Synthesis of Gold Colloid using *Zingiber officinale*: Catalytic Study

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Abstract

Aqueous extract of the root of ginger (Zingiber officinale) has been used to prepare gold nanoparticles. Almost spherical gold nanoparticles having diameter 3.22 ± 1.13nm have been revealed from transmission electron microscope image. Evidence of the existence of such small nanopartilces has been also demonstrated by their UV-Vis spectra.

FT-IR study was performed to know the interaction of the ingredients present in extract with the surface of nanoparticles. Catalytic efficiency of the gold nanoparticles was evaluated and reported in terms of catalytic activity parameter (κ), against the remediation of common environmental pollutants 4-nitro phenol and few organic dyes.

Keywords: *Zingiber officinale,* Gold Colloid, Catalyst.

Introduction

Metal nanoparticles have received considerable attention for their applications in diverse range of fields including sensing, catalysis, imaging, medicine etc.[1] From the past decade, tremendous research efforts have been devoted to develop low cost, convenient, eco-friendly protocol for synthesis of metal nanoparticles. Among various approaches which address the above criteria, reduction of metal ions and subsequent stabilization of the nanoparticles by phytochemicals present in the extract of different herbal plants may be considered as one of the promising protocols for synthesis of metal nanoparticles.[2-4]

Moreover, such nanoparticles in colloid states are more suitable for the biological applications as the formulations do not have any harmful chemicals. However, thorough screening is necessary in this context to find out the plants whose extracts have good reducing as well as stabilizing power. So far researchers have reported the successful synthesis of silver and gold nanoparticles using extracts of leaf, root and stem of different plants.[5-8]

Studies also reveal that phenolic compounds, flavonoids, terpenoids, polysaccharides, enzymes and other proteins, the key components present in the plants' extracts reduce the metal ions and also stabilize the nanoparticles by inhibiting their growth.[9] As a part of continuous efforts to find out plant extract having potential utility in synthesis of silver and gold nanoparticles,[10-14] in this report, we have studied the synthesis of gold nanoparticles using extract of root of a common herbal plant, Zingiber *officinale,* generally known as 'ginger'. This is a perennial herb and the root is most commonly used as spice as well as also for medicinal purposes in Asia.

Use as catalytic agent is one of the most promising applications of gold nanoparticles (AuNPs). Catalytic performance of our as-synthesized AuNPs has been evaluated to study the reduction of common pesticide, 4-nitro phenol(PNP) and industrial toxic dyes: Eosin blue (EB), Brilliant Cresyl Blue (BCB) and Erichrome black T (EBT).

Material and Methods

Preparation of Aqueous Extract of *Zingiber officinale*: Ginger root (*Zingiber officinale*) was purchased from local market of Jadavpur, Kolkata. The extract was prepared by boiling 10g of crushed root (the small pieces of roots were crushed in a mortar pestle) in 30ml of water for 5 min with constant stirring. The extract was filtered through Whatmann No. 1 filter paper to remove the insoluble matter and the filtrate was stored at 4^0C in refrigerator for future use.

Synthesis of gold Nanoparticles (AuNPs): For a typical synthesis, 0.1 ml of ginger extract was added into 10 ml of 0.2mM $HAuCl_4$. The solution was then incubated at 35^0C with continuous shaking for 24 hours. A purple colored solution appeared after completion of synthesis indicating formation of Au nanoparticles.

Characterization: The UV-Vis absorption spectra were recorded by Perkin Elmer UV spectrophotometer (model λ-25) at room temperature using a quartz cell (1 cm path length). The TEM study was carried out in a JEOL JEM 2100, working at an acceleration voltage of 200 kV. The deposition technique of the sample on carbon-coated copper grid was similar as described elsewhere.[15] FTIR spectra of the freeze-dried sample were taken using Perkin Elmer FT-IR Spectrometer Spectrum Two.

Catalytic Study: 4-NP, EBT, BCB, Sodium borohydride were purchased from Sigma (USA) and EB was purchased from Loba Chemie (India). For the catalytic study, 3.7 ml aqueous reaction mixture containing 4-NP (0.16mM), $NaBH_4$ (8mM) and 0.1ml as-synthesized AuNPs solution was introduced in standard quartz cell with 1 cm path length and reduction of 4-NP was examined by UV-Vis spectrophotometer with time at 25^0C.

Similar procedure was used for the catalytic reduction of BCB, EBT and EB dyes. The composition of the aqueous reaction mixture is given in the table 1.

Table 1
Composition of the different reaction mixtures

Total volume of reaction mixture (ml)	Name of the dyes	Concentration of dyes (mM)	Concentration of $NaBH_4$(mM)	Amount of Gold-colloid solution(ml)
3.7	EB	0.05	14	0.1
	EBT	1.7	80	0.1
	BCB	0.05	6	0.1

Results and Discussion

UV-Vis spectral and TEM study: After the addition of ginger extract into the $HAuCl_4$ solution, the colorless reaction mixture became purple in color (fig. 1 inset). Figure 1 shows the UV-Vis spectra of the reaction mixture containing 0.2mM $AuCl_4$ and 0.1ml ginger extract at different time interval. The characteristic plasmonic peak of the as-synthesized Au nanoparticles appeared at 548nm and increased in intensity with time.

A general view of the TEM micrograph of Au nanoparticles is shown in figure 2a. AuNPs are almost spherical in shape with an average particle size 3.22±1.13 nm (fig. 2b). Crystalline nature of the nanoparticle is confirmed by the HRTEM image of a single particle (fig. 2c) and the lattice spacing is 0.23nm. The selected area electron diffraction (SAED) pattern (fig. 2d) with bright spots also shows the crystalline nature of the particles.

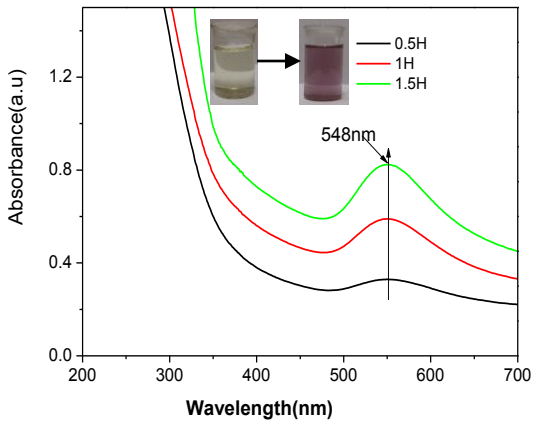

Fig. 1: UV-Vis spectra of the mixture of aqueous extract of ginger and $HAuCl_4$ at different time interval. Inset- Colour of the sample at initial stage and after 1.5hr

Fourier transform infrared spectroscopy analysis: FTIR spectrum of ginger-extract (fig. 3a) shows several absorption peaks which can be assigned for hydroxyl group (3450 cm^{-1}), carbonyl group of amide (1639 cm^{-1}), N-H bending and C-N str. vibration of amide (1531 cm^{-1}) methyl group (1402 cm^{-1}) and ether linkage (1108cm^{-1}). All these functional groups are related to flavonoids and peptides present in the extract.[10] Most of these peaks are shifted in the FTIR.

Catalytic Reduction of 4-nitrophenol: The aqueous solution of PNP is light yellow color and shows absorption peak at 317 nm. The addition of $NaBH_4$ into aqueous solution of PNP increases the pH of the solution and at this higher pH, PNP exists as phenolate ion. Due to formation of such phenolate ions, color of the solution changes to intense yellow and absorption peak of solution is shifted to 400nm.[10] Time-dependent UV-Vis spectra of aqueous solution of phenolate ion in presence of AuNPs and $NaBH_4$ show the gradual decrease in the intensity of absorption peak at 400 nm and concomitant development of a new peak at 290 nm which has been attributed to reduced product 4-amino phenol (fig. 4a). The reduction was completed within 1140 sec as the peak at 400nm fully disappeared after this time period. Also, ultimate bleaching of yellow color of 4-nitrophenol solution confirmed the completion of reduction process.

In contrast same amount of $NaBH_4$ without nanocatalyst can reduce 4-nitrophenol only in a small extent even after 1hr of reaction time. This result indicates that this thermodynamically feasible reduction of PNP ($E^0_{(PNP/4\text{-}AP)}$ = −0.76V) by $NaBH_4$ ($E^0_{(H3BO3/BH4-)}$ = −1.33 V) cannot occur without catalyst owing to its kinetic restriction. Since the concentration of $NaBH_4$ is high in comparison to 4-nitrophenol, the kinetics of reaction can be considered as pseudo- first- order with respect to 4-nitro phenol and the rate constant (k) of the reaction can be evaluated from the slope of the straight line obtained from the plot of ln (A_t/A_0) vs time (t). A_t and A_0 represent the absorbance of the reaction mixture at time t and initially when t=0 respectively.

A good linear correlation with a correlation coefficient R^2= 0.99, is obtained when ln (A_t/A_0) is plotted against time (t) (fig. 4b) and the corresponding rate constant is 0. 87 *10^{-3} s^{-1}.

In order to compare the catalytic performance of AuNP with respect to other literature value, a common quantity has been calculated[10]: the activity parameter (κ) = k/m [ratio of rate constant (k) to the total mass (m) of catalyst added]. In this study the obtained value for activity parameter (κ) is 225 $s^{-1}g^{-1}$. This value of activity parameter is slightly lower or comparable with the values obtained for AgNPs and Ag-Au bimetallic nanoparticles.[10,16,17]

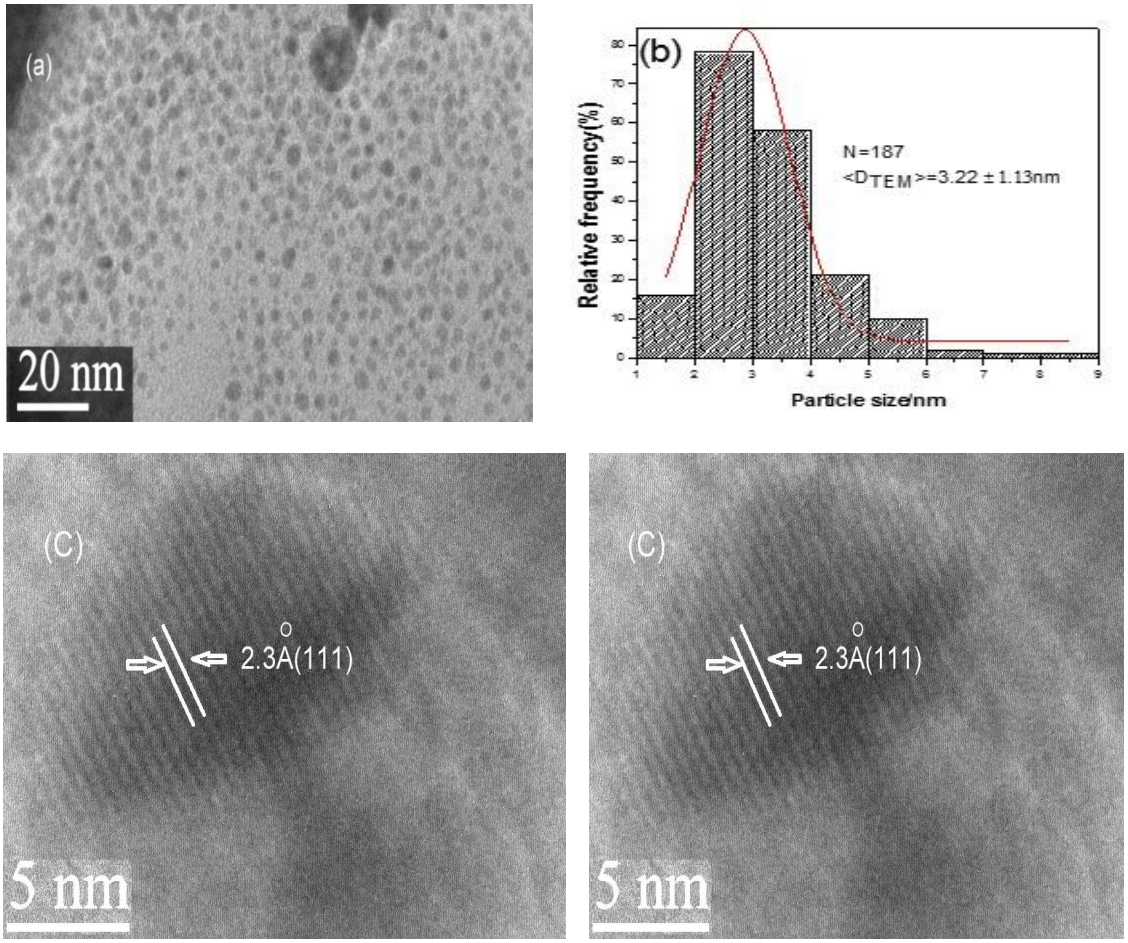

Fig. 2: (a) TEM micrograph of AuNPs (b)Particles size distribution histogram. (c) HR-TEM micrograph of AuNP with interplanar distance, (d) Selected area electron diffraction pattern (SAED) of AuNP

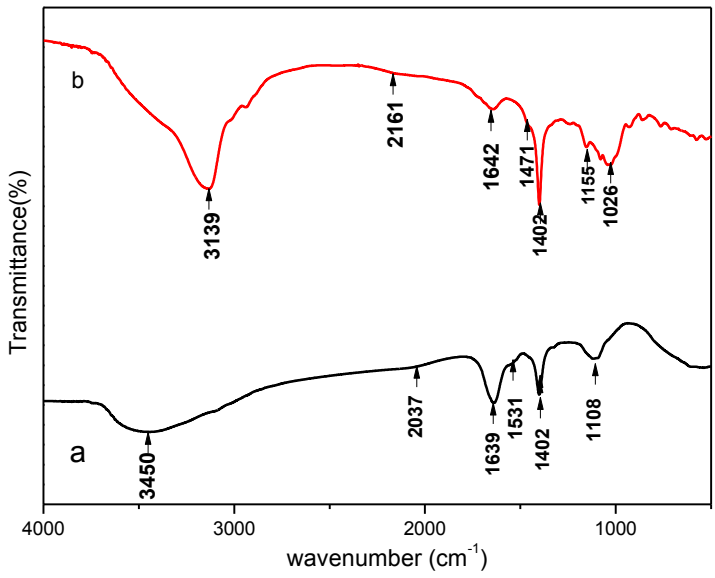

Fig. 3: FTIR spectrum of (a) ginger extract and (b) gold nanoparticles synthesized from $AuCl_4$ and ginger extract spectra AuNP-ginger extract suggesting the involvement of above mentioned functional groups to stabilize the gold nanoparticle.

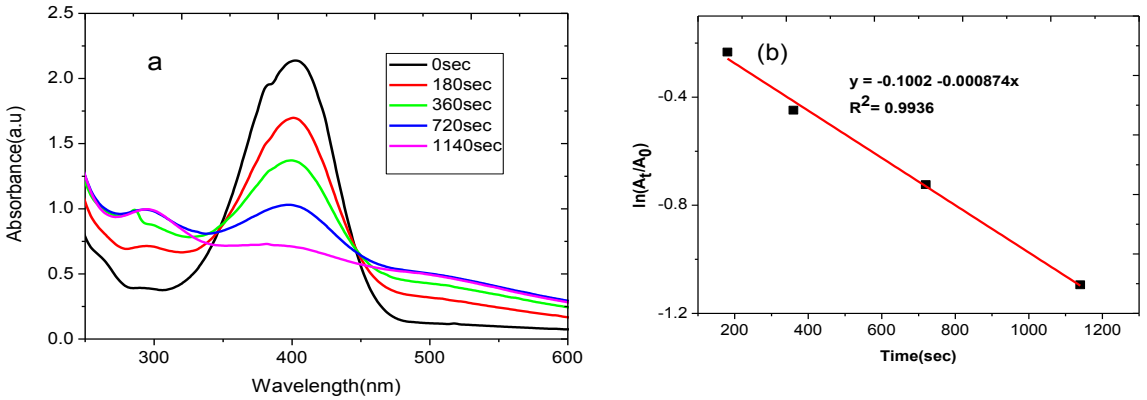

Fig. 4: (a) UV-Visible spectra of 4-nitrophenol mixed with $NaBH_4$ at different time intervals in presence of AuNPs. (b) Pseudo-first-order reactions kinetics followed by the reduction in presence of AuNPs

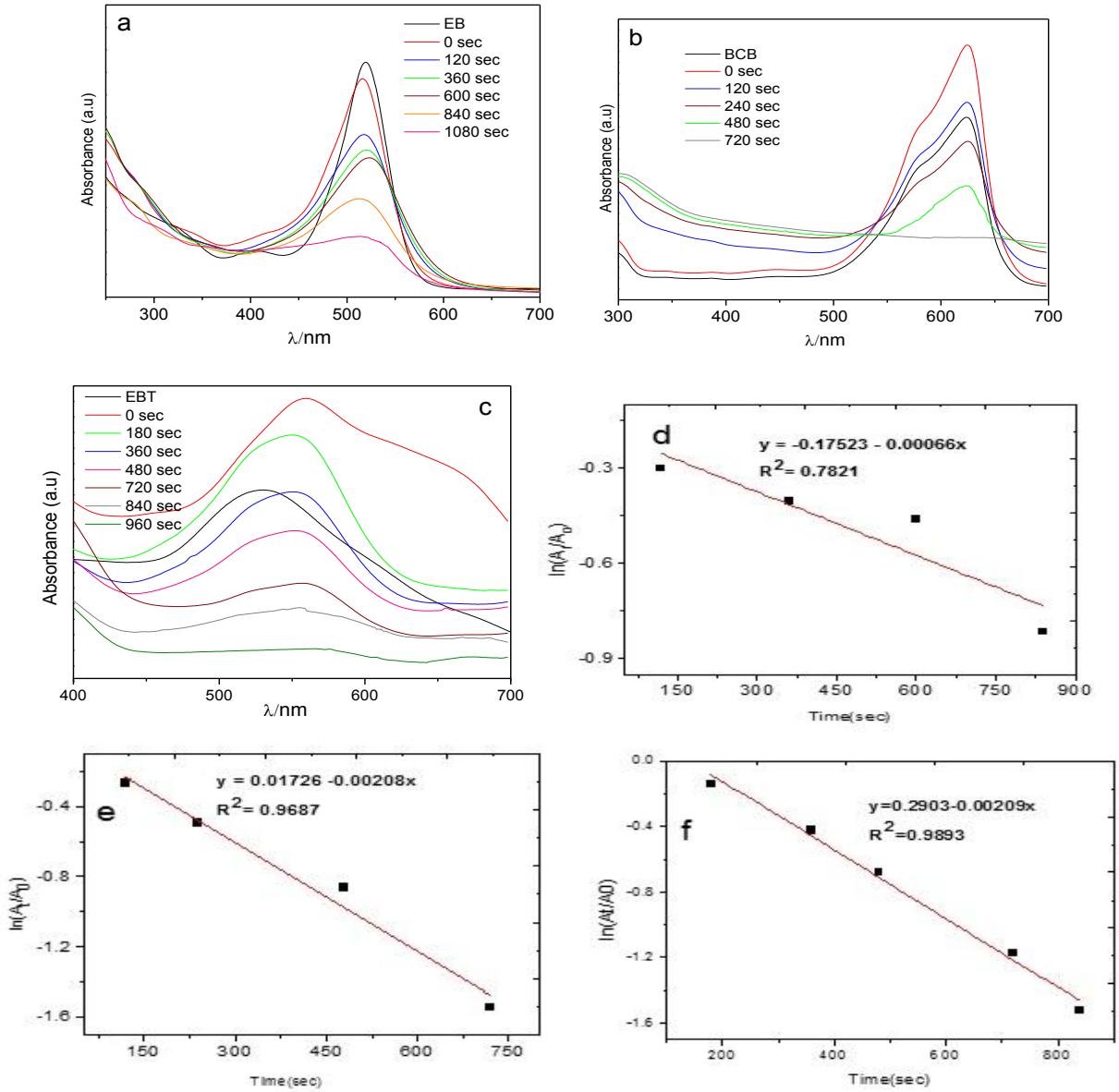

Fig. 5: UV-visible spectra of reduction of (a) EB, (b) BCB and (c) EBT mixed with $NaBH_4$ at different time intervals in presence of Au nanocatalyst. The pseudo-first-order reactions kinetics followed by the reduction (d) EB, (e) BCB and (f) EBT.

Table 2
Rate constant (k), correlation coefficient and activity parameters (κ) for the degradation processes for different dyes in presence of catalyst AuNPs

Name of substrate	Activity parameter κ ($s^{-1}g^{-1}$)	Rate constant k (s^{-1}) $\times 10^3$	correlation coefficient, R^2	Activity parameter κ ($s^{-1}g^{-1}$)
Eosin blue	218	0.66	0.78	171
BCB	1054	2.08	0.96	539
EBT	284	2.09	0.98	541

Degradation of organic dyes: The organic dyes are potential environmental pollutants because of their toxic nature and resistance to aerobic degradation. For remedial purposes, reductive degradation of such dyes into non-toxic components using noble metal nanoparticle as catalyst is a convenient, low cost, greener approach and the technique has been widely investigated to treat several dyes using Ag, Au, Pt noble metal nanocatalyst.[18] The catalytic activity of the as-synthesized AuNPs was further tested against the reduction of three dyes: EB, BCB and EBT. EB, BCB and EBT show the maximum absorption at the wave length (λ_{max}) of 519 nm, 624nm, 529nm (fig. 5 a, b, c) respectively.

λ_{max} decreased approximately 13% for EB and 30% for BCB after 1 hr reaction when those dyes were treated only with $NaBH_4$. Addition of $NaBH_4$. increases the pH of the solution and at this higher pH, phenolic OH group of the EBT exists as phenolate ion which increases the overall conjugation of EBT molecule. As a result, colour of the EBT solution changed red to violet and λ_{max} of the solution shifted from 529nm to 560nm (fig. 5 c). It is noted that in presence of $NaBH_4$ and AuNPs, the absorbance at λ_{max} decreases rapidly and ultimately reduction was almost completed within 1080sec, 720sec, 960sec for EB, BCB and EBT respectively (fig. 5 a, b, c).

Considering each reaction pseudo-first-order with respect to dye, the rate constant (k) has been evaluated from the slope of the straight line obtained from the plot of ln (A_t/A_0) vs time (t) (fig. 5 d, e, f). The values of calculated rate constant (k) along with correlation coefficient and activity parameters (κ) for all the degradation process for dyes in presence of AuNPs are summarized in table 2.

Conclusion

In summary, aqueous extract of ginger can successfully reduce Au ions to their metallic forms and it can also act as stabilizing agent to inhibit the growth of colloidal metal particles. As a result, the present eco-friendly and cheap technique can produce AuNPs which have appeared as efficient catalysts for the reduction of pollutants like 4-nitrophenol (4-NP) and dyes like Eosin Blue (EB), Brilliant cresyl blue (BCB) and Eriochrome black T (EBT).

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