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Green Synthesis of Gold Nanoparticles using *Crinum asiaticum* Leaf Extract and their Application in Size Dependent Catalytic Activity

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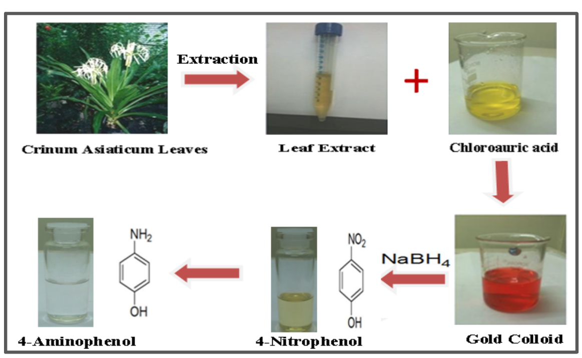
ABSTRACT

Use of non-toxic reagent, environmentally benign solvents and renewable materials are the key points of green methods. The present work explores green synthesis of gold nanoparticles (AuNPs) using crinum asiaticum aqueous leaf extract. In AuNPs synthesis Crinum asiaticum aqueous leaf extract is applied as a reducing as well as stabilizing agent. In the presence of sodium borohydride, synthesized gold nanoparticles exhibited size-dependent catalytic activity for reduction of 4-nitrophenol to 4-aminophenol. The effect of particle size on catalytic reduction of 4-nitrophenol was studied using UV-Visible spectrophotometers. The average particle size of AuNPs was found to be ~13 nm calculated using Scherrer equation. The formation of AuNPs was confirmed by various techniques as follows UV-Visible spectroscopy, X-ray diffraction, energy dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM).

Graphical Abstract



Process for the Synthesis of gold nanoparticles

Keywords: Gold nanoparticles, Crinum asiaticum, Green synthesis, Catalysis.

INTRODUCTION

There are various techniques available to synthesize nanoparticles in the form of clusters, powders, tubes, rods, and wires. Largely Chemical techniques are used to synthesize nanoparticles. But due to the hazards associated with chemical methods scientists around the world developed alternative methods. Green approach is a strategy, where utilization of biological material replaces the use of chemical reagents. Use of non-toxic reagent, environmentally benign solvents and renewable materials are the key points of green methods. There are various reports on green synthesis of nanoparticles using microorganism [**1, 2**], plant extract [**3**] and fungi [**4**], such work shows non-toxicity and friendliness with the environment and human health. Nanoparticles produced by plants are more stable and can be obtained in various shapes and sizes. Kemin wang *et al*., reported biosynthesis of gold nanoparticles using barbated skull cup herb extract and Daizy Philip *et al.*, reported green synthesis of gold nanoparticles using Trigonellafoenum-graecum extract. Literature survey reported that biosynthesis of gold nanoparticles using olive [**5**], tulsi [**6**], Mushroom [**7**], sugar beet [**8**], Honey [**9**] and citrus fruit [**10**] has been studied.

AuNPs have gained increasing interest due to their special features, such as unusual optical and electronic properties, high stability and biological compatibility, controllable morphology, size dispersion and easy surface functionalization [**11**]. AuNPs have shown potential applications in the field of chemistry, physics, biology, material, and medicine. AuNPs are the attractive member of the noble family because of their catalytic application [**12**], surface-enhanced Raman scattering [**13**] and drug delivery [**14**]. In this paper, we report a synthesis of gold nanoparticles using crinum asiaticum leaf extract as unreported efficient, economic and environmentally friendly reducing agent. As prepared gold nanoparticles show size-dependent catalytic activity for reduction of 4-nitrophenol to 4-aminophenol.

Crinum asiaticum can be found in China, Hong Kong, and Jeju-do in South Korea, India, Ryukyu Islands, Main land Japan and in Sri Lanka. This herb is cultivated in Indian gardens. It is used for the treatment of pain, swelling carbuncle, piles, earache, arthritis, skin disease (leprosy), cold and cough disorders, vomiting, worms infestation, disuria, polyuria, bowel complains, throat disorder, colic, dyiscrasia, flautulance, fever etc [**15-17**]. Crinum asiaticum is used traditionally for various purposes: (a) Action: Leaves and root are emetics, diaphoretic and purgative. (b) Uses: The paste of the tuber is tied over the wound for early recovery. Leaves of the herb smeared with castor oil and warmed is a useful remedy for inflammations at the end of toes and fingers. Alternatively, we can use bruised leaves of the herb mixed with castor oil for this purpose. The herb is also used to treat inflamed joints and sprains. For an earache and other ear complaints, use the slightly warmed juice of the leaves mixed with a little salt [**18**]. The bulbs are powerfully emetic and are used to produce vomiting in poisoning. Bruised leaves act as an effective insect repellent [**19-21**].

MATERIALS AND METHODS

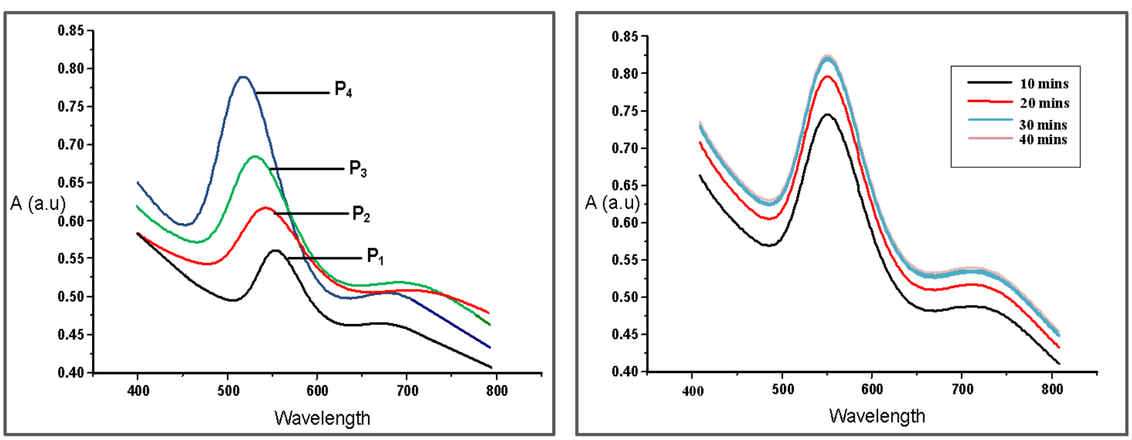
Materials: All chemicals were of A. R. grade and were used as received without any further purification. Chloroauric acid ($HAuCl_4$) was purchased from Sigma Aldrich,4-nitrophenol was provided by Loba Chemie, sodium borohydride ($NaBH_4$) was purchased from Merk India Ltd. All solutions were prepared using double distilled water. All experiments were performed at room temperature.

Preparation of gold nanoparticles: Plant leaves were collected from local area Mumbai, India. They have been thoroughly washed with distilled water, ethanol and sun-dried. 20 gm of the leaf was boiled in 100 mL of water for 10 min and filtered to get the extract. Chloroauric acid ($HAuCl_4$) is used as a source of Au3+. Gold nanoparticles prepared by adding 5 mL (P1), 10 mL (P2), 15 mL (P3) and 20 mL (P4) aqueous extract to the fixed volume (100 mL) of a 1mM chloroauric acid solution at room temperature. The mixture was stirred using magnetic stirrer at 150 rpm for 30 min. Formation of gold nanoparticles was confirmed by using various techniques.

Characterization of gold nanoparticles: The UV–Visible spectroscopy was carried out on a Shimadzu UV-2450 spectrophotometer with samples in a quartz cuvette operated from 200 to 800 nm. XRD analysis was carried out on an X-ray diffractometer (Shimadzu 7000S, Shimadzu Analytical, Japan) equipped with Cu Kα radiation (λ=0.154 nm). The FT-IR instrument used for characterization was from Perkin Elmer spectrum version 10.03.07. The spectra were collected in the wave number range between 400 and 4000 cm^{-1}. The scanning electron microscope employed for surface characterization was an FEI Quanta-200 model with an operating voltage of 20 kV. Energy dispersive x-ray spectroscopy (EDX) was carried out on FEI Quanta-200 model.

RESULTS AND DISCUSSION

UV-Visible spectroscopy: The addition of Crinum asiaticum leaf extract to 1mM HAuCl4 aqueous solution resulted in a color change from yellow to wine red due to the formation of gold nanoparticles. Colloidal solutions of gold show a very intense color due to surface plasmon resonance phenomenon [22]. Their origin is attributed to the collective oscillation of free conduction electrons induced by an interacting electromagnetic fields [23]. Figure 1(a) shows the formation of gold nanoparticles at fix concentration of 1 mM chloroauric acid and varying concentration of crinum asiaticum extracts 5 mL (P1), 10 mL (P2), 15 mL (P3) and 20 mL (P4). The color change was observed from pink to wine red to blue with varying concentration of crinum asiaticum extract due to different sizes of the gold nanoparticles. Gold colloids P1-P4 show SPR bands at 555 nm, 543nm, 536 nm and 528 nm respectively. From the spectra, it can be inferred that as a quantity of extract is increase the SPR band shifts towards lower wavelength due to the decrease in particle size of the nanoparticles. Figure 1(b) shows spectra recorded at the different time interval and it can be seen from the figure 1(b) that as time passes the SPR band becomes more intense indicating the formation of gold nanoparticles. After 30 mins there is not much difference in SPR band which shows that all Au^{3+} are reduced to Au.



(a) **(b)**

Figure 1. (a) UV-Visible Spectra of gold colloid by varying concentration of gold colloid, **(b).** UV–Vis spectra of AuNPs synthesized by reacting 1mM $HAuCl_4$ aqueous solution with crinum asiaticum leaf extract at different time intervals.

X-ray diffraction: Crystal structure of gold nanoparticles can be confirmed by measuring the XRD spectrum. Figure 2 shows the XRD pattern observed for P4 gold colloid. AuNPs give five peaks at 38.1º, 43.80º, 64.50º, 77.50º and 81.66º which correspond to (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes. The (1 1 1) plane is more intense than other planes, suggesting that (1 1 1) is in predominant orientation. XRD pattern further shows that gold nanoparticles are crystalline in nature and are face-centered cubic (fcc) in structure [24]. The average particle size of AuNPs was calculated using Scherrer equation [25]. There is no additional peak in XRD pattern, which indicates the high purity of AuNPs.

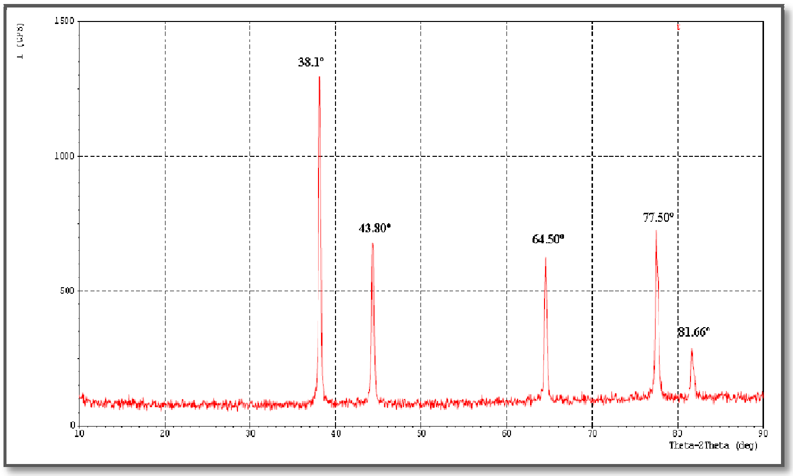
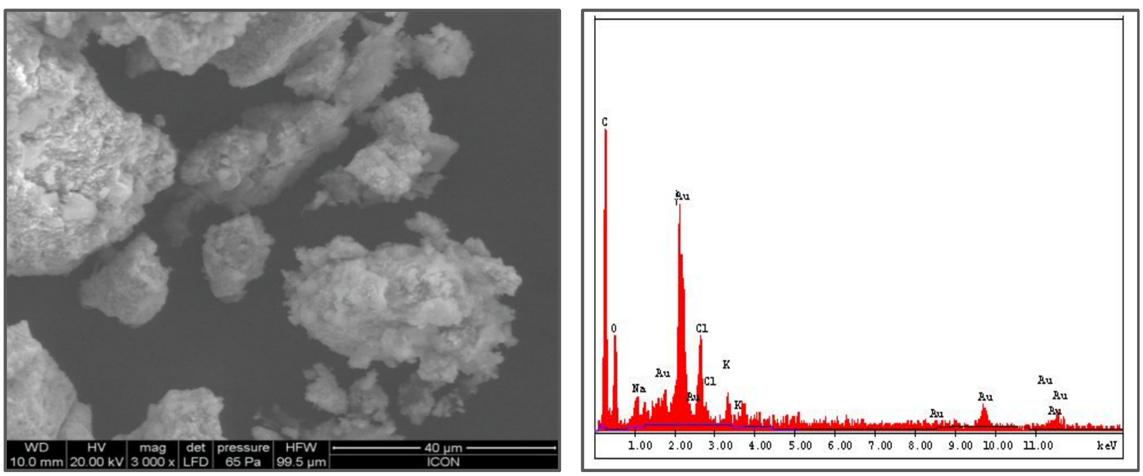


Figure 2. Representative XRD pattern of AuNPs.

Scanning electron microscopy and EDX analysis: Figure 3(a) shows the SEM image of gold colloid P4. SEM image shows the formation of clusters. Figure 3(b) is the Energy dispersive X-ray spectrum for P4 colloid which shows the strong Au peak along with weak peak Na, K, O, and C from the biomolecules present in the leaf extract. Probably these are the biomolecules responsible for the formation and high stability of gold nanoparticles.



(a) **(b)**

Figure 3. (**a**) SEM image of AuNP, (**b**). EDX spectrum of AuNPs

Catalytic activity of gold nanoparticles for reduction of 4-Nitrophenol: One of the main applications of gold nanoparticles is to catalyze reactions. To investigate catalytic activity of as-prepared gold nanoparticles, at first reduction of 4-nitrophenol with NaBH4 was carried out in the absence of AuNPs. The yellow color of the 4-nitrophenol became intense after addition of NaBH4 and red shift of the peak from 317 nm to 400 nm. This was due to conversion of 4-NP to 4-nitrophenolate ion. In the absence of AuNPs the absorption intensity remained at 400 nm even after several hours. After addition of gold nanoparticles reduction of 4-NP to 4-aminophenol started and color change was observed from yellow to colorless. In the present reaction (BH4-) acts as electron donor and 4-nitrophenolate ion as electron acceptor both are adsorbed on the surface of AuNPs. Gold nanoparticles provides surface for transfer of electron from BH4- to 4-nitrophenolate ion by lowering activation energy of the reaction. Thus AuNPs acts as efficient catalyst for reduction of 4-nitrophenol. UV-Visible spectra of gold colloid P4 are shown in the figure 4. The reduction is found to be complete in 6 min for P4 colloid as indicated by the disappearance of the yellow color. It is well known that size of nanoparticles play an important role in catalytic reduction. The effect of size on the rate of reaction was carried out and it was observed that as size of nanoparticles decrease directly proportional to the time of reduction. As shown in table1 time duration of different gold colloids p1-p4.

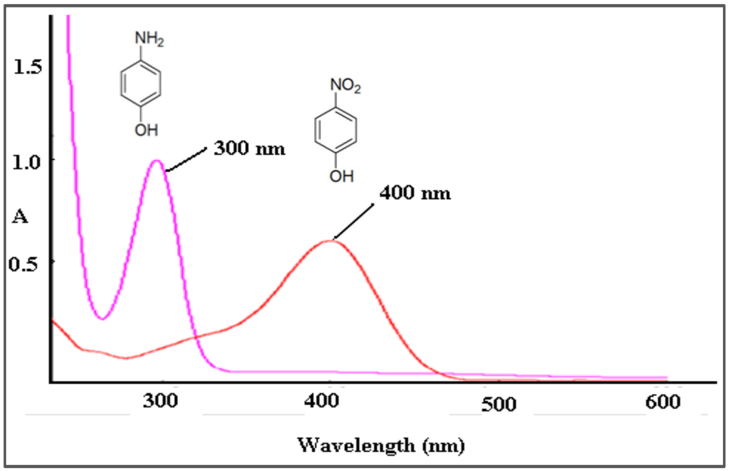


Figure 4. UV–Visible spectrum of the (—) mixture of 4-nitrophenol and $NaBH_4$, (—) mixture of 4-nitrophenoland $NaBH_4$, 7 min after the addition of gold colloid (P_4).

Table 1. Particle size obtained using Scherrer equation, λ_{max} and time taken for catalytic reduction of 4 nitrophenol

Colloid	Vol. of Extract (mL)	Particle Size (nm)	λ_{max} (nm)	Time require for Reduction of 4-NP (mins)
P_1	5.0	26.9	555	57.0
P_2	10.0	21.3	543	36.0
P_3	15.0	18.7	536	18.0
P_4	20.0	13.1	528	7.0

APPLICATION

As Prepared nanoparticles can be safely used for the various biomedical applications. The reducing agent and stabilizing agent used here is obtained from crinum asiaticum leaf extract. Hence, there might have the possibility of large-scale production of nanoparticles and their applications in industries. AuNPs can also be explored for its use as catalytic application in various organic transformations and drug delivery.

CONCLUSION

In the present work, we have successfully developed simple, non-toxic, efficient and economically favorable gold nanoparticles using crinum asiaticum leaf extract as a reducing and stabilizing agent. In the synthesis process, there is no use of toxic chemicals, organic solvent and all solutions prepared in double distilled water so the method is completely green and safe. The particles remain stable even after four months of reaction. A size of Gold nanoparticles varies with the quantity of extract; lower quantity of extract gives smaller size AuNPs. So, a quantity of extract and pH are two important factors for determining size distribution. Powder diffraction study showed the face center cubic structure of gold nanoparticles and the average size of nanoparticles was found to be 13 nm by using Scherrer method. As prepared AuNPs show good catalytic activity for reduction of 4-nitrophenol to 4-aminophenol. The size-dependent catalytic activity of gold nanoparticles was studied and it was found that as a size of the nanoparticles decrease the rate of reaction increase and shows the spontaneous reaction.

ACKNOWLEDGEMENT

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