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Research Article

Green Synthesis of Gold and Silver Nanoparticles Using *Averrhoa bilimbi* Fruit Extract

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We report on rapid one-step green synthesis of gold and silver nanoparticles using fruit extract of *Averrhoa bilimbi Linn*. UV-Vis absorption spectroscopy was used to monitor the quantitative formation of gold and silver nanoparticles. The characteristics of the obtained gold and silver nanoparticles were studied using UV-Vis absorption spectroscopy (UV/Vis), Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), and Energy-dispersive spectroscopy (EDX). UV/Vis spectrum showed Surface Plasmon Resonance (SPR) for both gold and silver nanoparticles at 540 and 420 nm. The EDX spectrum of the solution containing gold and silver nanoparticles confirmed the presence of elemental gold and silver signals. The average diameter of the prepared nanoparticles in solution was about 50–150 nm. Synthesized particles were either hexagonal or rhomboidal in shape. This synthesis approach of gold and silver nanoparticles is cost effective and can be widely used in biological systems. The effect of fruit extract and metal ion concentration was also studied.

1. Introduction

Nanotechnology is mainly concerned with the synthesis of nanoparticles and their application in various fields of medicine, chemistry, physics, materials science, and engineering. Metal nanoparticles such as gold (Au) and silver (Ag) have recognized importance in chemistry, physics, and biology because of their unique optical, electrical, and photothermal properties. Syntheses of nanoparticles are usually carried out by various physical and chemical methods which are not environmentally friendly. In recent years, researchers in the field of nanotechnology are finding that there is an expanding research in the synthesis of metal nanoparticles due to the potential applications for the development of novel technologies. Noble metal nanoparticles are extensively studied because of their wide applications [1–3]. Among the various noble metal nanoparticles, gold and silver have several applications in sensors, detectors, and antibacterial agents [4–6]. In ancient Indian medical system (Ayurveda), gold is used as medicine in the preparation of nano level Swarna Bhasma to treat tuberculosis, anemia, and cough and also believed to prevent ageing [7]. Silver has been described as therapeutic agent for many diseases and an efficacious antibacterial and antifungal agent [8].

Recently, the studies are focused towards greener methods for the synthesis of nanoparticles. Biosynthesis of nanoparticles gained lots of interest due to the use of mild experimental conditions such as temperature, pH and pressure. During the past several years, production of metallic nanoparticles using low cost biological resources such as plants, algae, fungi, and bacteria are reported [9–13]. As an alternative to synthetic chemicals, in the synthesis of nanoparticles fruit extracts are used successfully [14, 15]. If the exact mechanism of biological synthesis is explained, it could offer an extra advantage over the chemical methods by means of higher productivity and lower cost. Biologically synthesized gold and silver nanoparticles could be of immense use in medical and biomedical textiles for their efficient antibacterial and antimicrobial properties and also in other applications like spectrally-selective coatings for solar energy absorption and intercalation material for electrical batteries; they also find use as optical receptors and as catalysts in chemical reactions.

Averrhoa bilimbi Linn.

Classification:

Kingdom: Plantae-plants

Subkingdom: Tracheobionta-vascular plants

Super division: Spermatophyta-seed plants

Division: Magnoliophyta-flowering plants

Class: Dicotyledonae

Subclass: Rosidae

Order: Oxalidales

Family: Oxalidaceae

Genus: *Averrhoa*

Species: *bilimbi L.*

Figure 1: Snapshot showing the fruits of *A. bilimbi*.

Averrhoa bilimbi Linn. (Figure 1) *(Oxalidaceae,* Common name: *Bilimbi)* is a common plant in Asia growing up to 15 m tall and 30 cm in diameter [16]. Fruits are fairly cylindrical with five broad rounded longitudinal lobes and produced in clusters. During maturity stage the weight and size of the fruit increase to the maximum, and their external green colour changes into light yellow [17]. Bilimbi fruits are very sour and used in the production of vinegar, wine, and pickles and preparation of traditional dishes. The mature fruits can be eaten as such or processed into jams and jellies. The chemical constituents of *A. bilimbi* have been identified to include oxalic acid and vitamin C [16, 18]. It is widely used in traditional medicine as cure for cough, mumps, rheumatism, and pimples scurvy and also as an antioxidant [16, 19–21].

In the present work, a simple, low cost, and green method for the synthesis of gold and silver nanoparticles using the fruit extract of *A. bilimbi* was investigated. Synthesized nanoparticles were characterized by various methods, such as UV/Vis, FTIR, and SEM-EDX,

2. Materials and Methods

2.1. Materials. All chemical reagents including chloroauric acid ($HAuCl_4$) (LOBA Chemie Pvt, Ltd., Mumbai) and silver nitrate ($AgNO_3$) (Sd fine-chem Ltd., Mumbai) were obtained and used as received. All the chemicals used were of the highest purity available. Ultrapure water was used for all the experiments (Milli–Q System; Millipore Corp.). The *A. bilimbi* fruits used in these experiments were fresh and collected from a household garden and identified.

2.2. Extract Preparation. Fresh *A. bilimbi* fruits were cleaned, sliced (100 g), ground in an agate mortar, filtered through a mesh, and then centrifuged to remove any cell debris. The pH of the extract was found to be approximately 2.3. The extract was used as obtained in all the experiments unless otherwise stated.

2.3. Nanoparticle Synthesis. Aqueous solution (1 mM) of $AgNO_3$ and $HAuCl_4$ was prepared, and 5 mL of these solutions were reduced using 0.1 mL of *A. bilimbi* extract (ABE) at room temperature. The effects of various parameters such as the amount of extract (0.1 mL, 0.2 mL, 0.3 mL, 0.4 mL, and 0.5 mL), metal ion concentration (1 mM, 2 mM, and 3 mM), and reaction time were studied.

2.4. Characterization. The UV/Vis spectra of samples were analyzed using Systronics (India) double beam spectrophotometer (Model no. M2202) operated at a resolution of 2 nm with quartz cells with path length of 10 mm. Blanks were prepared with distilled and deionized (DI) water using a Milli-Q water purification system (Millipore Corp.).

The ATR-FTIR measurements were performed on a Bruker Eco Alpha-T FTIR spectrometer (Bruker, Karlsruhe, Germany) equipped with a mid-infrared (MIR) source (SiC) and a thermal detector, such as deuterated, L-alanine doped triglycine sulfate (DLaTGS) premium performance Pyroelectric detector. Spectra were collected at room temperature under atmospheric pressure, at an average of 64 scans with a resolution of 4 cm^{-1} resolution in ATR mode from 400 to 5000 cm^{-1}. In all experiments, background spectra were measured. FTIR spectroscopy measurements were carried out to recognize the biogroups that are attached on the surface of gold and silver nanoparticles from the ABE used for the synthesis. FTIR samples were prepared by drying ABE and ABE with nanoparticles at 60°C. The dried samples were subjected to FTIR measurement.

Scanning electron microscope (SEM) used was a Vega line (TESCAN) of scanning electron microscopes (TESCAN, VEGA3 SBU-EasyProbe compact SEM) from Czech Republic. The Vega column consists of a high brightness tungsten electron gun, an electromagnetic beam centering system below the anode, a doublet condenser lens system with a spray aperture, an intermediate lens with its own electromagnetic centering system, and a low-aberration conical objective lens with integrated scanning and stigmator coils. Vega SEM is fully integrated with a selected energy dispersive X-ray

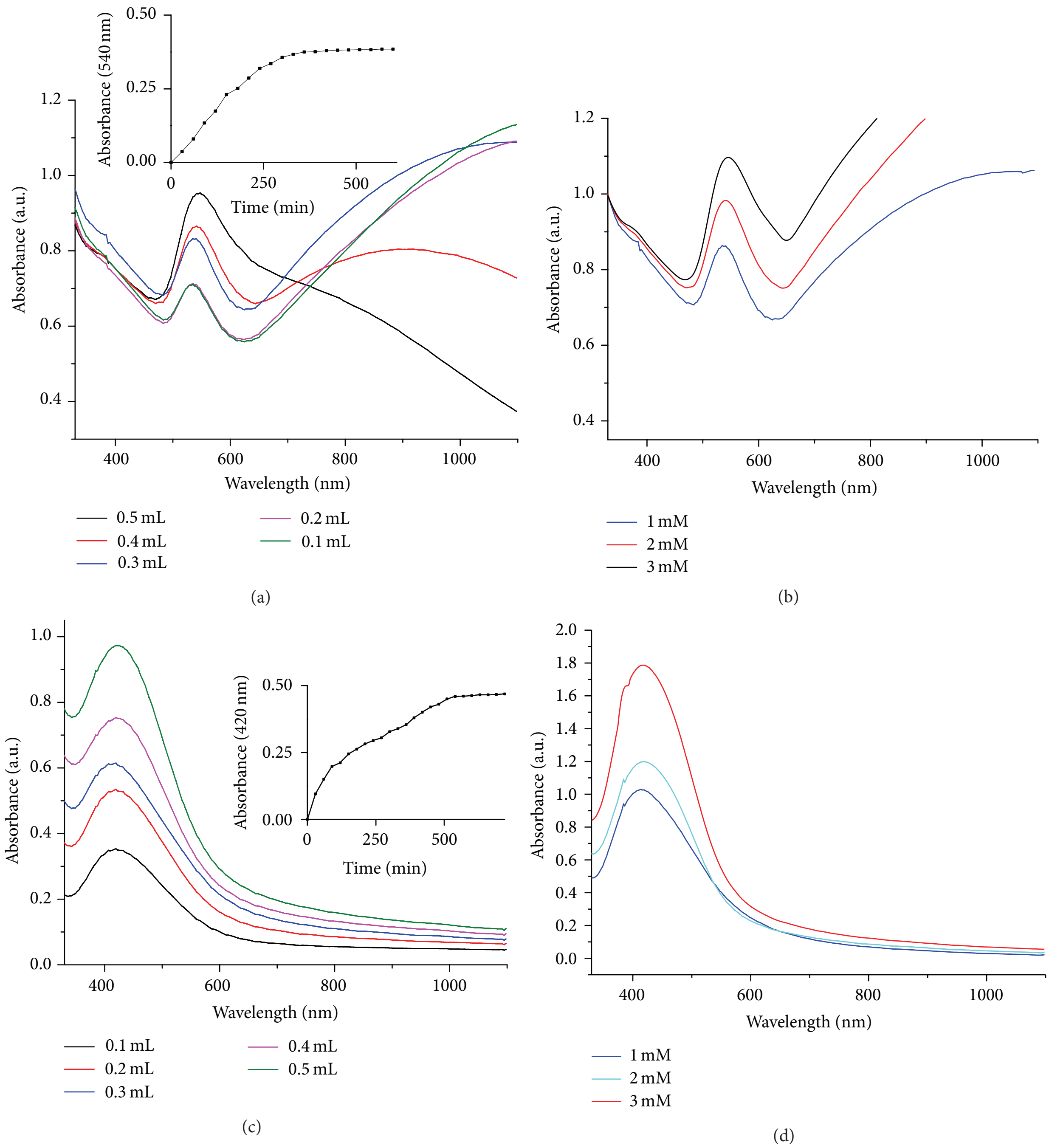

Figure 2: Effect of ABE extract with 1 mM metal salt concentration. (a) In synthesis of gold nanoparticles. (c) In synthesis of silver nanoparticles. Effect of metal ion concentration. (b) In synthesis of gold nanoparticles. (d) In synthesis of silver nanoparticles. Inset of (a) and (c), respectively, shows the change in SPR intensity over time for gold and silver nanoparticles synthesis.

microanalyser (EDX) for automatic quantitative elemental analysis and EasySEM software interface with One-Touch EDX toolbox. QUANTAX (Bruker AXS) energy dispersive X-ray micro- and nanoanalysis was integrated with TESCAN SEM to record the morphology (operated at 10 kV) and chemical composition of samples using QUANTAX EDX.

3. Results and Discussion

This work is focused on the synthesis of gold and silver nanoparticles using an environmentally friendly biosynthetic method. Both silver and gold nanoparticles were synthesized using ABE extract at room temperature. Due to the reaction of the metal salt and ABE, colour of the solutions changed to yellow and violet, indicating the formation of silver and gold nanoparticles, respectively [15, 22]. Experiment was carried out with varying ABE and salt concentrations. The SPR of gold and silver nanoparticles remained close to 540 nm and 420 nm (Figure 2); this shows the formation of gold and silver nanoparticles. The SPR wavelength of Au and Ag nanoparticles synthesized under different conditions varies with their size and shape. According to Mie theory, spherical nanoparticle of gold and silver will exhibit a single SPR band, whereas anisotropic particles will show 2 to 3 SPR bands [23]. The SPR band of Au nanoparticle shows an absorption peak at 540 nm resulting in out-of-plane quadrupole resonance. The absorption band in the region of 620–1100 is a result if in-plane dipole resonance [23, 24]. With increasing the ABE quantity from 0.1 to 0.5 mL in 5 mL of 1 mM metal ion solution, there is an increase in the UV/Vis absorbance spectrum for both Au and Ag nanoparticles (Figures 2(a) and 2(c)); this indicates a fast reaction as the ABE concentration is increased [25]. From the UV/vis absorption spectrum (Figures 2(a) and 2(c)), it was absorbed that there is a shift in wavelength from 534 to 545 nm for gold nanoparticles and from 418 to 422 nm for silver nanoparticles indicating a redshift with increase in ABE concentration. Accordingly, it can be concluded that with increase in ABE the size of Au and Ag nanoparticles increases [26]. The same phenomenon is observed with increase in metal ion concentration (Figures 2(b) and 2(d)). In the experiment carried out with varying metal ion concentration, the absorbance increased with increase in metal ion concentration (Figures 2(b) and 2(d)). The rate of formation of silver and gold nanoparticles was found to be slow at lowest concentration, and hence absorbance is also less. The inset (Figures 2(a) and 2(c)) shows the rate of gold and silver nanoparticles formation; the reaction is complete within 5 hrs for gold and 8 hrs for silver nanoparticles, and after that the absorbance is constant showing the completion of the reaction.

The mechanism for the reduction of Ag or Au ions to silver or gold could be due to the presence of water-soluble antioxidative substances like ascorbic acid which is present in the fruits of *A. Bilimbi*. Ascorbic acid is a reducing agent and can reduce, and thereby neutralize, reactive oxygen species leading to the formation of ascorbate radical and an electron. This free electron reduces the Ag^+ or Au^+ ions to Ag^0 or Au^0. The mechanism is shown in Figure 3.

The IR spectra (Figure 4) were recorded before and after adding the ABE extract solution. The FTIR bands are indexed in the figure. The FTIR spectra of the extract showed strong bands at 3353, 1633, and 1225 cm^{-1} assigned to O–H stretching vibration of alcohols and phenols [27], C=O stretching vibration of tertiary amines [28], and C–O stretching of aromatic ethers [29]. The IR spectra of gold nanoparticles showed bands at 3270, 1651, and 1023 cm^{-1} corresponding to O–H stretching vibration of alcohols and phenols, C=O stretching vibration of tertiary amides, and C–OH stretching of primary alcohols, the silver showed bands at 3285, 1633, and 1025 cm^{-1} assigned to O–H stretching vibration of alcohols and phenols, C=O stretching vibration of Tertiary amides, and C–OH stretching of primary alcohols. The amines and alcohols present in the sample along with ascorbic acid may

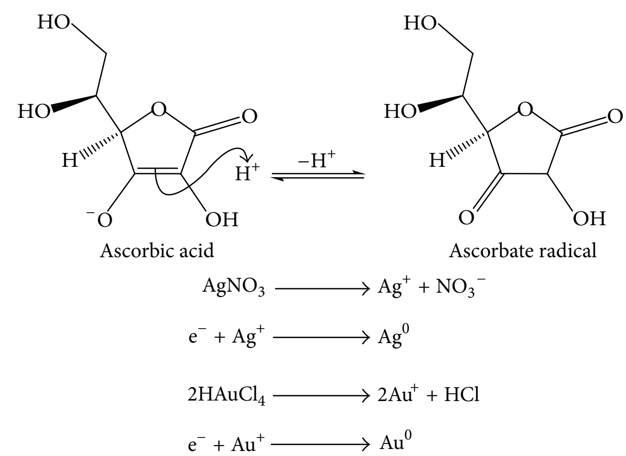

FIGURE 3: Ascorbic acid reduction of gold and silver ions to Au^0 and Ag^0 nanoparticles.

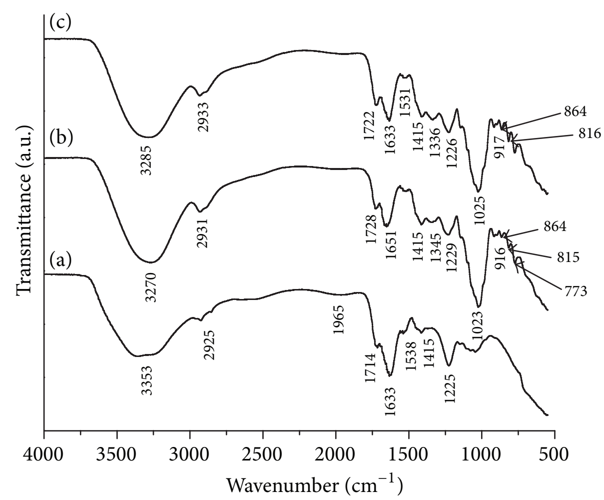

FIGURE 4: (a) FTIR spectra of ABE. (b) FTIR spectra of gold nanoparticles after synthesis. (c) FTIR spectra of silver nanoparticles after synthesis.

be responsible for the reduction and capping of gold and silver nanoparticles [30].

SEM image (Figures 5(a) and 5(b)) of biosynthesized gold (0.1 mL ABE and 1 mM salt concentration) and silver nanoparticles (0.1 mL ABE and 1 mM salt concentration) showed the presence of hexagonal or rhomboidal nanoparticles. The sizes of the silver nanoparticles were in the range of 50 to 175 nm. The sizes of gold nanoparticles were 75 to 150 nm. EDX spectrum (Figures 5(c) and 5(d)) shows peaks for gold and silver which reveals the presence of gold and silver nanoparticles along with aluminum (Al) as impurities coming from the sample substrate.

4. Conclusion

Here, we have demonstrated a low-cost and one-pot green synthesis approach for preparation of stable gold and silver

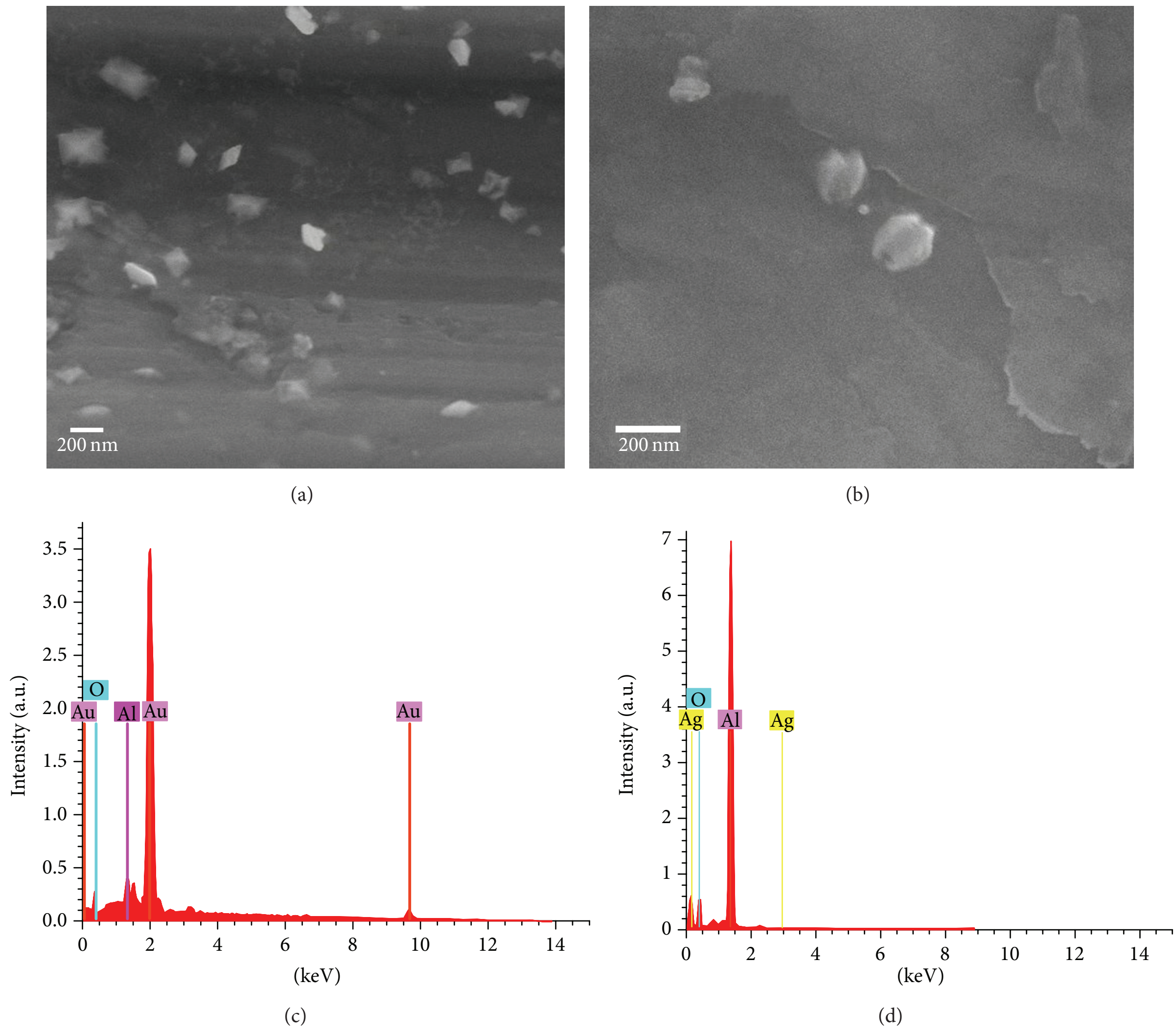

Figure 5: (a) SEM micrographs of gold nanoparticles. (b) SEM micrographs of silver nanoparticles. (c) EDX spectrum of gold nanoparticles. (d) EDX spectrum of silver nanoparticles.

nanoparticles. Gold and silver nanoparticles were synthesized by a rapid, eco-friendly (biogenic, green route) process using *Averrhoa bilimbi Linn.* fruit extract as a reducing agent. The alcohols, amines, and phenols present in the fruit extract might have caused the reduction and capping of the nanoparticles. The characteristics of the obtained gold and silver nanoparticles were studied using UV-Vis absorption spectroscopy (UV/Vis), Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), and Energy-dispersive spectroscopy (EDX). The EDX spectrum of the solution containing gold and silver nanoparticles confirmed the presence of elemental gold and silver signals along with aluminum (Al) as impurities coming from the sample substrate. The average diameter of the prepared nanoparticles in solution was about 50–150 nm.

The present method eludes the use of toxic chemicals for the synthesis of gold and silver nanoparticles so it can be used for biological applications. Synthesized particles were either hexagonal or rhomboidal in shape. This synthesis approach of gold and silver nanoparticles is cost effective and can be widely used in biological systems. Nanoparticles of free metals have been extensively researched because of their unique physical properties, chemical reactivity and potential applications in catalysis, biological labeling, biosensing, drug delivery, antibacterial and antiviral activity, detection of genetic disorders, gene therapy, and DNA sequencing.

Conflict of Interests

The authors do not have any conflict of interests with the content of the paper.

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