Research Article

Antioxidant and Catalytic Activity of Green Synthesized Gold Nanoparticles Using Gooseberry (*Emblica Officinalis*) Fruit Extract

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Abstract

The Green synthesis of gold nanoparticles (AuNPs) has become a promising field of research in present days. The present report is on the unexploited ecologically benign rapid synthesis of AuNPs (10±2 nm) using the gooseberry fruit extract. Studies on catalytic and anti-oxidant activities have been carried out. The synthesized AuNPs were characterized by various techniques. The formation of AuNPs was confirmed by surface plasmon resonance peaks using UV-Vis spectrophotometer and XRD studies indicated that the synthesized AuNPs were crystalline with face centered cubic geometry. The catalytic activity of the synthesized AuNPs was tested using the reduction of methylene blue in the presence of $NaBH_4$. The antioxidant activity was studied by radical scavenging (DPPH) assay.

Keywords: Gold nanoparticles, gooseberry fruit extract, antioxidant, methylene blue

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Introduction

Nanoscience and nanotechnology is an interdisciplinary field that uses principles of chemistry, biology, physics, and engineering to design and fabricate nanoscale materials [1-3]. It is already having a significant commercial impact, which will surely increase in the very near future. Metallic nanoparticles are definitely among the most widely studied systems in modern nanoscience due to the fact that metals often have totally different properties when bringing down to nanometer dimensions [4].

Metal nanoparticles are of most importance to research due to their extremely small size and large surface-to-volume ratio, metal nanoparticles are interesting for many applications such as antimicrobial activity, chemical sensors, catalysis, drug delivery systems, filters, and medical radiographic images. Among the metal nanoparticles, AuNPs shows distinguished surface plasmon resonance (SPR) absorption properties which are strongly related to their size, shape and inter particle distance. AuNPs have been exploited for various applications such as anti-bacterial activity, catalysis, photonics, drug delivery and sensors [5-7].

A large number of ways to synthesize AuNPs are reported and amongst them, the most common is the reduction of gold ions with reducing agents such as sodium borohydride, hydrazine, N, N-dimethyl formamide, citrate, or other organic compounds. However, using such reducing agents may associate with environmental toxicity or pose biological risks [8, 9].

To overcome such tedious techniques and replacement of non-ecofriendly synthesis, methods with non-toxic, clean and green chemistry methods is the current need in the synthesis of AuNPs. Several plants based biomolecules and biological systems such as fungi, bacteria and plant extracts can actively reduce metal ions to form metal nanoparticles in a green chemistry manner [10-12]. These biomolecules act as reducing and stabilizing agents in large scale commercial synthesis of AuNPs.

In this study, we focused on the synthesis of AuNPs using Indian gooseberry (*Emblica officinalis*) fruit extract. Gooseberry contains nutritional properties and extensively used as Ayurvedic medicine for treating diseases such as hepatitis, malaria, cancer and asthma dermatitis. This fruit contains a wide spectrum of components, including carbohydrates, alkaloids, benzenoids, flavonoids, steroids, coumarins and furanolactones [13, 14].

The present research studies gooseberry fruit extract is useful to produce AuNPs. The synthesized AuNPs were characterized by UV-Vis spectroscopy, FTIR spectroscopy, XRD and TEM. The synthesized nanoparticles were used as a catalyst for the reduction of methylene blue dye and antioxidant activity.

Experimental

Materials

$HAuCl_4.3H_2O$ was purchased from Sigma Aldrich, India and other chemicals were purchased from E. Merck (India). The glassware used in the current study was washed with aqua regia thoroughly and then rinsed with double distilled water.

Preparation of fruit extract solution

Fresh fruits of Gooseberry were collected in Palamuru university precincts, Mahabub Nagar. The fruit was washed thoroughly with double distilled water to remove the adhered dust particles present on the surface. Then the fruits (6g) were crushed and heated (64-70 ^oC) in 60mL of double distilled for 50 min and after cooling down to room temperature, the extract was filtered using filter papers.

Synthesis of gold nanoparticles

For the green synthesis of AuNPs, 4 mL of fruit extract was mixed with 3 mL of $HAuCl_4$. H_2O (1 mM) and the mixture was kept in an autoclave at 120^oC and 15 psi pressure for 15 min. The resulting solution was of blushing red colour, indicating the formation of AuNPs.

Characterization techniques

The resulting fruit extract capped AuNPs were analyzed by UV-Vis spectrophotometer (UV–Vis 3600 Shimadzu, Japan). FTIR spectra were recorded using IRAffinity-1, Shimadzu. XRD analysis carried out on a Rigaku-Miniflex method with Cu-Kα radiation. TEM images were recorded using 1200EX, JEOL Ltd., Japan.

Catalytic reduction of methylene dye

The catalytic reduction of methylene blue using sodium borohydride in the presence of AuNPs was carried out by using UV-Vis spectrophotometer. 1.6 mL of 1 mM methylene blue solution was mixed with 1 mL of 10 mM $NaBH_4$ and this mixture was made up to 8 mL using double distilled water, and stirred this mixture for 10 min. sufficient amount of synthesized AuNPs were added and UV-Vis spectra were recorded at regular intervals of time.

Antioxidant activity

The antioxidant activity of the green synthesized AuNPs was evaluated using the DPPH assay, this assay was done by following a previously described method with some modification [15]. Different volumes (6µL, 12µL, 18µL, 24µL, 30µL, and 36 µL) of AuNPs are made up to 60 µL with dimethyl sulfoxide and 2.56 mL DPPH (0.17 mM) solution is added. The mixture was shaken vigorously and kept in the dark for 40 min at room temperature. The absorbance measurements are read at 517 nm against a blank of DPPH and ascorbic acid used as a reference. The free radical scavenging activity was calculated using the following equation.

$$\text{DPPH scavenging effect (\%)} = [(A_0-A_t)/ A_0] \text{ X } 100$$

A_0 is the absorbance of the control and A_t is the absorbance of the sample

Studies on antioxidant, antibacterial and anticancer activities of the nanoparticles have been carried out.

Results and Discussion

AuNPs characterization

The formation of AuNPs was easily detected and characterized by UV-Vis spectroscopy owing to the SPR. The AuNPs were absorbed SPR strongly in the range of 520-530 nm in the visible region. The effect of fruit extract concentration (0.1-0.8%) on the formation of AuNPs was analyzed by UV-Vis spectroscopic studies and is given in **Figure 1a**. From the Figure1a, it is observed that the formation of AuNPs depends on the concentration of fruit extract and with the increase in extract concentration there is an enhancement in the formation of AuNPs. Figure 1b shows the effect of concentration of $HAuCl_4$ on the formation of AuNPs. From the Figure1b, it can be observed that the absorbance of AuNPs increased with increase of $HAuCl_4$ concentration [16].

FTIR spectra were recorded to identify the biomolecules that capped on AuNPs. The FTIR spectrum of fruit extract and synthesized AuNPs were shown in **Figure 2a**. Figure 2a curve (a) and curve (b) indicate the FTIR spectra of fruit extract and AuNPs respectively. The major peaks of fruit extract are observed at 3433, 1743, 1637, 1395, 1249 and 1030 cm^{-1} whereas the peaks of synthesized AuNPs are observed at 3376, 1751, 1593, 1402, 1217 and 1030 cm^{-1}. A shift in the peaks of the FTIR spectrum of synthesized AuNPs was observed from 3433 to 3376 cm^{-1}, 1743 to 1751 cm^{-1} and 1637 to 1593 cm^{-1}. Therefore, we believe that the presence of alcohols, carbonyl and amine groups present in the fruit extract might be a plausible reason for the reduction and stabilization of AuNPs.

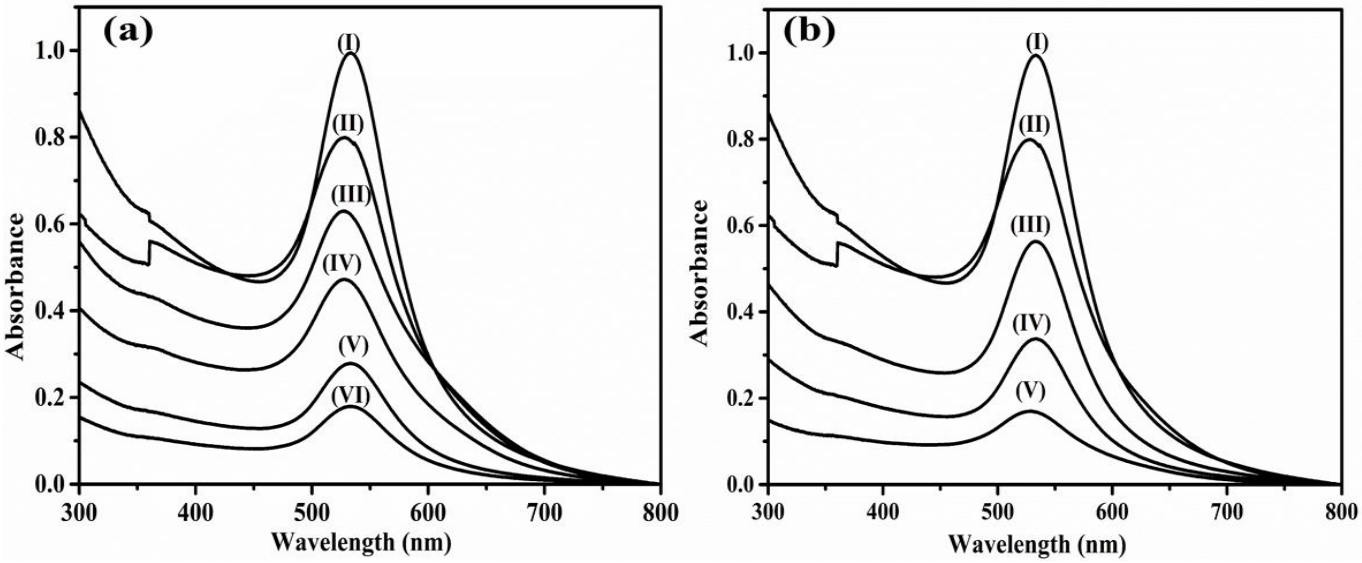

Figure 1 Absorption spectra of AuNPs systems synthesized (a) different fruit extract concentrations (I-0.8%, II-0.6%, III: 0.4%, IV-0.3%, V-0.2%, VI-0.1%) (b) Different concentrations of $HAuCl_4$ (I-2mM, II-1.5 mM, III: 1 mM, IV-0.5 mM, V-0.2 mM, VI-0.1 mM).

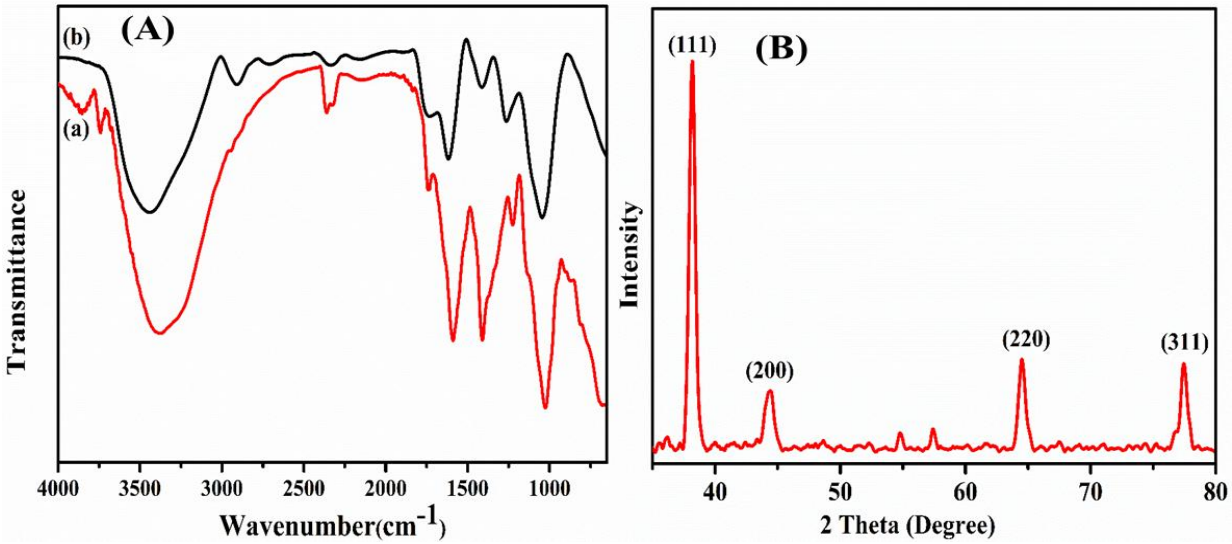

Figure 2 (A) FTIR spectra of the fruit extract (a) and fruit extract capped AuNPs (b), and (B) XRD pattern of synthesized AuNPs.

The XRD pattern of the synthesized AuNPs is shown in Figure 2b. The XRD peaks were observed at 2θ values of 38.15, 44.50, 64.51 and 77.42 could be attributed to the (111), (200), (220) and (311) respectively; these crystalline planes indicate the face centered cubic crystalline structure of AuNPs. The crystalline size of the AuNPs was calculated using Scherer's formula from the XRD graph and was found to be 8.5 nm.

The size and shape of synthesized AuNPs were analyzed by TEM. The TEM images (Figure 3a) revealed that AuNPs are predominantly spherical shapes. The average particle size was found to be 10 ±2 nm and the particle size distribution histogram (Figure 3b) was constructed.

Catalytic reduction of methylene blue

The catalytic activity of synthesized AuNPs was evaluated by using reduction of methylene blue to leuco methylene blue in the presence of $NaBH_4$. The reduction reaction was monitored by UV-Vis spectrophotometer at room temperature. In aqueous medium methylene blue shows an absorption bands at 664 nm with a shoulder peak at 614 nm [17, 18]. Figure 4a shows the methylene blue and $NaBH_4$ in the absence of catalyst for a time period of 60 min and it was observed that a small decreasing trend of the absorption maximum indicates the reduction of methylene blue, but in a slow process. Figure 4b shows UV-Vis spectrum of the reduction of methylene blue by $NaBH_4$ in the presence of AuNPs and it was observed that the absorption peak at 664 nm of methylene blue was found to decrease gradually with the increase in the reaction time. The rate constant (k) was calculated from the linear plot of ln (A_0/A_t) versus time (Figure 4c) in minutes. The reduction reaction follows a pseudo first order kinetics with respect to methylene blue. The reaction rate constant was calculated and was found to be 0.291 min^{-1}.

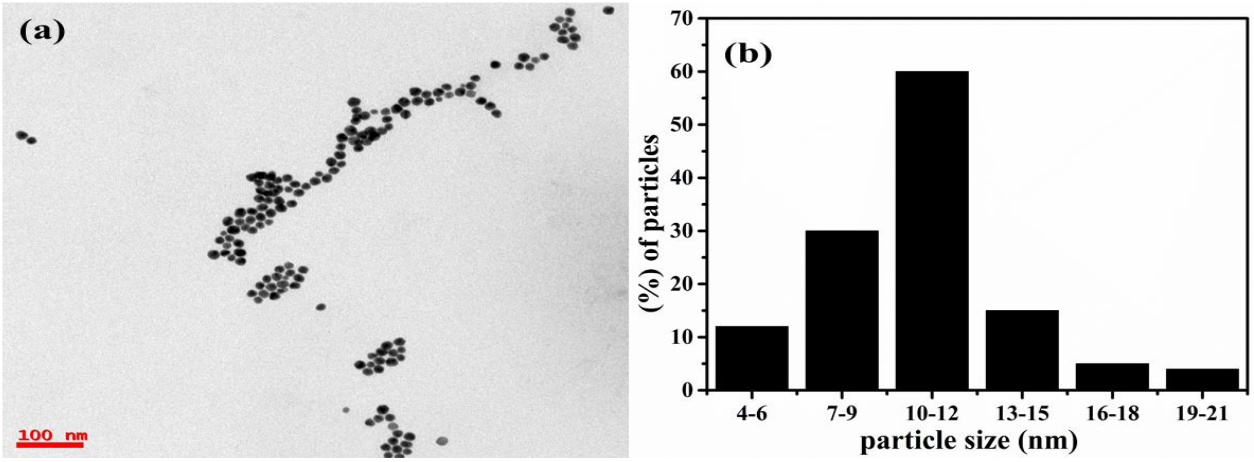

Figure 3 (a) TEM images of synthesized AuNPs and (b) The particle size distribution histogram of AuNPs

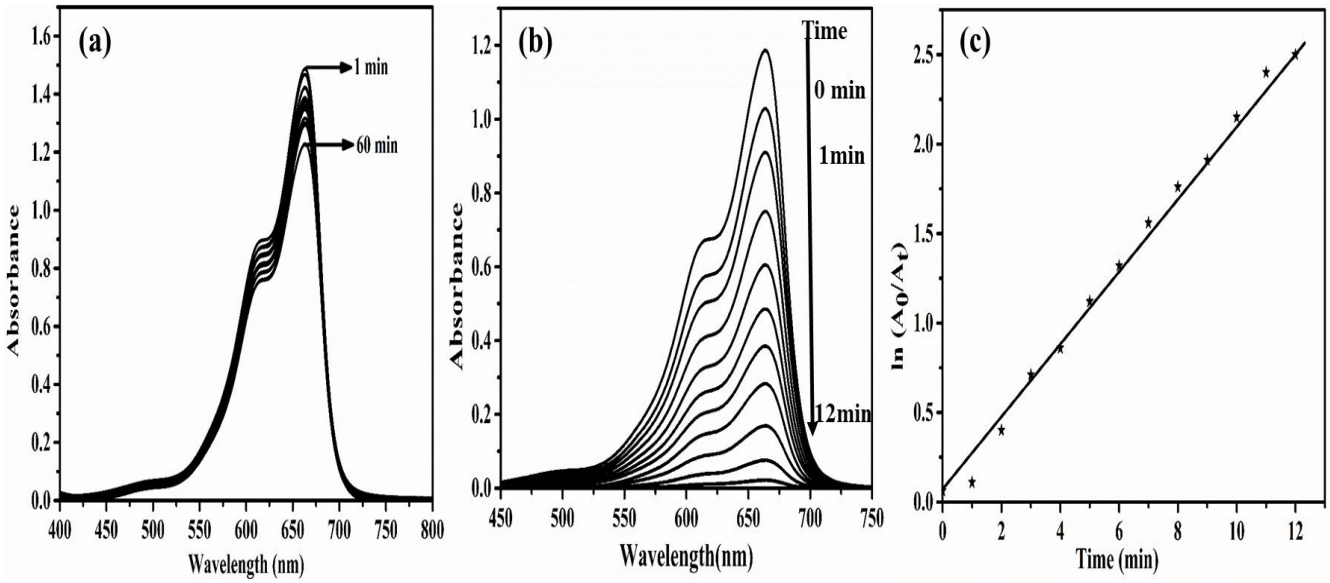

Figure 4 Reduction of methylene blue dye in the presence of $NaBH_4$ and absence of AuNPs (b) Time-dependent UV–Vis spectra for the catalytic reduction of methylene blue to leuco methylene blue by $NaBH_4$ in the presence of AuNPs (c) The plot of ln(A_0/A_t) versus time for the reduction of methylene blue

Anti-oxidation studies

The synthesized AuNPs antioxidant activity was evaluated using DPPH assay using ascorbic acid as reference. The antioxidant activity of synthesized AuNPs was assessed in terms of percentage inhibition of DPPH radicals. The DPPH is considered more stable nitrogen centered free radical due to exhibiting a higher degree of accepting hydrogen atoms or electrons from antioxidant materials. The change in color of the DPPH solution was observed with the addition of AuNPs, which is due to the scavenging action of DPPH by addition of hydrogen to form the yellow colored DPPH solution. Figure 5 shows the inhibition activity of AuNPs in comparison to the ascorbic acid (standard) and it is observed that the DPPH radical inhibition activity was increased with the concentration of AuNPs. Scavenging rate of AuNPs 23.2, 45.6, 59.1, 56.3, 63.1and 65.25 % at 6µL, 12µL, 18µL, 24µL, 30µL, and 36 µL respectively. When compared to ascorbic acid, the AuNPs shows enhanced antioxidant activity [15].

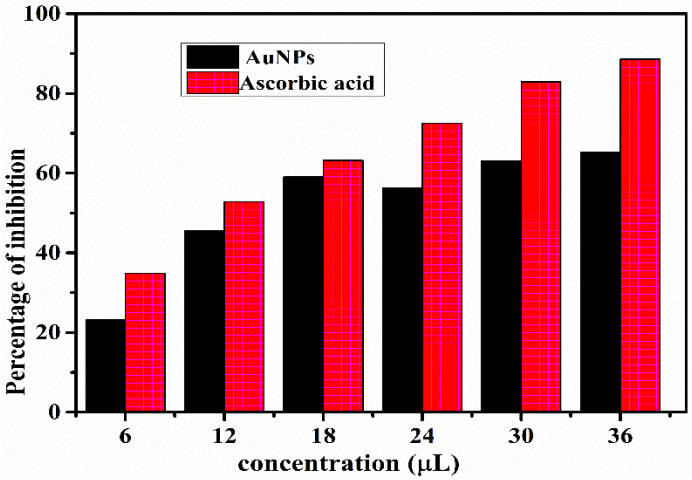

Figure 5 Antioxidant property of AuNPs

Conclusion

The present investigation reports the facile synthesis of AuNPs using gooseberry fruit extract. The gooseberry fruit extract acted as both reducing and stabilizing agent in the formation of AuNPs. The size and shape of the AuNPs were found to be mostly spherical and average particle size is 10±2 nm. The crystalline nature of the AuNPs was confirmed by XRD analysis. The AuNPs exhibit good catalytic activity for the reduction of methylene blue in aqueous phase. The prepared AuNPs have excellent antioxidant property.

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Publication History
Received 04th Jan 2018
Revised 25th Jan 2018
Accepted 05th Feb 2018
Online 28th Feb 2018