Advances in Nano Research, *Vol. 5 No. 3 (2017) 253-260*
DOI: https://doi.org/10.12989/anr.2017.5.3.253

Synthesis of gold nanoparticles using *Coffea Arabica* fruit extract

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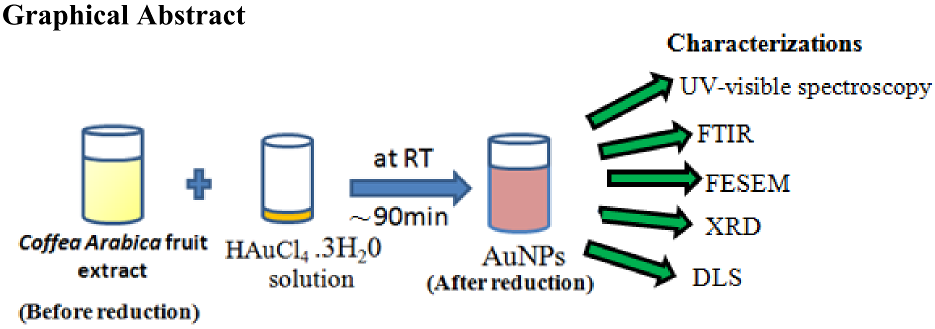
(*Received January 15, 2017, Revised May 29, 2017, Accepted August 01, 2017*)

Abstract. We report a simple eco-friendly process for the synthesis of gold nanoparticles (AuNPs) using aqueous extract from *Coffea Arabica* fruit. The formation of AuNPs was confirmed using absorption spectroscopy and scanning electron microscopy images. FT-IR analysis demonstrates the major functional groups present in *Coffee Arabica* fruit extract before and after synthesizing AuNPs. The Face Center Cubic (FCC) polycrystalline nature of these particles was identified by X-Ray diffraction (XRD) analysis. Taking into account the contribution of the biomass surrounding the AuNPs, dynamic light scattering (DLS) results revealed an average particle size of ~59 nm.

Keywords: green synthesis; AuNPs; FCC; *Coffea Arabica*; FE-SEM; DLS

Graphical Abstract



1. Introduction

In recent years nanoparticles are widely used in fabrication of advanced materials, optical displays, super computers, energy storage devices and biomedical devices (Daniel and Astruc 2003). Based on the size and shape of metallic nanoparticles (NPs), distinct features in mechanical (capillary forces), chemical (catalysis), thermal (melting point), electrical (tunneling current),

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http://www.techno-press.org/?journal=anr&subpage=5 ISSN: 2287-237X (Print), 2287-2388 (Online)

magnetic (super paramagnetic effect) and optical (scattering, absorption) properties can be observed. Among the various physical and chemical routes to synthesize metal nanoparticles, majority of them have been synthesized using expensive hazardous toxic solvents / reducing agents such as hydrazine (Guzmán *et al*. 2008), dimethyl formamide (DFM) (Pastoriza-Santos and Liz-Marzán 2002) and amino acids (Maruyama *et al*. 2015). Additionally polymers or surfactants have been used as capping or stabilizing agents (Azim *et al*. 2009). To overcome the difficulties of physical and chemical routes, several plant-mediated reducing agents have been proposed (also named as green nanotechnology). Green nanotechnology integrates the principles of green chemistry to produce safe, eco-friendly and non-toxic nanoparticles (Philip 2009). In modern science, green-energy technologies have received tremendous amount of attention for the production of metal nanoparticles. In general, metal NPs have an excellent electro-catalytic ability. Specifically gold nanoparticles (AuNPs) with broad spectrum of physical, chemical and optical properties (Tapan and Andrey 2009) give rise to several applications, such as immunoassays (Peng *et al*. 2009), biosensors (Singh *et al*. 2013), cancer treatment (Tapan and Andrey 2009), drug delivery (Hu *et al*. 2006) and photo thermal therapeutics. Preparation of AuNPs using green synthesis has been already reported through lemon grass leaf (Shankar *et al*. 2005), *rosa damascena* (Ghoreishi *et al*. 2011), diethylaminoethyl dextran chloride (DEAE-D) polymer (Singh *et al*. 2013), and immunoglobulin (Huang *et al*. 2006). As AuNPs are promising supports due to their available surface area for the attached catalyst and avoid aggregation, it is essential for the progress of sustained catalytic efficiency (Radha and Mostafa 2005). Previously reported preparation of Ag NPs using *Coffee Arabica* (Nadagouda and Varma 2008 and Vivek *et al*. 2016).

In this work, we explore an alternative green, novel and eco-compatible reducing precursor for the synthesis of polycrystalline AuNPs, i.e., *Coffea Arabica* fruit (CAF) extract solution as a natural reducing and stabilizing agents. To best of our knowledge there are no reports on the synthesis of AuNPs using CAF extract and their corresponding application towards the reduction of 4-Nitrophenol, till now. The *Coffea Arabica* seed, commonly called “coffee bean” is a seed of the coffee plant and is the source for coffee. The *CAF* is also called as stone/coffee fruit. It belongs to *rubiaceae* family and with the binomial name of *Coffea Arabica*, 75-80% of the coffee produced worldwide is Coffea Arabica. It consists of 0.8-1.4% caffeine (1,3,7-trimethyl-xanthine) and alkaloids.

2. Materials and methods

Chloroauric acid ($HAuCl_4.3H_2O$) and all other reagents used were of analytical grade. *Coffea Arabica* fruits were collected from Cuernavaca, Morelos, Mexico. The fruit was dried and stored in ambient conditions. For the preparation of coffee fruit extract, 50 mg of finely dried powder was mixed in 100 mL of deionized water and kept in temperature controlled water bath at ~85±5°C for 25 min. Then the extract was filtered using cellulose filter paper. The natural pH of *Coffea Arabica* fruit extract is~6.3, without contribution of any chemical reagent (acid).

$HAuCl_4.3H_2O$ (20 mL; 4 mM) was added to 100 mL of freshly prepared extract in the ratio of 1:5. The gradual formation of AuNPs was observed by visual colour change from light yellow to violet, which was confirmed by Perkin-Elmer Lambda 950 UV-Visible dual beam spectrophotometer The XRD analyses of AuNPs were carried out by Bruker D8 Advance eco diffractometer. The spectra were recorded in the scanning range of 10° to 90°. Field Emission Scanning Electron Microscopy (FESEM) analysis was done using a Hitachi SU5000 Schottky FESEM. Dynamic Light Scattering (Malvern zetasizer, Model nano ZS) was used to determine the average particle size and distribution of AuNPs. FT-IR measurements were carried using Varian 660-IR FT-IR spectrophotometer, to confirm the functional groups present in the CAF extract. In order to confirm the catalytic efficiency, the reduction of 4-Nitrophenol (4-NP) (with $NaBH_4$) using Au nanoparticles as catalyst, was studied as a model reaction. Catalytic activity of Au nanoparticles (catalyst) was performed by reducing 4-NP to 4- Aminophenol (4-AP) in the presence of $NaBH_4$. The reduction of 4-NP was monitored and recorded using UV-visible spectrophotometer at regular time intervals. The kinetic study was determined by measuring change in initially observed absorbance peak at 400 nm as a function of time.

3. Result and discussion

AuNPs were synthesized using different parameters, such as concentration and volumetric proportion of coffee fruit extract with respect to the gold salt. Six different concentrations of *CAF* extract (from 1 mg/10 mL–6 mg/10 mL of freshly dried CAF powder) with a constant concentration of gold salt (4 mM; $HAuCl_4.3H_2O$) were prepared to test the minimum concentration necessary for reducing the Au salt. Visual color change and monitoring of the reaction through UV-visible spectroscopy reveals that a certain minimum (5 mg/10 mL) concentration is necessary to reduce Au^{+3} to Au^0. Additionally, 5:1 volumetric ratio of extract to salt precursor (5 mg/10 mL extract: (4 mM) $HAuCl_4.3H_2O$) was found to be optimum to obtain minimum polydispersity and maximum concentration of AuNPs (Fig. 1).

Fig. 1 demonstrates the UV-vis spectra of gold colloids with a maximum absorbance (λ_{max}) at 557 nm, due to surface plasmon resonance (SPR) band. Particle size, shape and interaction with the medium have been found to influence the shape of SPR band (Daniel and Astruc 2003).

FTIR spectrum analysis (Fig. 2) was carried out to identify the functional groups/ biomolecules responsible for reduction and stabilization of the synthesized AuNPs. The most intense bands of the pure extract, found at 1624 cm^{-1} (carboxyl –C = O stretching) and 3074-3430 cm^{-1} (–OH

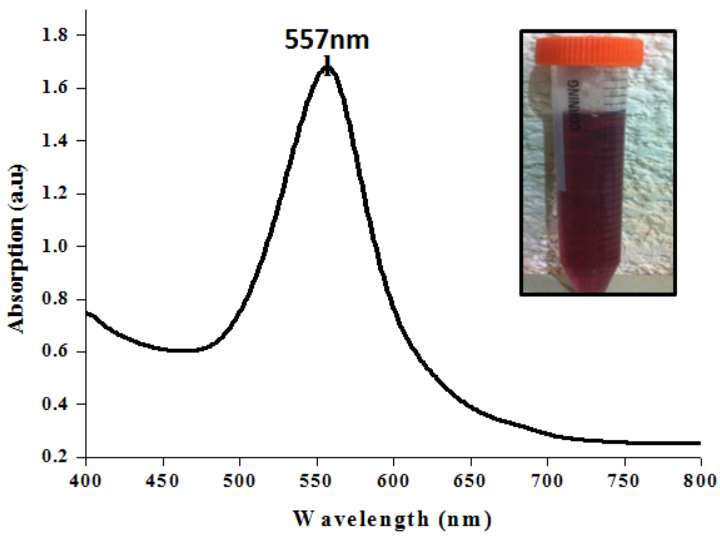

Fig. 1 Absorbance spectra of the AuNPs formed with 5 mg/10 mL concentration of CAF Exctract in the volumetric proportion of 5:1 with Au salt (inset: photograph of AuNPs)

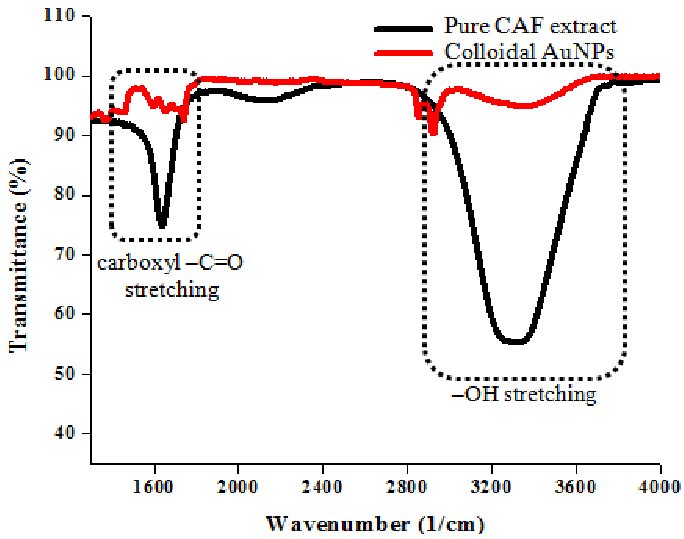

Fig. 2 FTIR spectra of pure CAF extract and colloidal AuNPs

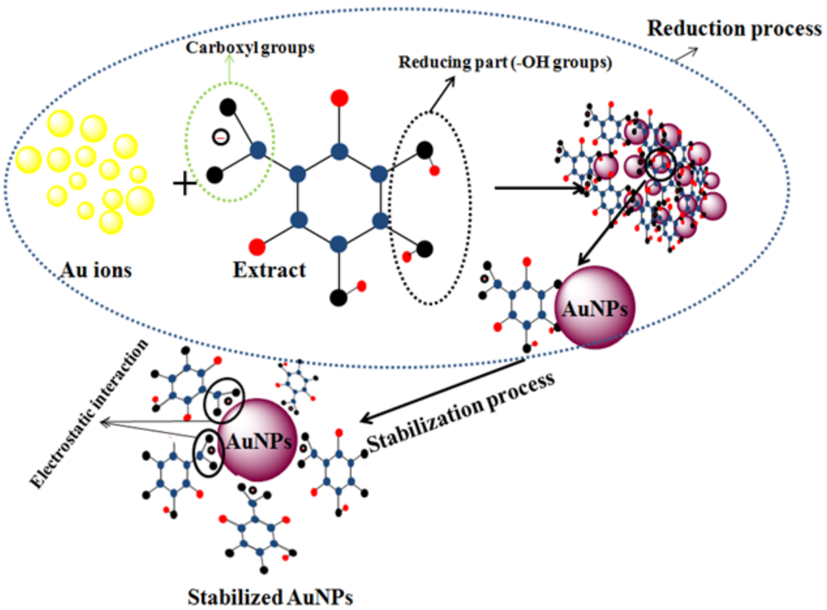

Fig. 3 Plausible mechanism involved in the formation of colloidal AuNPs

stretching), correspond to the phenolic compounds (Maruyama *et al*. 2015). IR spectrum of AuNPs shows similar bands at 1624 cm^{-1} and 3074-3430 cm^{-1}. Significant change in the IR bands of the extract, before and after the synthesis of the AuNPs, is due to the reduction and stabilization process. The possible mechanism corresponding to the reduction of Au^{+} to Au^{0} can be explained as follows: phenolic –OH groups present in extract can form intermediary structures with Au^{+} ions, which accordingly undertake reduction to quinine forms with successive reduction of Au^{+} to Au^{0}

form. Small entities of reduced Au^0 (AuNPs) combine with carboxyl groups then form stabilized AuNPs.

$$\text{Gold salt } (HAuCl_4.3H_2O) + H_2O \rightarrow Au^+ \text{ ions}$$

$$Au^+ \text{ ions + extract (–OH groups + carboxyl groups)} \rightarrow Au^0 \text{ (AuNPs) + extract (carboxyl groups)}$$
{Reduction process}

$$Au^0 \text{ (AuNPs) + extract (carboxyl groups)} \rightarrow \text{Stabilized AuNPs}$$
{Stabilization process}

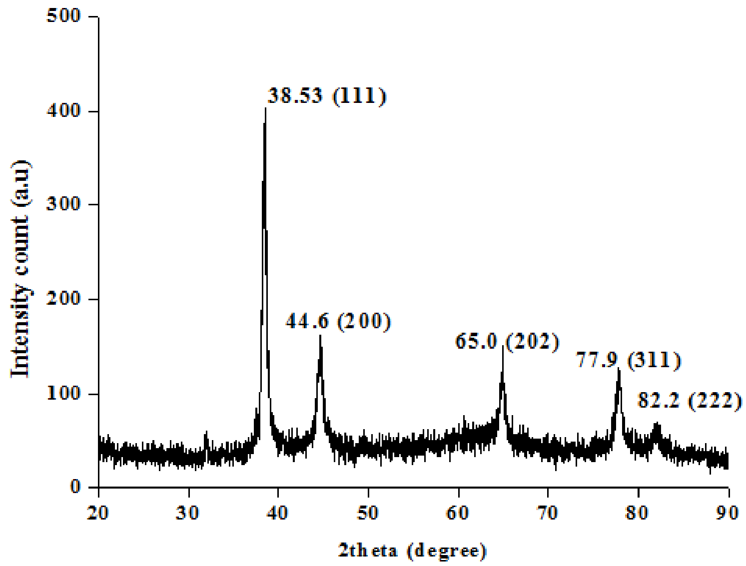

Fig. 4 X-Ray diffraction pattern of synthesized colloidal AuNPs

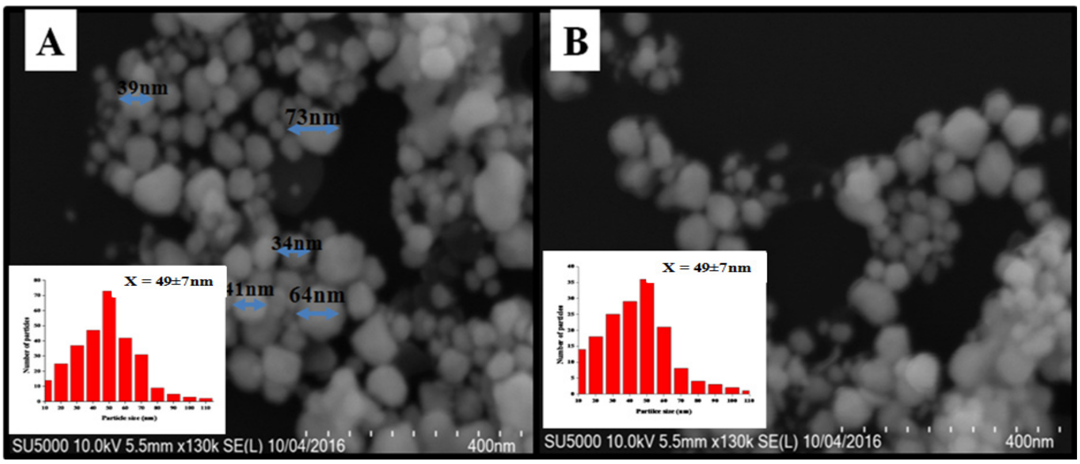

Fig. 5 Two different SEM images with the same magnification of colloidal AuNPs (inset: size dependent histogram of AuNPs)

The schematic of the plausible mechanism involved in the formation of colloidal AuNPs (proposed from FTIR studies) is shown in Fig. 3. The XRD results of the synthesized AuNPs (Fig. 4) show the Bragg's diffraction peaks at 38.5^0, 44.6^0, 65.0^0, 77.9^0 and 82.2^0, indexed corresponding to the planes (111), (200), (202), (311) and (222) respectively. The (200), (202), (311) and (222) Bragg reflection are weak and broad relative to the intense (111) reflection (Philip 2009). The average crystallite size (D) was calculated using Debye-Scherrer's relationship $D = k\lambda/\beta\cos(\theta)$, where k – Scherrer coefficient (0.9), λ - X-ray wavelength ($\lambda = 1.54A^0$), β – full width half maxima (FWHM) in radians and θ - Bragg's angle. The average crystallite size of ~49 nm was calculated from the high intensity narrow (111) peak.

Two different SEM images with the same magnification of AuNPs are shown in Fig. 5, providing information about their size, shape and structure. Polydispersity with the average particle size of 49±3 nm is evident from the SEM images. Additionally, we can observe the biomass around the NPs which stabilizes the AuNPs. In Fig. 5 insets show the size distribution histograms of colloidal AuNPs.

The size distribution of AuNPs obtained from DLS is found to be in good agreement with the values obtained from SEM and XRD measurements. The average hydrodynamic size of AuNPs was found to be ~59 nm (Fig. 6). The higher size of AuNPs from DLS measurements as compared to SEM histogram and XRD results is attributed to the additional contribution from biomass (confirmed through SEM).

Catalytic reduction of 4-NP: As aqueous 4-NP (10^{-1} M; 2 mL; pale yellow) shows absorbance maxima (λ_{max}) at 317 nm (Fig. 7), an addition of $NaBH_4$ to 4-NP results in visual color change (10^{-1} M; 2 mL; intense yellow color) due to the formation of 4-nitrophenolate ion i.e., the absorbance maxima was shifted from 317 to 400 nm. An addition of AuNPs as catalyst (27.8 μg), the absorption peak at 400 nm decreases linearly with an increase in the reaction time. Appearance

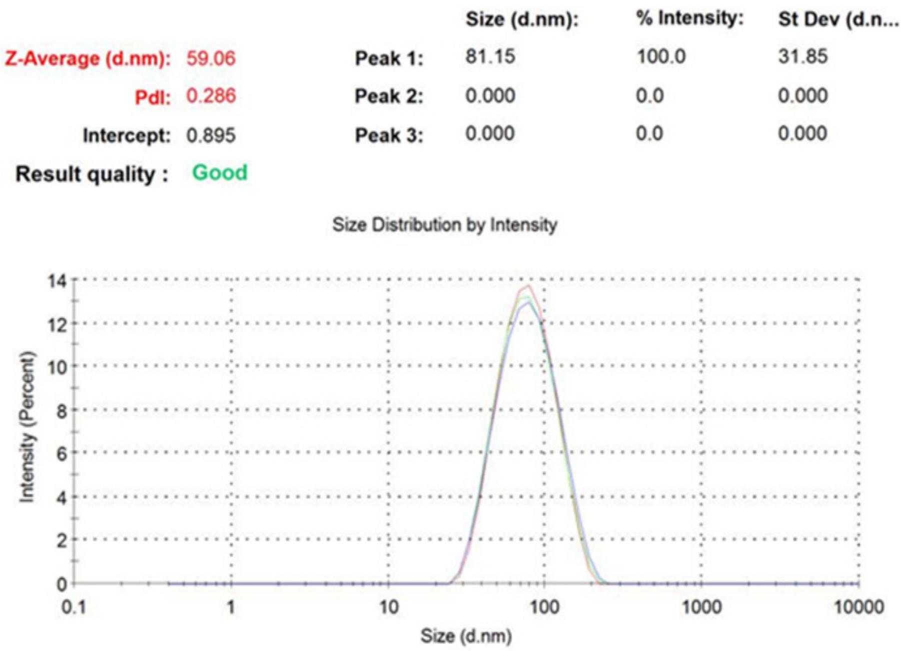

Fig. 6 Average particle size of synthesized colloidal AuNPs from DLS

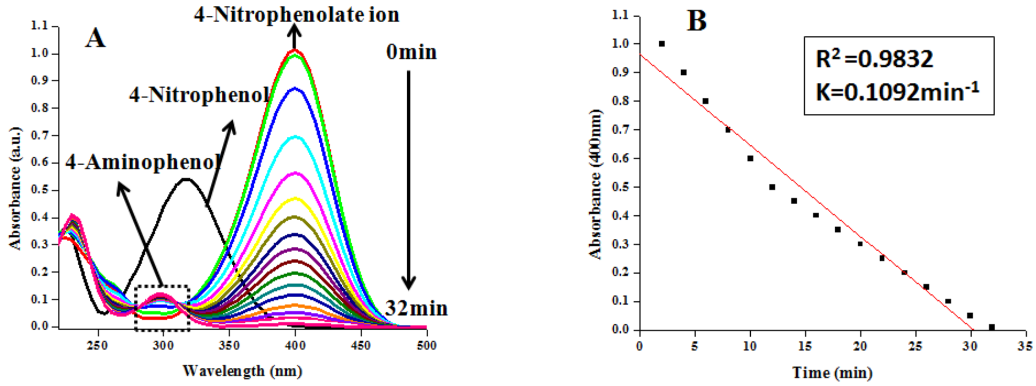

Fig. 7 (a) UV-visible; and (b) kinetic study of Au nanoparticles catalytic reduction of 4-NP

of a new absorption peak at ~299 nm, characteristic to the formation of 4-aminophenol confirms the reduction of 4-NP. Finally the reaction stops with a visual color change from dark yellow to colour less within 32 min. A linear fit in the kinetics plot (Fig. 7(b)) gives the rate constant "*k*" (0.1092 min^{-1}) corresponding to the pseudo first order reaction.

4. Conclusions

Green synthesis of AuNPs using *Coffea Arabica* fruit extract has been demonstrated for the first time, revealing a relatively broad size distribution and comparable catalytic efficiency with respect to the AuNPs prepared with conventional methods (Francyelle *et al*. 2016, Fenger *et al*. 2012). SEM and XRD measurements reveal the average crystallite size of around ~49±3 nm and ~49 nm respectively. The well-defined formation of AuNPs confirms the multifunctional nature (reducing and stabilizing agent) of *coffee Arabica* extract. Due to presence of biomass, the average NPs size from DLS and XRD/SEM is found to be different by 10%.

Changing the pH and/or the temperature of Au salt/*Coffea Arabica* fruit extract might give a possible solution for controlling the size distribution of the Au nanoparticles, which can replace both physical and chemical methods for different application fields.

Acknowledgments

The work has been financially supported by CONACyT CIAM -188657. BNK Reddy acknowledges the CONACyT Ph.D. scholarship no. 614234.

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