Prayogik Rasayan

Ficus carica Linn (*Dumur*) Fruit Extract Mediated Green Synthesis of Gold Nanoparticles and its Application in Catalytic Reduction

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Abstract

The fruit extract of *Ficus carica Linn* (Dumur) is rich in different types of plant secondary metabolites such as terpenoids, polyphenols including flavanoids, etc. We have demonstrated the use of the fruit extract for the synthesis of gold nanoparticles in water at room temperature under very mild conditions. There was no need of additional stabilizing or capping agents and the synthesis of the gold nanoparticles was complete in several minutes. The gold nanoparticles were characterized by HRTEM, EDX, SAED, Surface Plasmon Resonance Spectroscopy and X-Ray diffraction studies. The freshly prepared gold nanoparticles have been used as an efficient catalyst for the sodium borohydride reduction of 4-nitrophenol to 4-aminophenol in water at room temperature and the kinetics of the reduction reaction have been studied spectrophotometrically.

Keywords: green synthesis; gold nanoparticles; catalytic reduction; *Ficus carica Linn* (Dumur)

1. Introduction

Gold, the commonly used ornamental metal in the bulk state, has become an area of intense research in the nano scale because of its unique optical, electronic and magnetic properties and also because of its applications in diversified areas of science and technology [1,2,3,4]. Biocompatibility of gold nanoparticles (AuNPs) in combination with its resistance to oxidation have made it useful for its biological applications especially in biodiagnostics,[5] drug delivery,[6] medicine and biotechnology.[7] In contrast to metallic gold that is inactive in the bulk state, the AuNPs with very large surface to volume ratio, show excellent catalytic properties in the nanoscale for different types of chemical transformations [8,9,10]. AuNPs exhibit unique color depending upon its size, shape, coordinating ligands, medium etc. due to Surface Plasmon Resonance (SPR), a phenomenon arising due to collective oscillation of conduction electrons upon optical excitation [11]. Various preparative methods for AuNPs broadly under the categories of 'top-down' (physical manipulation) and 'bottom-up' (chemical transformation) have been reported [12]. Among these synthetic methods, the plant extract based 'bottom-up' approach involving the solution phase reduction of Au(III) to Au(0) utilizing plant metabolites, has gained profound significance in recent years because such methods will lead to "green" and "sustainable" development [13]. The non-toxic and renewable nature of the plant extracts, eco-friendly aqueous medium and mild reaction conditions make the method advantageous over other hazardous methods. Moreover, as the plant extracts themselves act as stabilizers and no additional stabilizers or capping agents are needed, this method is more advantageous over other synthetic methods. During our investigations on plant based triterpenoids as renewable functional nano-entities [14,15,16,17,18], we have also demonstrated the eco-friendly green synthesis of AuNPs from the extracts of *Punica granatum* juice [19], *Saraca indica* bark [20], *Terminalia arjuna bark* [21] and *Ocimum sanctum stem* [22]. *Ficus carica Linn* (dumur) is a small tree grown in various parts of the world for its edible fruits and various parts of the plant have also been utilized as medicines for the treatment of different diseases. Herein, we report a very mild and environment friendly method for the synthesis of AuNPs from the fruit extract of *Ficus carica Linn* without any additional capping or stabilizing agents. The stabilized colloidal AuNPs were characterized by High Resolution Transmission Electron Microscopy (HRTEM), Energy Dispersive X-ray spectroscopy (EDX), Selected Area Electron Diffraction (SAED), SPR spectroscopy, X-Ray diffraction and FTIR studies. Catalytic activity of the freshly synthesized colloidal AuNPs have been demonstrated for the sodium borohydride reduction of 4-nitrophenol to 4-aminophenol in water at room temperature and the kinetics of the reduction reaction have been investigated spectrophotometrically.

2. Experimental

2.1 Synthesis and Characterization of AuNPs

Chloroauric acid ($HAuCl_4$) was purchased from SRL (Sisco Research Laboratory) and used without purification. $HAuCl_4$ (35.4 mg) was dissolved in distilled water (10 mL) to obtain a 10.7 mM Au(III) stock solution. Aliquots of Au (III) solution (0.16 mL, 10.7 mM each) were added drop-wise to the *Ficus carica Linn* fruit extract (see supporting information) to prepare stabilized AuNPs where concentration of the fruit extract varied from 200 to 1000 mgL^{-1} keeping the concentration of Au(III) ion fixed at 0.42 mM. UV-visible measurements of the gold colloids were carried out after 6

hrs of mixing. HRTEM images of AuNPs were recorded in JEOL JEM-2100 instrument. X-ray Diffraction (XRD) patterns of the stabilized AuNPs were recorded using PAN analytical X'Pert PRO diffractometer with Cu-Kα radiation (λ=1.54 Å). Mass spectral analysis of the samples were carried out in Shimadzu GCMS QP 2100 Plus instrument. UV-visible spectra of the samples were recorded in Shimadzu 1601 spectrophotometer. FTIR spectra of the samples were recorded using a Perkin Elmer Spectrum 2 instrument with a resolution of 1 cm^{-1}.

3. Result and Discussion

Ficus carica Linn, a moderate sized tree growing up to 15 meter in height, is widely found throughout the world. It is one of the first plants cultivated by human for the dry and fresh consumption of its edible "fruits". Various parts of the plant are used in different medicines like Ayurveda, Siddha and Homoeopathy. The fruits are considered to be very effective in the treatments of various ailments such as diabetes, skin diseases, ulcers, stomachache, etc. Different bio-active compounds have been isolated from this plant [23].

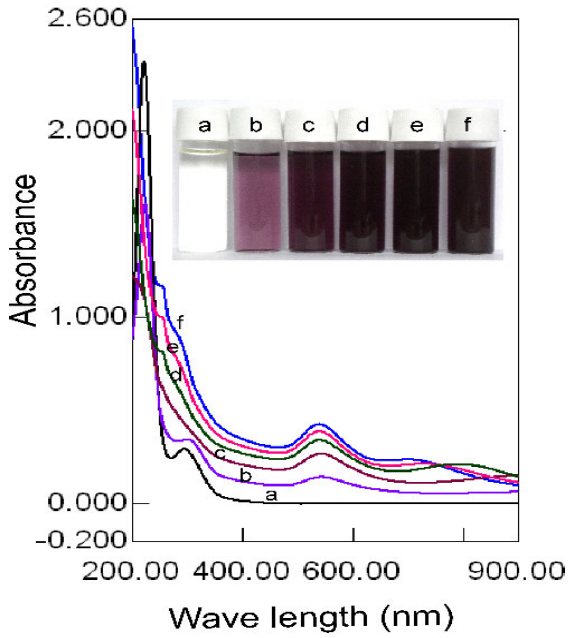

Figure 1: UV-visible spectra of: (a) $HAuCl_4$, (b-f) AuNPs at 200, 400, 600, 800, 1000 mgL^{-1} concentration of the fruit extract. Inset: photograph of vials containing AuNPs.

Presence of different types of plant secondary metabolites such as polyphenols, flavanoids, antioxidants etc. have been reported in the fruit extract of *Ficus carica Linn* [24,25]. Evidence for the presence of phenolic compounds in the fruit extract was obtained from ferric chloride test (see supporting information). Additonnal evidence for the presence of flavanoids along with terpenoids, steroids and hydroxy acids, etc. were obtained from mass spectral analysis (supporting information Figure S2). Since these compounds have high oxidation-reduction potential, they can easily reduce Au(III) ions to metallic Au(0) with concomitant oxidation to the corresponding quinones. The Au(0) atoms thus formed, may undergo collision with its neighbouring Au(0) atoms forming AuNPs and gain stability by the newly generated quinone derivatives, polyphenols and other coordinating phytochemicals. To test this, we treated aqueous solutions of $HAuCl_4$ with increasing concentrations of the fruit extract of *Ficus carica Linn*. Interestingly, we observed the appearance of pinkish red color indicating the formation of AuNPs. The color intensity of the mixtures increased on standing at room temperature for several hours.

3.1 UV-visible spectroscopy and HRTEM Studies:

The charge transfer interactions between the metal and the chloro ligands resulted in a strong absorption peak at 220 nm and a shoulder peak at 290 nm in the UV-visible spectrum of $HAuCl_4$ (Figure 1a). Colloidal AuNPs show a very intense color, in contrast to the bulk metallic gold. This is due to the combined oscillation of free conduction electrons induced by an interacting electromagnetic component of the visible radiation. The formation of gold nanoparticles from *Ficus carica Linn* fruit extract was evident from the UV–visible spectroscopy studies as shown in Figure 1. The appearance of the SPR band in the region of 539-543 nm suggested that AuNPs were formed upon addition of $HAuCl_4$ solution to the fruit extract. On increasing the concentration of the fruit extract, no significant blue shift of the SPR band was observed indicating that the formation of AuNPs were of almost similar average sizes. This observation was also in consistent with the HRTEM studies (vide infra).

The morphology and average particle sizes of the *Ficus carica Linn* fruit extract stabilized gold nanoparticles was investigated by high resolution transmission electorn microscopy (HRTEM) analysis (Figure 2 and supporting information Figure S3). Aliquots of the samples were placed on carbon coated copper grids (300 mesh) and dried initially in air and then under reduced pressure. Mostly spherical shaped AuNPs were observed by HRTEM along with certain percentage of trigonal, tetragonal and rod-like particles. The average particle size of the AuNPs measured from the HRTEM images of the samples from the vials containing 800 mgL^{-1} (Figure 2 a-c) and 1000 mgL^{-1} (Figure 2 d, e) concentration of the fruit extract (Figure 2 g, h) were 13-14 nm. This observation also supported the results obtained by UV-visible spectroscopy studies (discussed above). No aggregation of the colloidal AuNPs was observed on standing the sample vials at room temperature for several days indicating the stability of the AuNPs. Selected Area Electron Diffraction (SAED) pattern revealed four rings of Brags reflections corresponding to (111), (200), (220) and (311) planes of fcc crystalline Au suggesting crystalline nature of AuNPs (Figure 2f). EDX analysis of the AuNPs revealed the presence of elemental gold embedded in organic matrix (see supporting information Figure S4). The presence of organic matrix was also evident from HRTEM studies (see supporting information Figure S3).

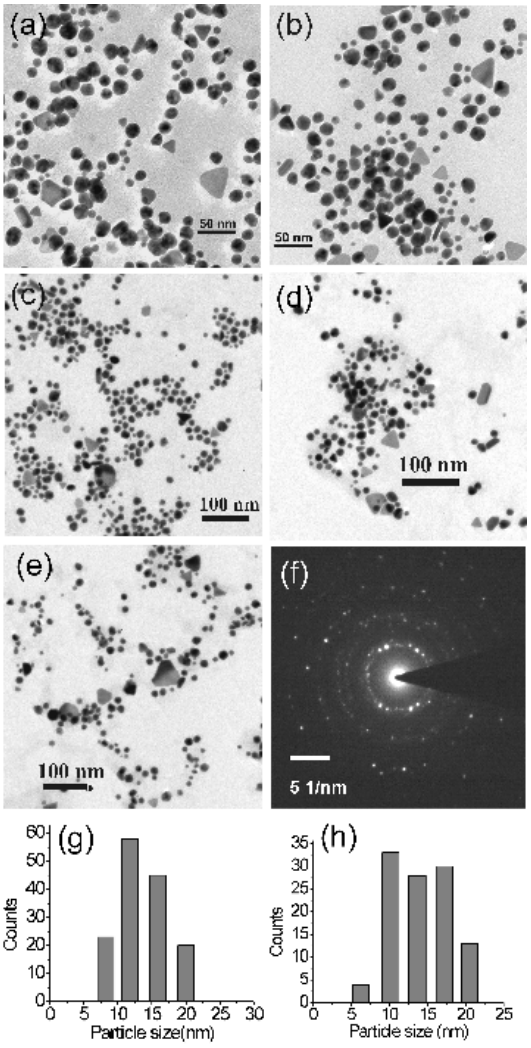

Figure 2: HRTEM images of stabilized AuNPs at various concentration of the fruit extract: (a,b,c) concentration = 800 mgL^{-1} ; (d,e) concentration = 1000 mgL^{-1} ; (f) SAED image of AuNPs and (g,h) histograms showing particle size distribution at 800 and 1000 mgL^{-1} concentration of the fruit extract.

3.2 X-Ray diffraction and FTIR Studies:

The XRD pattern of AuNPs synthesized from *Ficus carica Linn* fruit extract is given in Figure 3. The intense diffractions peaks due to AuNPs were clearly observed at 2θ = 38.3°, 44.3°, 64.8°, 77.9° and 81.8° which can be indexed to the (111), (200), (220), (311) and (222) Bragg reflections respectively. This confirmed the reduction of Au(III) to Au(0) by the phytochemicals present in the fruit extract. These values agreed well with the reported standards given in JCPDS file no. 04-0784. The intensity of (111) plane is comparatively larger than the other peaks is indicative of the predominant orientation of the (111) plane. This study suggested that the AuNPs obtained during biosynthesis were crystalline in nature.

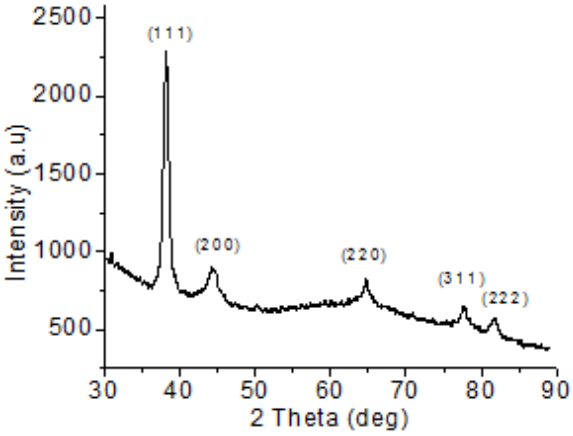

Figure 3: XRD pattern of AuNPs

We have performed FTIR analysis of *Ficus carica Linn* fruit extract and the stabilized AuNPs to investigate the participation of various functional groups for the synthesis and stability of the AuNPs (Figure 4). In the FTIR spectrum of *Ficus carica Linn* fruit extract, a broad absorption band was observed around 3390 cm^{-1} due to hydrogen bonded 'O-H' stretching vibration of polyphenols, flavanoids etc. Additionally, a weaker peak was observed at 1205 cm^{-1} due to stretching vibrations of 'C-O' in polyphenols. The 'C–H' stretching vibration modes in hydrocarbon chains appeared at 2918.5 cm^{-1}. The presence of sharp peaks in the region of 1611-1445 cm^{-1} are attributed to 'C=C' stretching vibrations of aromatic rings. However, in the FTIR spectrum of AuNPs, the peak for the 'O-H' groups became slightly narrower indicating the interaction of this group with the AuNPs. The in-plane bending of the OH groups in the fruit extract appeared at 1372 cm^{-1}. This frequency became much weaker in the stabilized AuNPs (Figure 4b).

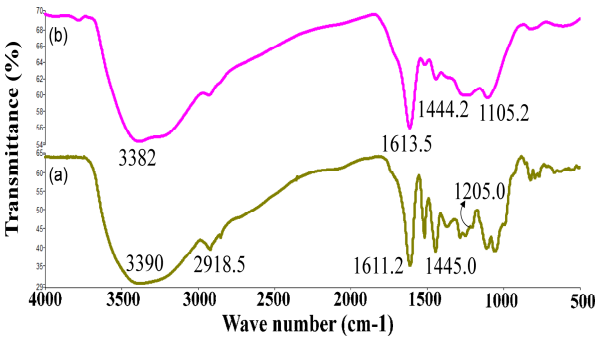

Figure 4: FTIR spectra of (a) *Ficus carica Linn* fruit extract and (b) stable AuNPs

3.3 Reaction Mechanism:

The fruit extract of *Ficus carica Linn* is rich in different types of plant secondary metabolites. Mass spectral analysis

carried out by us indicated the presence of different types of polyphenols including flavanoids (supporting information Figure S1). The presence of the phenolic compounds in the fruit extract was evident from positive ferric chloride test (see supporting information). Easy oxidation of phenolic compounds by transition metal ions at a higher oxidation state are known. These electron rich o-dihydroxy-compounds present in the fruit extract can easily form a five-membered chelate ring with the Au(III) ions.

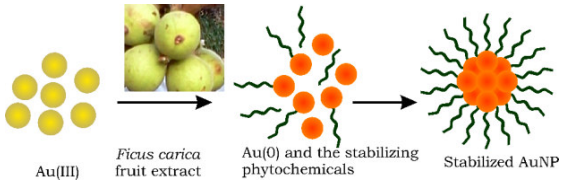

Figure 5: Mechanism of the formation and stabilization of AuNPs by polyphenolic compounds present in *Ficus carica Linn* fruit extract.

A schematic representation for the formation of AuNPs is given in Figure 5. The redox reaction can take place in the chelate complex where the o-dihydroxy compounds can be oxidized to corresponding quinones with concomitant reduction of Au(III) ions to Au(0). The neighboring Au(0) atoms can collide with each other forming the nano-sized gold particles and the AuNPs can be stabilized by the quinones, phenolic compounds, as well as other coordinating phytochemicals present in the fruit extract. The stabilizing ligands surrounding the AuNPs prevent further metallic aggregation.

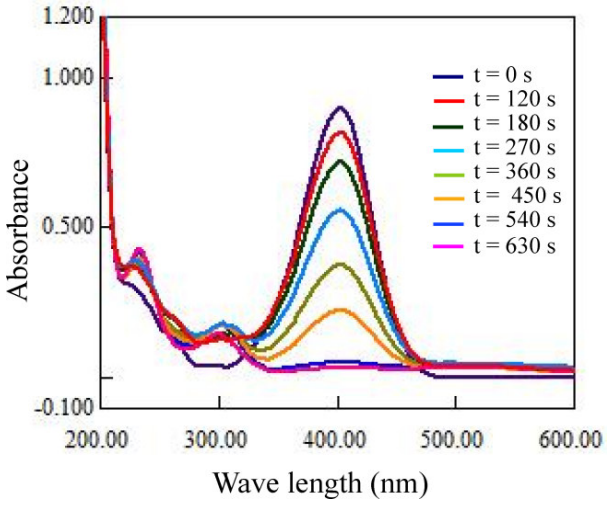

Figure 6: Overlay of UV-visible spectrum at various time intervals during catalytic reduction of 4-nitrophenol to 4-aminophenol.

3.4 Catalytic Application of AuNPs:

The catalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) in the presence of metal nanoparticles and sodium borohydride ($NaBH_4$), has become an area of intense research in recent years because of its usefulness as analgesic and antipyretic drugs, photographic developer, corrosion inhibitor, etc. [26]. To test whether the AuNPs synthesized by us can be used as a catalyst, we have designed the following experiment. In the absence of catalyst the absorption peak of the mixture of 4-NP and $NaBH_4$ appear at 402 nm due to the formation of 4-nitrophenolate ion in the alkaline medium [19]. But no reduction of 4-NP to 4-AP took place on standing the reaction mixture for a longer period due to large kinetic barrier of the reduction reaction. Interestingly, on addition of the freshly prepared colloidal AuNPs (0.1 mL, synthesized with 200 mgL^{-1} of the fruit extract) to the reaction mixture, the absorption intensity due to 4-nitrophenolate at 402 nm decreased with concomitant appearance of a new peak around 300 nm. This was due to the formation of 4-AP indicating the catalytic property of the stabilized AuNPs for the reduction reaction. The progress of the reaction could be monitored by UV-visible spectroscopy at various time intervals (Figure 6). As excess of $NaBH_4$ was used for the reduction reaction, the rate of the reaction could be measured assuming pseudo-first-order rate kinetics. From the plot of ln (C_t/C_0) vs time a linear correlation was obtained (supporting information Figure S5). From the slope of linear plot, the rate was calculated to be 0.59 X 10^{-2} sec^{-1} that was comparable to the rate constant obtained by us previously [27,28].

4. Conclusion

Fruit extract of *Ficus carica Linn (Dumur)* has been utilized for the synthesis of polyshaped gold nanoparticles under very mild conditions. The phytochemicals including polyphenolic compounds present in the fruit extract act as effective reducing as well as stabilizing agent and gold nanoparticles of 13-14 nm size were obtained without any additional capping or stabilizing agents. The stabilized gold nanoparticles have been characterized by HRTEM, EDX, SAED, surface plasmon resonance spectroscopy, XRD and FTIR studies. According to our knowledge, this is the first report of the synthesis of stabilized colloidal AuNPs using the fruit extract of *Ficus carica Linn*. Catalytic application of the freshly synthesized colloidal AuNPs has been demonstrated for the sodium borohydride reduction of 4-nitrophenol to 4-aminophenol in aqueous medium at room temperature. Kinetic studies for the catalytic reduction have also been carried out spectrophotometrically. As the fruit extract has tremendous medicinal significance, the results described here will also be useful for its application in pharmacology and biomedicine.

5. Acknowledgements

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6. References

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