Research Article

Rapid biosynthesis of *Areca nut* seed extract mediated gold nanoparticles and its use in catalytic reduction of 4-nitrophenol to 4-aminophenol

Shib Shankar Dash*

Department of Chemistry, Government General Degree College, Salboni, Paschim Medinipur, 721 516, West Bengal, India

Received: 1 February 2019 Revised: 21 March 2019 Accepted: 30 March 2019

Abstract

Objective: *Areca nut* seed commonly used as ingredients in the preparation of betel has tremendous medicinal significance, is rich in different types of primary and secondary plant metabolites. In this work, the seed extract has been utilized in the synthesis of gold nanoparticles at room temperature under very mild conditions. **Material and methods:** The synthesis of the gold nanoparticles occurred rapidly and no extra stabilizing or capping agents were necessary. The gold nanoparticles were characterized by Surface Plasmon Resonance Spectroscopy, HRTEM, FTIR and X-ray Diffraction studies. **Results and conclusion:** The synthesized gold nanoparticles are almost spherical in shape with average size 15 nm. The Catalytic property of gold nanoparticles towards the reduction of 4-nitrophenol to 4-aminophenol has also been demonstrated. The results described here will be useful in nanoscience and nanotechnology.

Keywords: *Areca nut*, gold nanoparticles, green synthesis, catalytic reduction

Introduction

In recent years metal nanoparticles in the size range of 1-100 nm has also drawn considerable attention to the Scientists due to their unique properties and wide range of applications in our daily life (Jain et al., 2008; Daniel et al., 2004; Dykman et al., 2012; Murphy et al., 2008; Saha et al., 2012). Several considerable methods for the synthesis of metal nanoparticles are well reported in the literature includes reduction of metal salt using reducing agents such as sodium borohydride, N,N-dimethyl formamide, trisodium citrate, etc (Mittal et al., 2013). But major drawbacks of these methods associated with toxicity and chemical hazards. Currently, green chemistry has been introduced in the nano-science and nanotechnology as the principles, includes non toxicity and environmentally benign to nature. Recently, green synthesis of metal nanoparticles using bio molecules such as polyphenols, anthocyanins, organic acids etc has drawn much attention to the scientific community because of renewable nature and no other stabilizing agents are necessary for the metal nanoparticles (Anastas et al., 2002; Aromal et al., 2012; Chandran et al., 2006; Montes et al., 2011). Areca nut usually referred as *betel nut* is frequently grown around us has tremendous medicinal significance includes elimination of tapeworms and any intestinal parasites. It is use as major ingredients in the preparation of betel leaf and also used in ayurbedic medicine. In this study, the seed extract has also been utilized in the synthesis of AuNPs at room temperature under mild condition without any extra stabilizing or capping agents. The characterization of AuNPs has been carried out by Surface Plasmon Resonance spectroscopy, High Resolution Transmission Electron Microscopy (HRTEM), X-ray Diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). Recently, AuNPs plays key role in the field of catalysis (Zhang et al., 2012; Majumdar et al., 2012; Shiv et al., 2004). 4-nitrophenol (4-NP) is toxic in nature, strong skin irritant and imparts odor to water and used as building blocks of many dyes, explosives, pesticides. It has adverse effect on human health. So, several attempt has been taken to develop the method for its conversation to 4-aminophenol (4-AP). Here a safe and efficient method for the conversion of 4-NP to 4-AP utilizing *Areca nut* embedded stabilized AuNPs has been reported and rate constant of the reduction reaction has been calculated spectrophotometrically.

Address for Corresponding Author:
Shib Shankar Dash
Department of Chemistry, Government General Degree College, Salboni, Paschim Medinipur, 721 516, West Bengal, India
Email: shiba.chem@gmail.com

DOI: https://doi.org/10.31024/ajpp.2019.5.5.6

Material and Methods

Plant materials

Areca nut seeds were collected from local area, identified properly and the specimen was deposited in the College.

Chemicals

All chemicals used in the experiment were analytical reagent (AR) grade. Chloroauric acid ($HAuCl_4.H_2O$) was purchased from Merck and used as such. 4-nitrophenol and sodium borohydride were purchased from Nice Chemicals. Double distilled water was used for the experiments.

Synthesis of AuNPs

$HAuCl_4$ (13 mg) was dissolved in deionized water (10 mL) to obtain a 3.83 mM Au(III) stock solution. Aliquots of Au (III) solution (0.2 mL, 3.83 mM) were added drop-wise to the seed extract of *Areca nut* to prepare a series of stabilized AuNPs where concentration of the seed extract varied from 100-400 mg/L and the concentration of Au (III) remained fixed at 0.2 mM). UV-vis spectroscopy of the solutions was carried out after 1 hrs of mixing $HAuCl_4$ and the seed extract and a band in the vicinity of 545 nm confirm the formation of gold nanoparticles.

Catalytic properties of AuNPs for 4-NP reduction

The reduction of 4-nitrophenol to 4-aminophenol in the presence of $NaBH_4$ and AuNPs was studied as model reaction to confirm the catalytic activity of AuNPs. Aliquot of 4-nitrophenol (0.2 mL, 1 mM) was treated with freshly prepared sodium borohydride solution (3.4 mL, 16.4 mM) and 0.2 mL freshly prepared colloidal AuNPs (synthesized with 100 mgL^{-1} plant extract) in a 10 mm quartz cuvette. Then the reaction mixture was shaken thoroughly and the UV-visible spectrum was recorded at room temperature (23 - 27°C). The progress of the reaction was monitored properly.

Characterization of prepared AuNPs

The microstructural analysis of gold nanoparticles was carried out using several techniques. The size, shape and composition of the AuNPs were analyzed using high-resolution images obtained with a JEOL 2100 transmission electron microscope at an accelerating voltage of 200 KV. The X-ray diffraction (XRD) patterns of the stabilized AuNPs was acquired by Bruker D2 phase diffractometer with Cu-Kα radiation (λ = 1.542 Ǻ). UV-visible spectrum was carried out in Shimadzu spectrophotometer. FTIR spectra of the samples (with KBr pellet) were recorded using a Perkin Elmer Spectrum 2 instrument.

Results and discussion

The seed extract of *Areca nut* contains a large number of plant secondary metabolites including sugars, poly phenols, steroids, terpenoids, fatty acids, flavanoids, anthocyanines, etc. (Bhat et al., 2013). The antioxidant flavanoids and anthocyanines provide the *Areca nut* seed extract a brilliant red color. Several poly phenolic compounds with o-dihydroxy moiety such as gallic acid, quinic acid, caffeic acid, catechin, epicatechin, quercetin, etc. present in the seed extract of *Areca nut* plays the key role in reducing the chloroaurate ion and stabilizing the Au (0) atoms. Thus these compounds served as an effective reducing agent for Au (III) which has a high oxidation-reduction potential (Ferrer et al., 1999). The Au (0) thus formed undergo collision with its neighbours and form AuNPs and get stabilized by the benzoquinone derivatives obtained from the oxidation of poly phenols (Kim et al., 2005). The AuNPs particles are exceptionally stable as no agglomeration takes place on standing the solution for several months.

UV-visible spectroscopic analysis

The formation of AuNPs by the plant phytochemicals present in the seed extract of *Areca nut* was confirmed from the characteristic surface Plasmon resonance (SPR) band in the UV-visible spectra of the resulting solution containing seed extract and $HAuCl_4$ together (Figure 1). In this study a series of plant extracts with varied concentration (100-400 mg/L) were prepared by diluting the stock solution of seed extract in water (1000 mg/L). Aliquot of aqueous $HAuCl_4$ (0.4 ml, 3.8 mM) was added to the seed extract in a vial (4 ml) and resulting solution was mixed thoroughly and

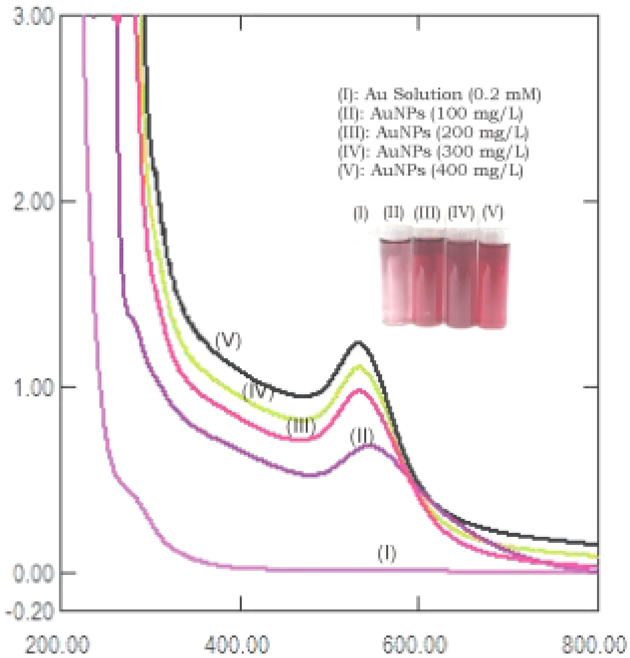

Figure 1. UV-vis spectra of (I) $HAuCl_4$ (0.2 mM), (II-V) AuNP's at 100, 200, 300, 400 mgL^{-1} concentrations of *Areca nut* seed extract respectively. Inset: Photograph of the vials containing the solutions (after 15 min of mixing).

allowed to keep at room temperature. After 15 minutes the color of the solution turns into red color indicating the formation of AuNPs. In the UV-visible spectroscopy a strong absorption peak at 545 nm was observed confirm its formation. With increasing concentration of the *Areca nut* seed extract, the intensities of these peaks increased attributed to the formation of more AuNPs in the media (Esumi et al., 2000; Beeram et al., 2010). A small blue-shift of the SPR band from 545 nm to 533 nm perhaps due to formation of smaller sized nanoparticles. Above the concentration 400 mg/L no further increase of the SPR band was observed due to complete reduction of the accessible Au (III) ions (Huang et al., 2010).

Micro structural analysis

XRD Studies

The crystallinity of the gold nanoparticles were confirmed from the five intense peaks in wide angle X-ray Diffraction of gold nanoparticles at 2ϴ = 37.9, 44.1, 63.9, and 77.4 which can be indexed as (111), (200), (220) and (311) reflections respectively based on the comparison with the standard data given by JCPDS file no. 04-0784 (Figure 2).

HRTEM, SAED and EDX Analysis

The size, shape and morphologies of the AuNPs obtained at different concentration of the *Areca nut* seed extract were characterized by Transmission Electron Microscopy (Figure 3). The average particle size of the nanoparticles is 15 nm. Nanoparticles formed were of spherical shaped. All the particles are well separated and no agglomeration was noticed. Selected Area Electron Diffraction (SAED) pattern revealed four rings of Brags reflections corresponding to crystalline fcc nature for AuNPs (Figure 2f). Energy Disperse X-ray (EDX) Spectroscopy was also performed to know the composition of the nanoparticles. The data revealed the presence of bio molecules consisting of carbon and oxygen along with the metallic gold.

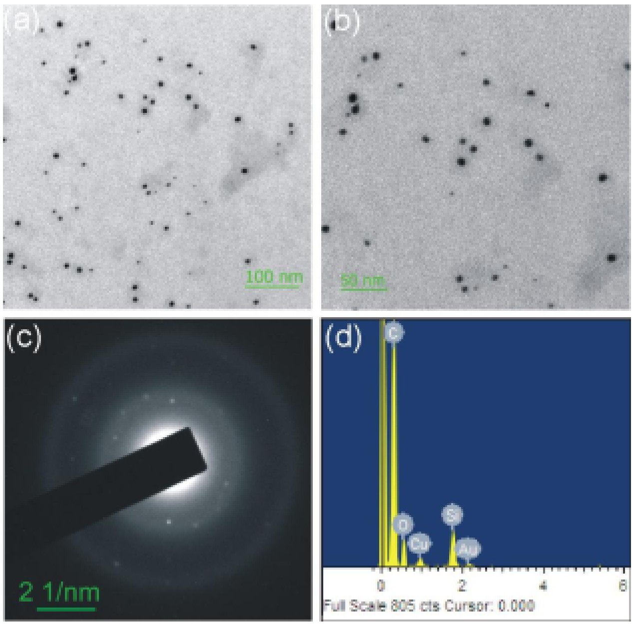

Figure 3. (a, and b) TEM Images of AuNPs (concentration of seed extract = 100 mgL^{-1}); (c) SAED image of AuNPs and (d) Energy dispersive X-ray spectroscopy.

FTIR Studies

In order to investigate the various types functional groups present in the bio molecules and their interactions with AuNPs, the FTIR spectra of seed extract and seed mediated AuNPs were compared (Figure 4). The –OH or -OH/-NH functionality of the bio molecules present in the seed extract was confirmed by a peak near 3300 cm^{-1}. A band nearly at 2915 cm^{-1} is due to aliphatic C-H stretching. The presence of carboxyl group in the biomass was confirmed from the strong absorption band at 1736 cm^{-1}. The presence of aromatic ring containing compounds was confirmed from the peak at 1605 and 1520 cm^{-1}. In case of colloidal AuNPs,

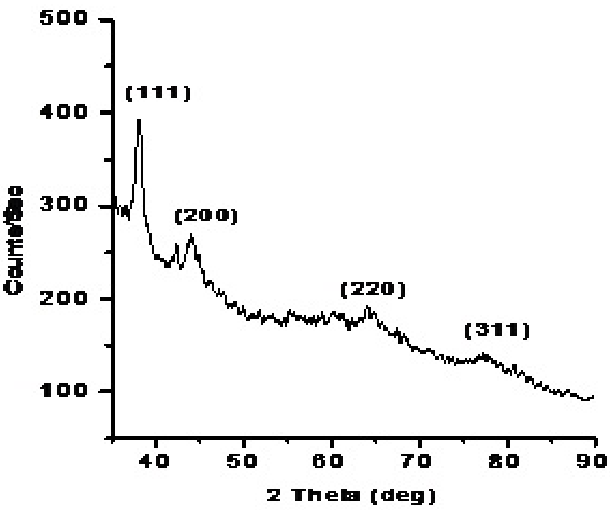

Figure 2. X-ray diffraction pattern of stabilized AuNPs

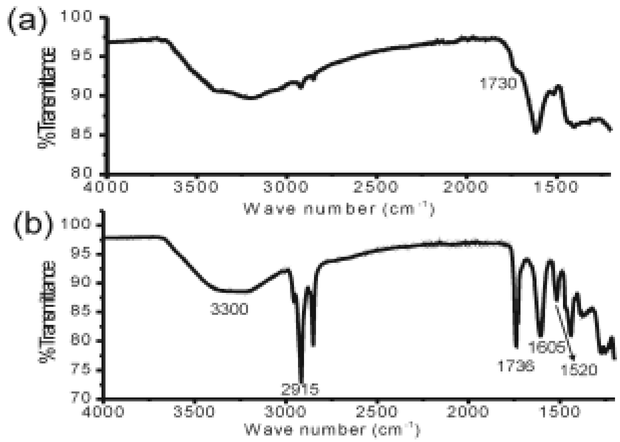

Figure 4. FTIR spectrum of (a) stable AuNPs and (b) *Areca nut* seed extract

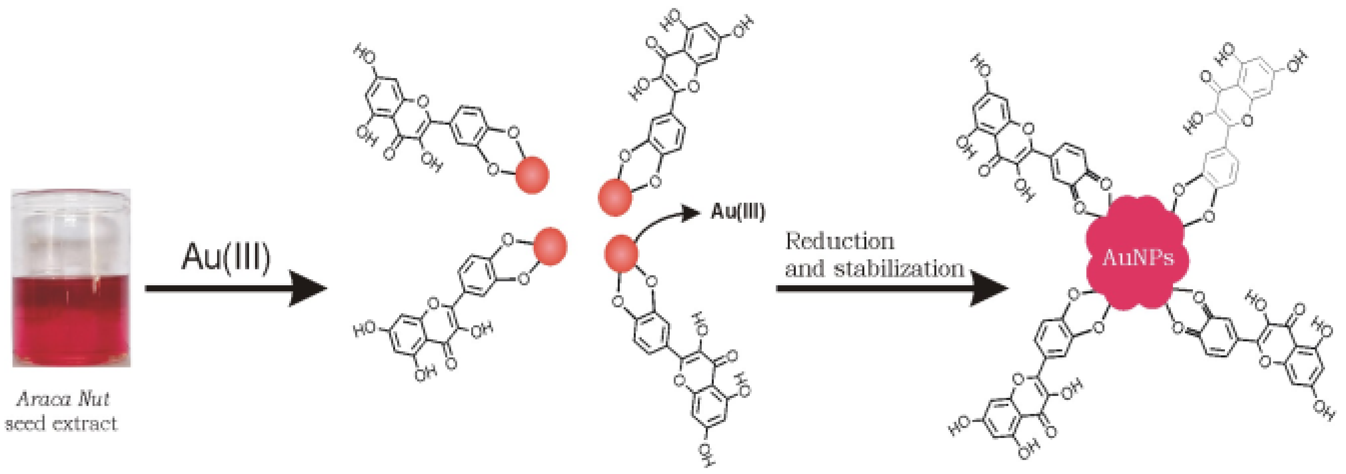

Figure 5. Mechanism of the formation and stabilization of AuNPs by polyphenolic compounds present in *Areca nut* seed extract

the peak due to -OH/-NH groups became narrower indicating the interaction with AuNPs. The peak due to carbonyl became significantly weaker due to interaction of carbonyl groups with AuNPs.

Mechanism of AuNPs formation and stabilization

Schematic illustration regarding AuNPs formation and its stabilization by the various types of bio molecules especially polyphenols present in the seed extract is shown in figure 5. Polyphenolic compound with vicinal diol moiety form five membered chelate ring with Au^{3+} ion and reduced them into Au^0 atoms and itself oxidized to quinones, as evident from the high oxidation-reduction potential of Au^{3+}/Au^0 couple compare to phenol/quinone. Au^0 thus formed collide with each other to form AuNPs and get stabilized by the quinones and as well as unreacted polyphenolic compounds (Huang et al., 2010; Prakash et al., 2011).

Catalytic properties of AuNPs

In recent years materials of nanoscale dimension have drawn much attention owing their unique application as catalyst in chemical transformations, which are normally restricted due to the large activation energy (Kim et al., 2009). The electrochemical potential value (E^0) suggest that the reduction of 4-NP to 4-AP by sodium borohydride ($NaBH_4$) is a thermodynamically allowed reaction (E_0 for 4-NP/4-AP -0.76 and for H_3BO_3/BH_4^- -1.33 V). In the UV-visible spectroscopy the absorption maxima of 4-NP (0.05 mM) appeared at 319.5 nm. However, on treatment with a freshly prepared aqueous solution of $NaBH_4$ (15 mM), the color of the solution changes to deep yellow and bathochromic shift of the absorption maxima takes place at 401.0 nm due to the formation of stable 4-nitrophenolate ion (Figure 6). But the reduction of the nitro group to amino group does not occur on standing the reaction mixture for several days due to high activation energy. However, on addition of seed extract mediated freshly prepared colloidal AuNPs (0.1 mL, 100 mg/L) to the reaction mixture, surprisingly, the absorption intensity at 401.0 nm reduces with concomitant formation

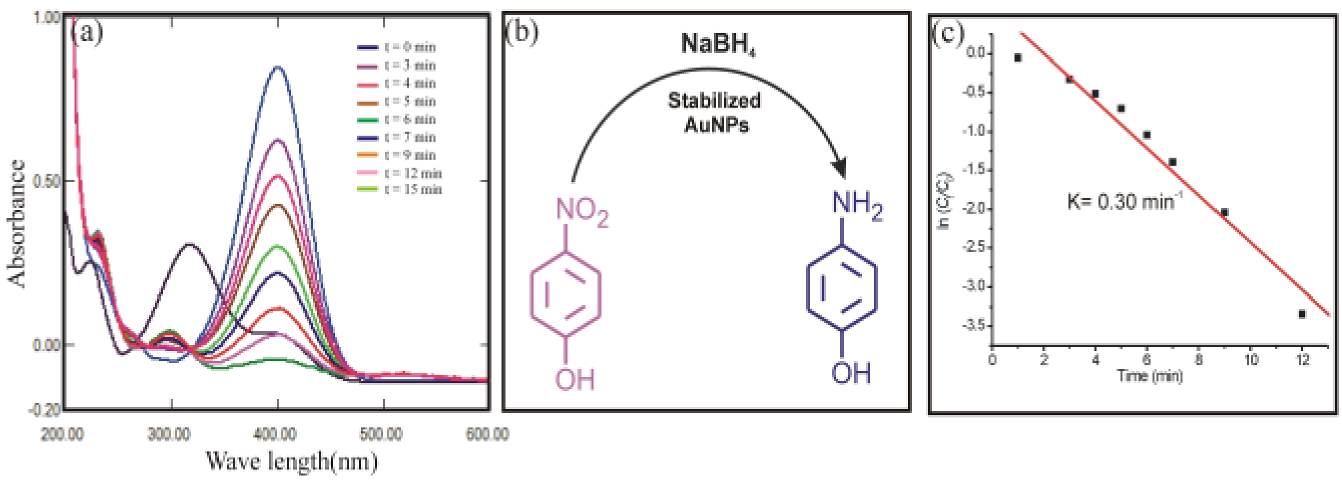

Figure 6. (a) UV-visible spectrum of 4-nitrophenol in the presence of sodium borohydride (15 mM) and AuNPs (100 mg/L) catalyst in the reaction mixture; (b) scheme of the reduction reaction and (c) plot of ln (C_t/C_0) vs time.

of a new peak at 297.5 nm indicating the formation of 4-AP. Therefore, it is evident that the reduction of 4-NP is solely activated by the presence of seed extract. The generation of H_2 gas helps the reaction mixture to keep in the stirring condition (Wei et al., 2010). Complete disappearance of the 401.0 nm peak was observed within 15 minutes. As the concentration of BH_4^- was much larger than that of 4-NP the reaction rate is independent on the $NaBH_4$ concentration. Therefore, a pseudo-first-order rate kinetics is used to evaluate the rate of the reaction and calculated to be 0.30 min^{-1}. This rate constant value was comparable to the reported values in the literature (Gangula et al., 2011).

Conclusions

In this paper an eco friendly method for synthesis of AuNPs has been described using the seed extract of *Areca nut*, well known medicinally important ingredients in our daily life. Various types of bio molecules present in the seed extract plays key role in reducing and stabilizing the AuNPs where no additional reagent is necessary for the stabilization. Micro structural analysis revealed that the AuNPs are almost spherical shaped with average size15 nm. The as synthesized colloidal AuNPs have also been utilized as an efficient catalyst for the reduction of 4-nitrophenol to 4-aminophenol in the presence of $NaBH_4$. As seed extract of *Areca nut* has medicinal significance the results described here will be useful for its use in biomedical science as well as nanoscience and nanotechnology.

Competing interests

The author declares that he has no competing interests.

References

Anastas PT, Kirchhoff MM. 2002. Origins, Current Status, and Future Challenges of Green Chemistry Accounts of Chemical Research, 35: 686-694.

Aromal SA, Philip D. 2012. Facile one- pot synthesis of gold nanoparticles using tannic acid and its application in catalysis. Physica E, 44:1692.

Aromal SA, Vidhu VK, Philip D. 2012. Green synthesis of well-dispersed gold nanoparticles using Macrotyloma uniflorum. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 85: 99-104.

Beeram SR, Zamborini FP. 2010. Purification of Gold Nanoplates Grown Directly on Surfaces for Enhanced Localized Surface Plasmon Resonance Biosensing, ACS Nano, 4: 3633–3646.

Bhat R, Ganachari S, Deshpande R, Ravindra G, Venkataraman A. 2013. Rapid Biosynthesis of Silver Nanoparticles Using Areca Nut (*Areca catechu*) Extract Under Microwave-Assistance. Journal of Cluster Science, 24: 107-114.

Chandran SP, Chaudhary M, Pasricha R, Ahmad A, Sastry M. 2006. Synthesis of gold nanotriangles and silver nanoparticles using Aloe vera plant extracts. Biotechnology Progress, 22:577–583.

Daniel MC, Astruc D. 2004. Gold nanoparticles: assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology. Chemical Review, 104:293.

Dykman L, Khlebtsov N. 2012. Gold nanoparticles in biomedical applications: recent advances and perspectives. Chemical Society Review, 41:2256-82.

Esumi K, Suzuki A, Yamahira A, Torigoe K. 2000. Role of Poly (amidoamine) Dendrimers for Preparing Nanoparticles of Gold, Platinum, and Silver. Langmuir, 16:2604-08.

Ferrer M, Reina R, Rossell O, Seco M. 1999. Anionic iron clusters as building blocks for the synthesis of higher nuclearity compounds containing 11- and 12-group elements Coordin. Coordination Chemistry Review, 193-5:619-42.

Gangula A, Podila R, Ramakrishna M, Karanam L, Janardhana C, Rao AM. 2011. Catalytic Reduction of 4-Nitrophenol using Biogenic Gold and Silver Nanoparticles Derived from Breynia rhamnoides. Langmuir, 27: 15268-15274.

Huang X, Wu H, Liao X, Shia B. 2010. One-step, size-controlled synthesis of gold nanoparticles at room temperature using plant tannin. Green Chemistry, 12:395–99.

Jain PK, Huang X, El-Sayed IH, El-Sayed MA. 2008. Noble Metals on the Nanoscale: Optical and Photothermal Properties and Some Applications in Imaging, Sensing, Biology, and Medicine. Accounts of Chemical Research, 41:1578-86.

Kim YH, Nakano Y. 2005. Adsorption mechanism of palladium by redox within condensed-tannin gel. Water Research, 39:1324-30.

Majumdar R, Bag BG. 2012. Terminalia arjuna bark extract mediated size controlled synthesis of polyshaped gold nanoparticles and its application in catalysis. International Journal of Research in Chemistry and Environment, 2: 338-342.

Mittal AK, Chisti Y, Banerjee UC. 2013. Synthesis of metallic nanoparticles using plant extracts, Biotechnology Advances, 31:346–356.

Montes MO, Maoral A, Deepak FL, Parsons JG, Yacaman JM, Peralta-Videa JR, Gardea-Torresdey JL. 2011. Anisotropic gold nanoparticles and gold plates biosynthesis using alfalfa extracts. Journal of Nanoparticle Research, 13:3113-21.

Murphy CJ, Gole AM, Stone JW, Sisco, PN, Alkilany AM, Goldsmith EC, Baxter SC. 2008. Gold Nanoparticles in Biology: Beyond Toxicity to Cellular Imaging, Accounts of Chemistry Research, 41:1721 – 1730.

Prakash CVS, Prakash I. 2011. Bioactive Chemical Constituents from Pomegranate (*Punica granatum*) Juice, Seed and Peel-A Review. International Journal of Research in Chemistry and Environment, 1:1-18.

Saha K, Agasti SS, Kim C, Li X, Rotello VM. 2012. Gold Nanoparticles in Chemical and Biological Sensing. Chemical Review, 112:2739.

Shiv SS, Rai A, Ahmad A, Sastry M. 2004. Rapid synthesis of Au, Ag, and bimetallic Au core–Ag shell nanoparticles using Neem (Azadirachta indica) leaf broth. Journal of Colloid and Interface Science, 275(2): 496.

Zhang Y, Cui X, Shi F, Deng Y. 2012. Nano-Gold Catalysis in Fine Chemical Synthesis. Chemical Review, 112: 2467.

Wei D, Ye Y, Jia X, Yuan C, Qian W. 2010. Chitosan as an active support for assembly of metal nanoparticles and application of the resultant bioconjugates in catalysis. Carbohydrate Research, 345:74.