I placed a droplet of silver nanoparticles on a fresh piece of silicon wafer, which I allowed to dry via evaporation at room temperature. Once dried, I added a thin layer of carbon film on top of the dried nanoparticles to mitigate charging, and then I was able to analyze the elemental composition of the sample.

Transmission Electron Microscopy (TEM)

Morphological characterization of the nanoparticles was done by the Leo 912 AB transmission electron microscope which is a high-performance electron microscope, and it is operated at 120 kV. For this analysis, a sample of the synthesized silver nanoparticles solution was placed on the carbon-coated copper grid, which was dried before the microscopy analysis.

Free Radical Scavenging Evaluation of the Synthesized Nanoparticles

Antioxidant Activity of the AgNPs against 2, 2- diphenyl-1-picrylhydrazyl (DPPH)

2,2-diphenyl-1-picrylhydrazyl is used to test preliminary radical scavenging activity on a compound or nanoparticles. Antioxidant activity was made by the modified DPPH that was reported by [9]. The DPPH methanolic solution was made by measuring 0.04g DPPH in 1000ml methanol, taking the optical density of the solution at 517nm. To find the antioxidant activity, the synthesized silver nanoparticles were made at concentrations of 50, 100, and 150µg/ml and were each challenged with 4ml of methanolic DPPH. The samples, for then, were allowed to scavenge DPPH for 30 minutes in the dark. The absorbance at 517 nm was measured with a UV-visible spectrophotometer. The scavenging percentage was calculated using the formula below:

DPPH scavenging (%) $= \frac{Absorbance\ control - Absorbance\ of\ sample}{Absorbance\ control} \times 100\%$

Total Phenolics content of the bio-fabricated nanoparticles

For the bio-fabricated silver nanoparticles, the total phenolics content (TPC) was determined using the Folin Ciolcateau assay [8]. 1 ml of AgNPs with differing concentrations (50, 100, 150 µg/mL) was reacted with 10 ml of distilled water and 1.5 ml Folin Ciolcateau reagent. After a mixture was allowed to sit for 5 minutes, 4 ml of 20% sodium carbonate was added. 25 ml of distilled water was added and allowed to incubate for 30 min at ± 28 ºC. Determination of total phenolic content was done using UV-Vis spectrophotometry and 765 nm. The results were expressed as gallic acid (GA) equivalent (µg/g).

Results and Discussion

Bio-fabrication of the Silver Nanoparticles

In the study, the reduction and capping agent (plant extract) was first reacted with the precursor (silver nitrate solution) during photoactivation, and then the mixture transitioned through a series of color changes over 38 minutes, due to the reduction of Ag + to Ag° with the silver nanoparticles excitement in the Surface Plasmon Resonance (SPR) [10] and the stabilized silver nanoparticles produced a reddish-brown coloration (Fig. 1). The nanoparticles have been reported to exhibit various colors ranging from cherry red, yellowish brown, reddish brown, pale yellow, greenish brown to dark green [11, 12, 13, 14]. This variation in color demonstrated the presence and activity of biomolecules in the reducing and capping agent, in this case, the Vigna unguiculata extract, which was used in the bio-fabrication of the nanoparticles. The presence of various macromolecules, particularly proteins, and phenolic compounds, contributed to the catalytic and stabilization of the formation of the silver nanoparticles which further emphasizes the effectiveness of the reducing agent.[8].

Characterization of the Bio-fabricated Silver Nanoparticles

Figure 2 displays the UV-Vis spectrum of the silver nanoparticles. The spectrum shows a maximum absorbance at a wavelength of 448.0 nm, showing surface plasmon resonance is in the 350–450 nm range. [15] reported that silver nanoparticles synthesized from Cucumis prophetarum aqueous leaf extract with UV-Vis spectrum absorbance shows a characteristic surface plasmon resonance peak of 420 nm. [13] the spectrum indicates there is absorption peak at 439 nm and is a result of a color changing of the mixture after adding the capping/reducing agent (H. Colorata extract).. [10] had also reported a peak at 417 nm on a UV-Vis spectrophotometer for silver nanoparticles which had been synthesized using Eugenia roxburghii extract. The spectrum of the Synthesized silver nanoparticles (Looking at Fig. 3) for the Fourier Transform Infrared spectroscopy showed the following strong peaks of 3430.17, 2966.0, 2587.73, 2538.0, 2357.63, 1753.52, 1686.39, 1608.09, 1417.29, 1309.0, 1190.44, 1017.61 and 1017.61 cm-1 which indicates proteins and phenolic compounds which acted as capping and stabilizing agents in the biotransformation process of the synthesized AgNPs. The peak 3430.17 cm-1 is associated with the amine N-H and the peaks at 2416.71, 1753.52, 1686.39, 1608.09, 1417.29, 1309.0, 1190.44, 1017.61 and 1017.61 cm-1 pertains to the methyl and thiol groups, the stretch of alkenes, and the amide [16]. The silver nanoparticles core was likely shield and encapsulated by the silver coated phytochemicals from the aqueous extract of Vigna unguiculata. The silver nanoparticles (Fig. 4) had a spherical shape and were 1.22–3.82 nm in diameter (Fig. 5). This is supported by [8] which also reported sizes in the range of 10–80 nm.

Free Radical Scavenging Activities of the Silver nanoparticles

Antioxidant Activity of the AgNPs against 2, 2- diphenyl-1-picryhydrazyl (DPPH)

The passage of time allows the investigation of the activity of the silver nanoparticles against DPPH to be done for the three concentrations of 50, 100, and 150 µg/ml (Table 1). DPPH is a stable free radical, thus a suitable candidate to investigate the free radical scavenging properties of the silver nanoparticles and many other nanoparticles [17]. It was seen that when the concentration of the Silver nanoparticles was increased, the free radical scavenging activities decreased. For the concentrations of 50, 100, and 150 µg/ml the free radical scavenging activities were 59.46 ± 0.2a, 50.15 ± 0.2a and 43.18 ± 0.3a respectively while for the control, Gallic acid, the activities were 74.27 ± 0.2a, 61.00 ± 0.2b, and 55.96 ± 0.2b for 50, 100, and 150 µg/ml respectively.

The total phenolics content of the AgNPs was evaluated at three different concentrations of 50, 100 and 150 µg/ml as presented in Table 2. Phenolic compounds are known to be important bioactive molecules found in plants [18] that contribute significantly to the antioxidant properties of various materials including green synthesized nanoparticles [17]. The results showed that as the concentrations increased, the total phenolics content of the BH AgNPs declined. At 50 µg/ml, the phenolics content was 59.46 ± 0.2a, which decreased to 50.15 ± 0.2a at 100 µg/ml, and further reduced to 43.18 ± 0.3a at the highest concentration of 150 µg/ml. this trend was observed in the control (Gallic acid) at 50 µg/ml, the phenolic content of the control was 74.27 ± 0.2a, at 100 µg/ml it was 61.00 ± 0.2b, and 55.96 ± 0.2b at 150 µg/ml.

Table 1
Free radical scavenging activities of BH AgNPs against DPPH

Sample	50	100	150
	(ug/ml)		
BHNps	56.49 ± 0.2^{a}	52.55 ± 0.2^{a}	48.09 ± 0.3^{b}
Gallic Acid (control)	78.46 ± 0.2^{b}	61.29 ± 0.2^{b}	50.11 ± 0.2^{b}

Table 2
Total Phenolics Content of the BH AgNPs

Samples	50 (ug/ml)	100	150
BHNps	59.46 ± 0.2[a]	50.15 ± 0.2[a]	43.18 ± 0.3[a]
Gallic Acid (control)	74.27 ± 0.2[a]	61.00 ± 0.2[b]	55.96 ± 0.2[b]

The strong free radical scavenging activity exhibited by the *Vigna unguiculata* husk-mediated silver nanoparticles demonstrates their potential as effective modulators of oxidative stress. This finding is constituent with broader evidence that nanoparticles can attenuate redox imbalances in biological systems. [7] reported that foliar application of nanoceria enhanced antioxidant enzyme activity and mitigated cadmium-induced oxidative damage in *Abelmoschus esculentus*. While the study on *Vigna unguiculata* focuses on silver nanoparticles synthesized from agro-waste and applied toward indoor environmental applications, both studies states the central role of nanoparticles in reducing oxidative stress through free radical scavenging. These studies reinforce the versatility of nanoparticle-based approaches for health and environmental protection.

The use of plant-based silver nanoparticles which are accessible biologically will help reduce the impact of oxidative stress. These silver nanoparticles will help oxidants dissolve, and there are many natural antioxidants which will help aid in the process. During the process of the silver nanoparticles biosynthesis, other plant materials, flavonoids, polyphenols, and terpenoids that have phytochemical and antioxidant properties will also be used to increase the antimicrobial and antioxidant activities of the silver particles. [2, 17]. These green-synthesized nanoparticles can be strategically incorporated into building materials, air filtration systems, surface coatings, paint formulations, textile treatments, and HVAC components to provide continuous antioxidant protection throughout indoor environments, effectively intercepting reactive species before they reach cellular targets and creating a protective barrier that preserves cellular integrity and function [2, 19]. The versatility of plant-based silver nanoparticles allows them to address multiple sources of oxidative stress simultaneously, including radiation-induced oxidative stress from electromagnetic-emitting building materials through incorporation into shielding materials and surface treatments that provide both electromagnetic protection and antioxidant activity. Studies have demonstrated that cytotoxic effects of various indoor pollutants through ROS generation can be mitigated through systematic antioxidants such as N-acetylcysteine (NAC), and plant-based silver nanoparticles offer superior advantages by providing sustained, localized antioxidant activity directly within the indoor environment, reducing the need for continuous systemic antioxidant supplementation while providing targeted protection against specific sources of oxidative stress [3, 4, 19].

The integration of green synthesized silver nanoparticles from *Vigna unguiculata* husk aqueous extract into indoor environmental systems represents promising innovative approach toward multifunctional, sustainable air quality management, and lasting solutions that address the growing challenges of indoor air pollution and its associated health effects on inhabitants. Recent innovative research on nanomaterial applications in sustainable indoor environments has demonstrated the exceptional potential of green synthesized nanoparticles in creating healthier indoor environments through their free radical scavenging properties [20, 21]. The incorporation of green-synthesized metallic nanoparticles, especially silver nanoparticles, into indoor air filtration systems has shown unprecedented efficacy in scavenging harmful ROS and RNS while simultaneously removing particulate matter, as evidenced by recent reports showing that silver nanoparticle-embedded filters can achieve better pollutant removal efficiency compared to conventional filtration technologies [22]. Also, the bio-fabrication of silver nanocluster composite coatings for air filtration applications has proven effective in providing effective defense system against biological and chemical indoor air contaminants [23, 24, 25].

Conclusion

This study adds to the use of agro-waste in the synthesis of environmentally friendly nanoparticles which can be used in capturing free radicals in the indoor environment. Use of plant-based silver nanoparticles in indoor environments directly contributes to the United Nations Sustainable Development Goal 3 (Good Health and Well-being) by lowering environmental health risks and encouraging preventive health care. It also contributes to SDG 11 (Sustainable Cities and Communities) by improving building sustainability, health, and urban environment, and to SDG 12 (Responsible Consumption and Production) by the use of nanotechnology which has lower environmental impacts and utilizes plant resources to antimicrobial silver nanoparticles in prepare green silver safer prepare silver nanoparticles. It greatly contributes to the 3 goals in a safe and innovative manner by addressing oxidative stress in indoor environments which is a critical public health concern considering the modern population spends 90% of their time indoors.

Declarations

Ethics Declaration

Not Applicable

Consent to Publish Declaration

Not Applicable

Consent to Participate Declaration

Not Applicable

Conflicts of Interest

All authors declare that they have no conflicts of interest.

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No funding was received for this research work.

Data Availability

All data that support the findings of this study are available from any of the corresponding authors upon request.

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Figures

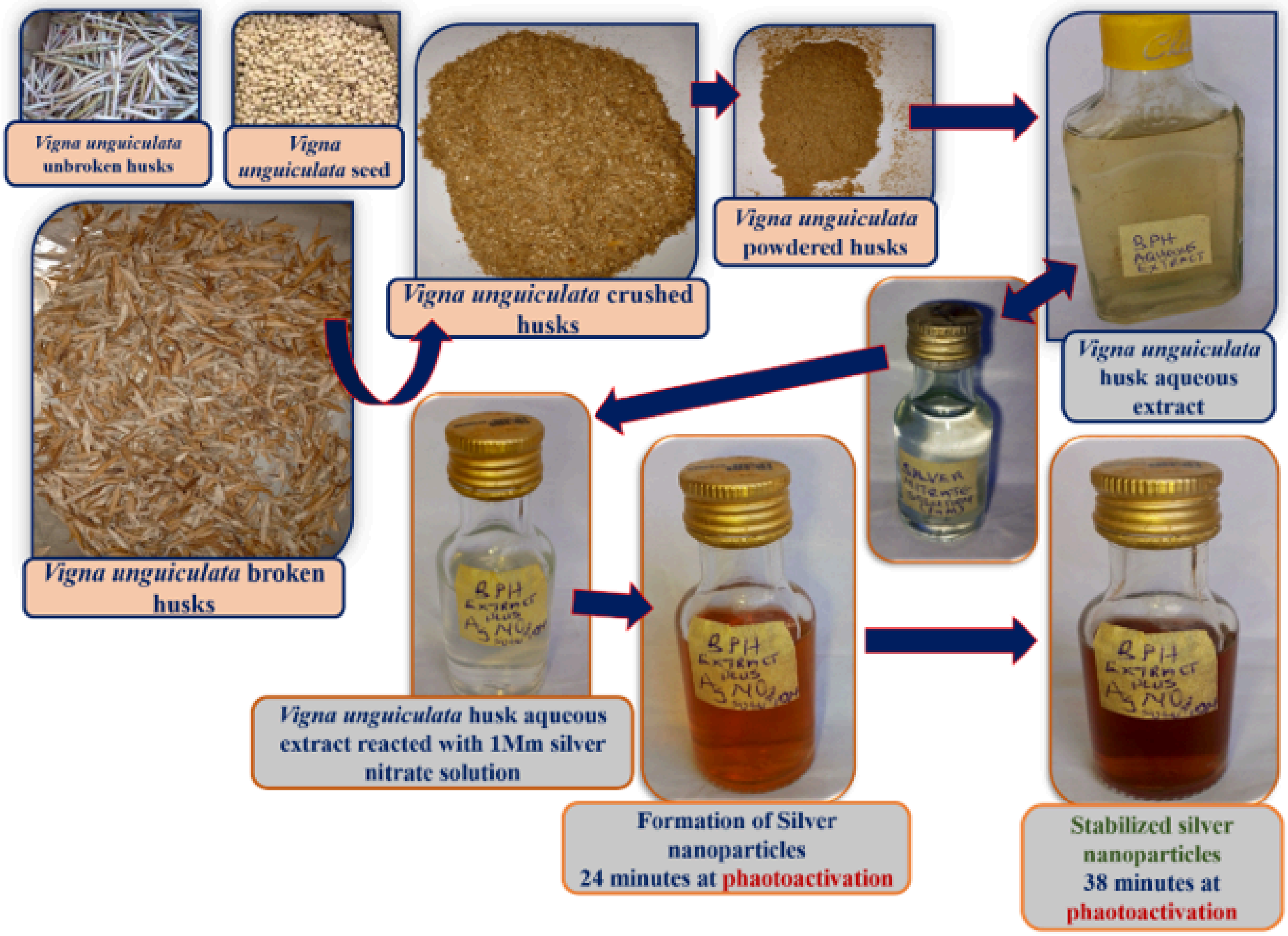

Figure 1

Green synthesis of *Vigna unguiculata* mediated silver nanoparticles

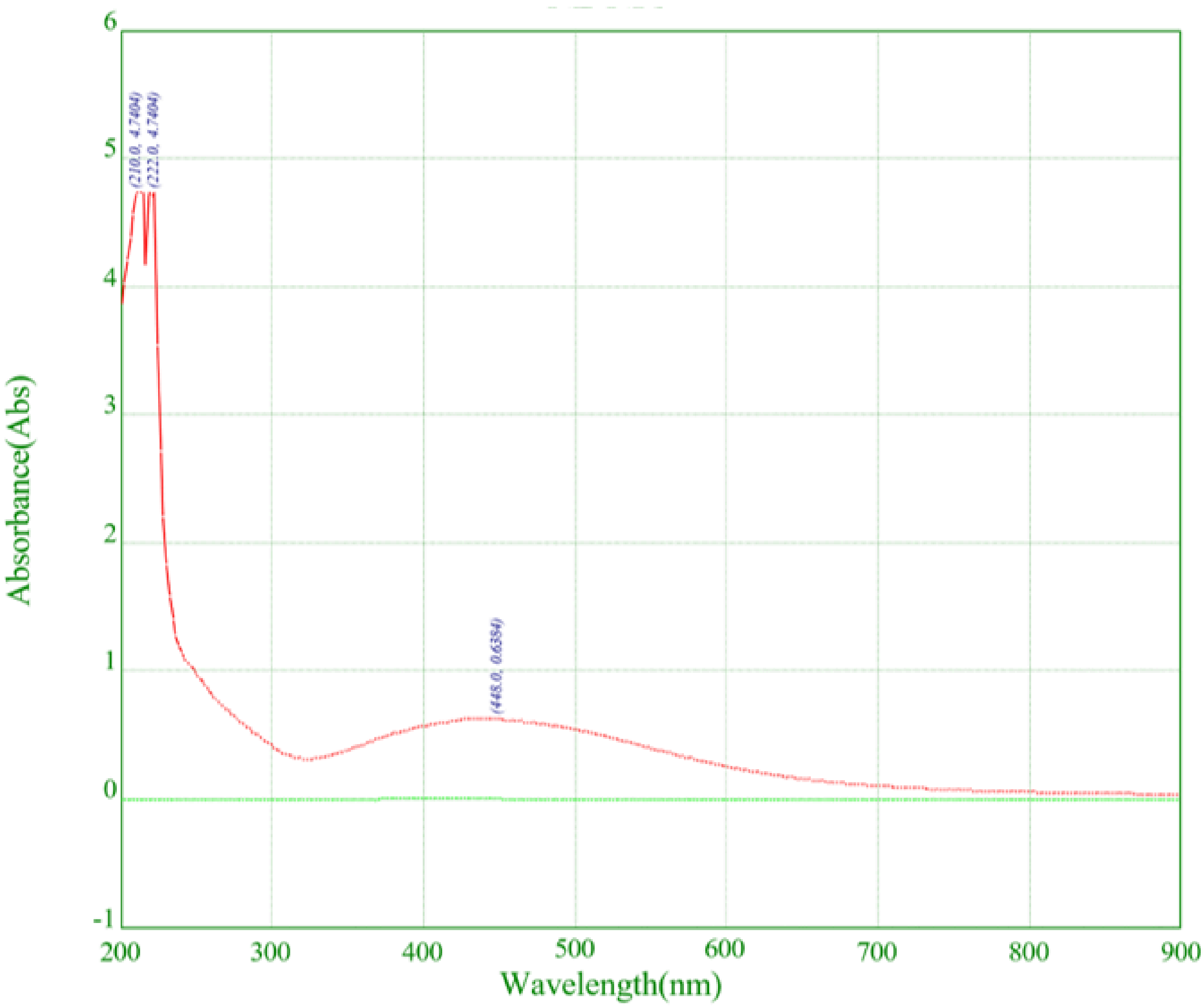

Figure 2

Uv-Vis spectrum of the synthesized silver nanoparticles

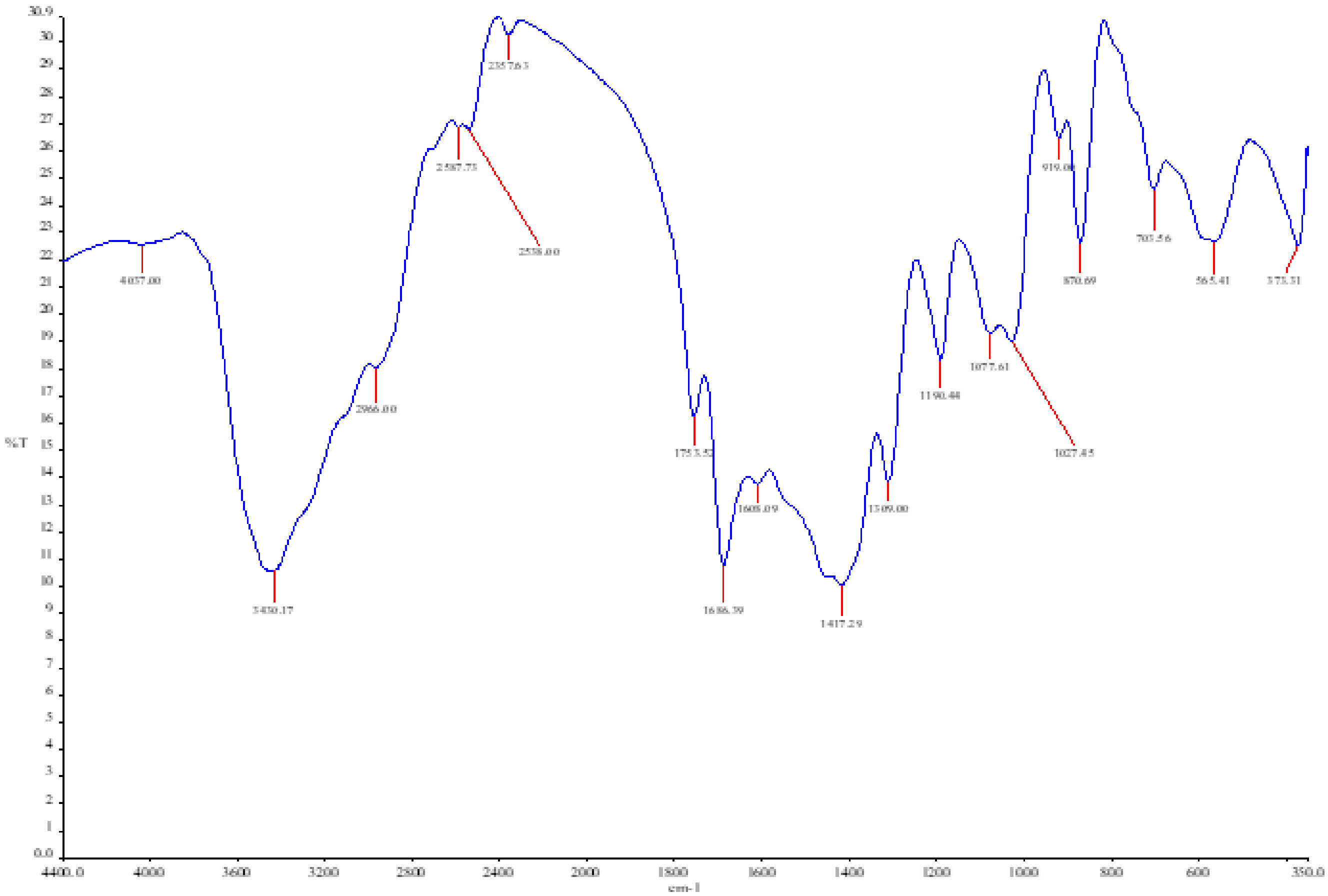

Figure 3

FTIR Spectrum of the synthesized silver nanoparticles

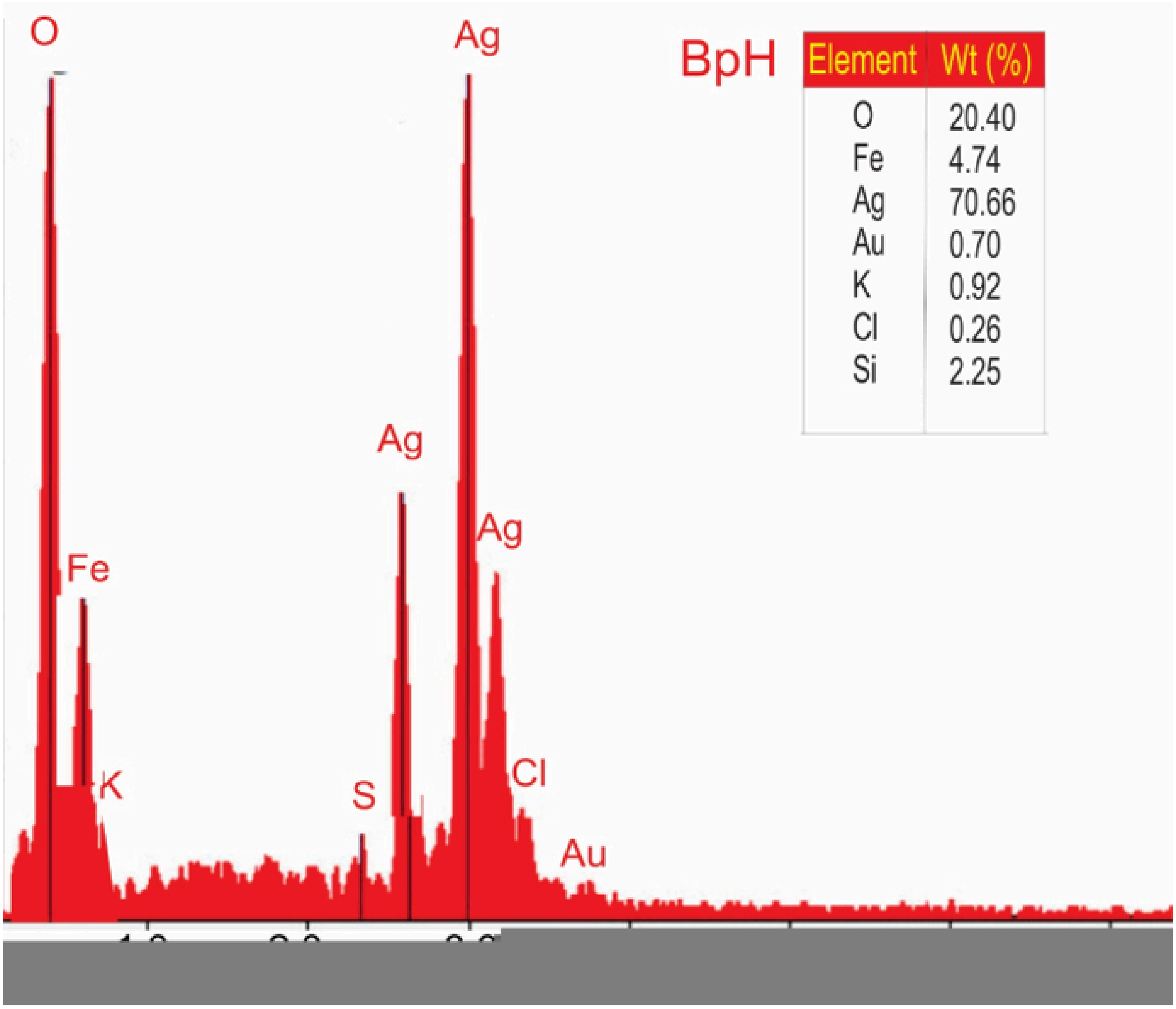

Figure 4

EDX spectrum of the synthesized silver nanoparticles

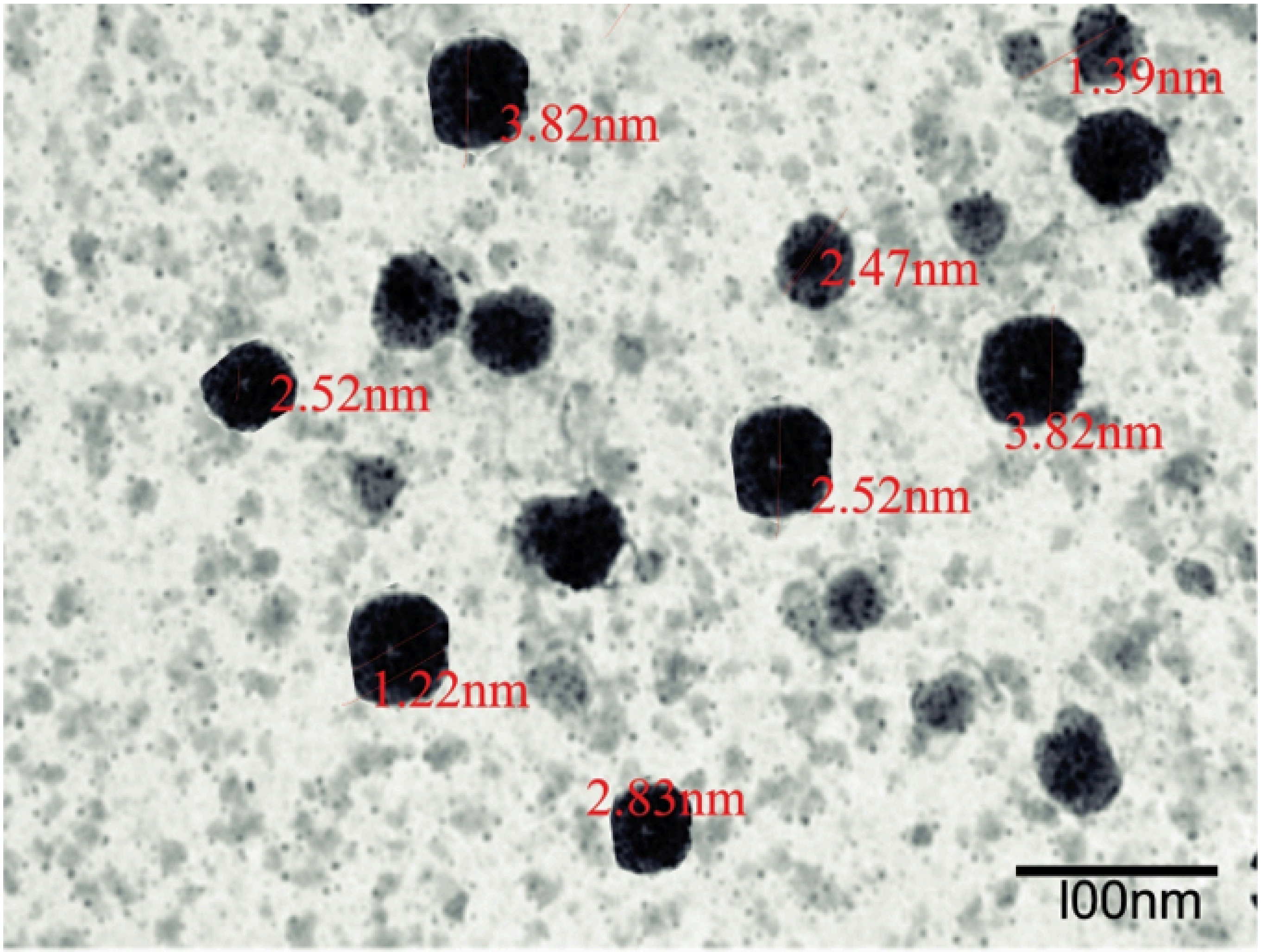

Figure 5

Transmission Electron Micrograph of the synthesized Nanoparticles