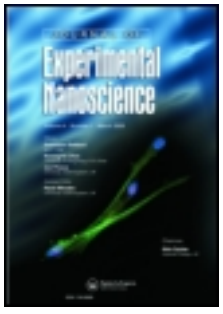

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Gold nanoparticles by Terminalia bellirica aqueous extract - a rapid green method

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Gold nanoparticles by *Terminalia bellirica* aqueous extract – a rapid green method

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Synthesis of metal nanoparticles (NPs) using plant extracts as reducing agents is of great interest due to its ease and environmental friendly process. Reports show biogenic green synthesis reaction times in forming gold metal nanoparticles (Au NPs) varying from minutes to several hours. In this article, an instantaneous (less than 10 s) method for the green synthesis of gold NPs using aqueous extract of *Terminalia bellirica* as a reducing and stabilising agent has been reported. Formation of Au NPs was instantaneous and confirmed by UV-Vis spectroscopy where surface plasmon resonance band centred at 530 nm. Formation of anisotropic Au NPs was evidenced from transmission electron microscope studies. High levels of polyphenols in *T. bellirica* were responsible for the rapid reduction and stabilisation. The Au NPs did not display toxicity when tested by the brine shrimp (*Artemia salina*) assay.

Keywords: *Terminalia bellirica*; anisotropic Au NPs; brine shrimp

1. Introduction

Gold nanoparticles (Au NPs) with flexible properties have been used in biomedical applications mainly in drug delivery, cellular imaging, etc. [1]. Since Au NPs are used in many human contact applications, it is necessary to avoid the toxic chemicals and stabilisers involved in the synthesis process of Au NPs. In this context, biogenic green methods stand as the finest technique to synthesise Au NPs. These green techniques use no toxic chemical/hazardous materials and hence eco-friendly.

In recent years, many researchers have brought out the potential of plants in synthesising Au NPs [2–10]. But most of these green techniques require more reaction times from several minutes to hours [2–11]. Recently, rapid synthesis of Au NPs was reported using the extracts of *Mangifera indica* leaf [2] and Tansy fruit [3] where formation of NPs was observed within 2 and 20 min, respectively. More rapid reduction at high temperatures using *Murraya koenigii* leaf [4] extract was demonstrated. In this study, a rapid technique to synthesise Au NPs where phenolic rich [12] aqueous extract of *Terminalia bellirica* used for reduction and stabilisation has been explored and the impact of Au NPs against brine shrimp (*Artemia salina*) was studied following brine shrimp lethality assay [13]. To our knowledge, this article reports *T. bellirica* mediated rapid and green synthesis of Au NPs for the first time.

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2. Experimental

2.1. *Synthesis of gold NPs*

One gram of finely powdered *T. bellirica* dry fruit pericarp (local purchase) was added to 100 mL of deionised water and heated at 90°C in a temperature controlled water bath for 1 h, cooled and filtered using 0.2 μm cellulose nitrate membrane filter paper. About 200 μL of freshly prepared warm extract was added to 2 mL of 1 mM $HAuCl_4$ (Sigma Aldrich, India) and mixed thoroughly. Instantaneous colour change was observed from yellow to reddish pink which indicated the formation of Au NPs. The solid Au NPs were separated out by centrifugation at 15,000 rpm and washed thrice with deionised water followed by air drying.

2.2. *Brine shrimp lethality assay*

About 1 g of *A. salina* (Linnaeus) cysts (Sanders Great Salt Lake, Brine Shrimp Company L.C., USA) was freshly hatched and free-swimming nauplii were used for the bioassay in this study. The assay system was prepared with 2 mL of filtered seawater containing 20 nauplii. The Au NPs at 250, 500 and 1000 mg/L were used as test samples to check the brine shrimp lethality assay in triplicates. In each test container, 20 nauplii were transferred and the setup was allowed to remain for 24–48 h under constant illumination. After 24–48 h, the dead nauplii were counted with a hand lens.

2.3. *Characterisation of Au NPs*

The preliminary characterisation of synthesised Au nanocolloids was carried out using UV-Vis spectroscopy. The UV-Vis absorption spectra of thus obtained Au nanocolloids were monitored using a Jasco V-670 UV-Vis spectrophotometer after 5-fold dilution with deionised water.

The purified solid Au NPs obtained after centrifugation at 15,000 rpm was subjected to powder X-ray analysis. Powder X-ray diffraction (XRD) analysis was done using Bruker D8 Advance Diffractometer (Bruker AXS, Germany) with Cu-Kα radiation ($\lambda = 1.54$ Å). XRD pattern of Au NPs was recorded over a 2θ range of 10–90° with scanning rate 4°/min and with a step size of 0.02°.

Morphology, crystalline nature and size of Au NPs were determined by HRTEM (JEOL JEM 2100 high resolution transmission electron microscope) operated at an accelerating voltage of 200 kV. Sampling was done by dispersing the sample using an ultrasonic bath and a drop of the dispersion was applied on a Cu grid with ultrathin Cu on a holey C-film and allowed to dry in vacuum. EDAX (energy-dispersive X-ray spectroscopy) pattern was recorded in order to check the surface inter-atomic distribution.

FT-IR measurements were carried out for solid Au NPs on a JASCO FT-IR 4100 instrument at room temperature with a resolution of 4 cm^{-1} in KBr pellets against *T. bellirica* pericarp powder as control.

3. Results and discussion

The formation of Au NPs was evidenced *in situ* by the visible colour change from yellow to reddish pink on addition of *T. bellirica* extract to chloroauric acid. UV-Vis spectroscopic studies (Figure 1a) on Au nanocolloids showed two distinct surface plasmon resonance (SPR) bands: one was in the visible region around 530 nm and other broad band appeared very close to the near-infrared (NIR) region. The latter band indicated the anisotropic nature of the NPs [14]. It is well known that the uniform spherical NPs show only one SPR band, whereas the anisotropic NPs show two or more bands because of quadrupole and multipole plasmon excitations [15]. The absorption of NPs in the NIR region makes them useful for fabricating

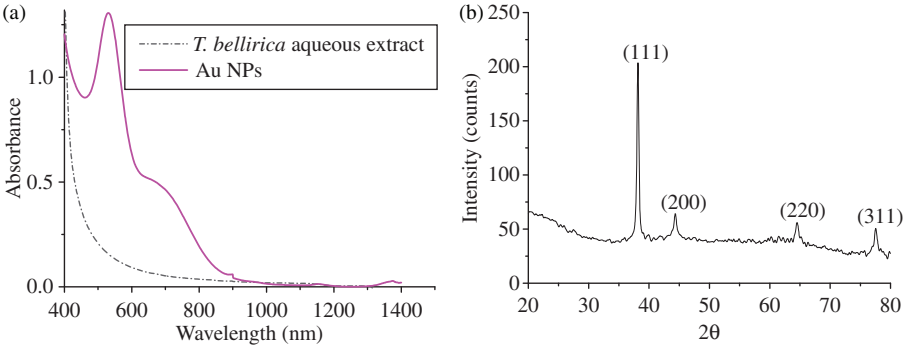

Figure 1. (a) UV-Vis spectrum of Au nanocolloids and (b) powder XRD pattern of Au NPs.

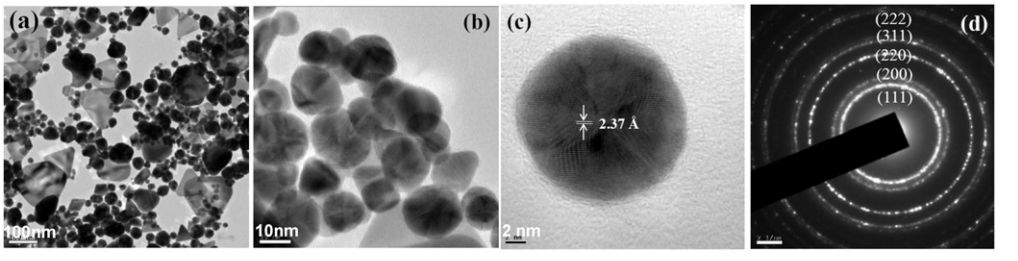

Figure 2. Study of morphology of Au NPs: (a, b) TEM, (c) HRTEM and (d) SAED pattern of Au NPs.

medical and sensing devices [16,17]. No visible sedimentation was observed even after 2 months suggesting that the synthesised Au NPs were stabilised by oxidised polyphenols.

The XRD pattern of the synthesised Au NPs is shown in Figure 1(b). It is clear that the Au NPs formed were crystalline in nature. The XRD pattern showed four distinct peaks at 38.16, 44.33, 64.51 and 77.54 which could be indexed to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of cubic Au NPs, respectively, and were in conformity with the JCPDS database (JCPDS no. 00-004-0784).

HRTEM images at different magnifications and selected area electron diffraction (SAED) pattern are shown in Figure 2. The sizes of the NPs formed were in the range of 10–130 nm (Figure 2a and b). It is clear from the TEM image that the synthesised Au NPs consisted of majority of spheres, few triangles, pentagons and hexagons which circuitously supported the broad band formed close to the NIR region due to formation of anisotropic Au NPs (Figure 2a). The spherical NPs formed initially were stable because of sufficient amount of reduced polyphenols available for protecting Au NPs by co-ordination of carbonyl groups present in oxidised polyphenols. The NPs which formed later were less stable due to insufficiency in available protective oxidised polyphenols; hence thermodynamically unstable [18,19]. Because of rapid reduction, room temperature sintering and assembly, the unprotected spherical NPs lead to the formation of various crystal structures such as triangular, pentagonal and hexagonal Au NPs [19]. In order to minimise the surface energy of freshly formed triangles and pentagons, these NPs endured a shrinking process which resulted in blunted angel anisotropic NPs. Similar reports can be seen in Au NPs synthesised using *Coleus amboinicus lour* [17], *Terminalia chebula* [11] and apiin [5]. Although the detailed study on the concentration of polyphenol in plant

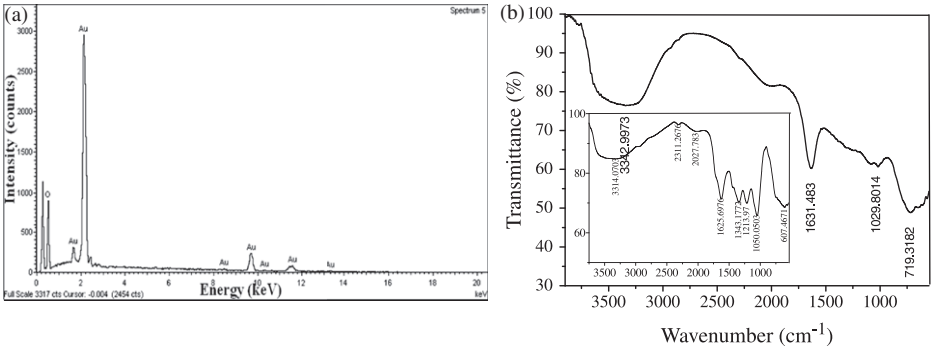

Figure 3. (a) EDAX pattern of Au NPs and (b) FT-IR spectra of Au NPs. Inset: FT-IR spectrum of *T. bellirica* dry fruit pericarp powder.

extract *versus* morphology of Au NPs is missing in the literature, Smitha et al. [15] demonstrated that the increase in quantity of extract lead to the formation of uniform and finely dispersed spherical Au NPs because of higher availability of protecting molecules which bound the freshly budding nanocrystals, while reduction with lower quantity of extracts ended with anisotropic structures due to lack of protecting molecules. The spacing between the fringes was 2.37 Å (Figure 2c) which was in close agreement with spacing of (1 1 1) planes of FCC gold (JCPDS no. 00-004-0784). The SAED pattern shows that the formed NPs were polycrystalline in nature and the patterns were assigned as (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) reflections (Figure 2d). Simultaneous EDAX spectrum was recorded which showed only the signals of gold and no other peaks were observed which indicated that the synthesised Au NPs were essentially pure (Figure 3a).

FT-IR analysis was done for the synthesised Au NPs and *T. bellirica* dry fruit pericarp powder in order to check the capping of bio-molecules onto the surface of Au NPs. FT-IR analysis (Figure 3b) of *T. bellirica* powder showed the strong IR bands at 3314, 1625, 1343, 1213 and 1050 cm^{-1}. The bands observed at 3314 and 1625 cm^{-1} correspond to –OH and –C=O stretching modes, respectively. The bands at 1343, 1213 and 1050 cm^{-1} were due to –C–O stretching, –C–O–H bending and –C–O–C stretching modes, respectively. FT-IR spectrum of Au NPs showed the strong IR bands at 3342, 1631 and 1029 cm^{-1} which were due to –O–H, –C=O and –C–O–C stretching modes, respectively. So, this observation confirmed the capping of bio-molecules on Au NPs. In the FT-IR spectrum of Au NPs, the intense peak at 1631 cm^{-1} of –C=O stretching mainly indicated that the enhanced stability was due to capping of oxidised polyphenols by the co-ordination of carbonyl groups on the Au NPs surface. Similar type of strong interaction between carbonyl group of polyvinylpyrrolidone and Au core was demonstrated by Zhou et al. [20]. The brine shrimp lethality assay was done for Au NPs which showed no drop in survival of nauplii (*A. salina*) within 48 h which suggested non-toxic nature of the synthesised Au NPs up to 1000 mg/L.

The recent literature for synthesising Au NPs using *Mentha piperita* [21], palm oil [22], sugar beet pulp [23] and *Zingiber officinale* [24] required 24 h, 48 h, 48 h and 20 min, respectively. When compared with the previous literature, the present method to synthesise Au NPs required very less time. Time required for the complete conversion of Au^{3+} to Au NPs was less than a minute. Thus obtained Au nanocolloids were stable for a period of 2 months due to the co-ordination of carbonyl groups of oxidised polyphenols onto the surface of Au NPs. In addition, Au nanocolloids did not show any toxicity when tested by the brine shrimp (*A. salina*) assay up

to 1000 mg/L. Because of non-toxic nature, these Au NPs can be used in a wide range of biological and organic applications.

4. Conclusion

An *in situ* green method using *T. bellirica* dry fruit pericarp aqueous extract has been demonstrated and confirmed the formation of anisotropic Au NPs by both UV-Vis and TEM studies. Capping of Au NPs by oxidised polyphenols which was evidenced by FT-IR, indeed enhanced stability of Au NPs more than 2 months. Also the synthesised Au NPs were benign to *Artemia nauplii* up to 1000 mg/L. Since the obtained Au NPs were free from toxic impurities, it can be used in a variety of medical and biological applications.

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References

[1] S.H. Huang, *Gold nanoparticle-based immunochromatographic test for identification of* Staphylococcus aureus *from clinical specimen*, Clin. Chim. Acta 373 (2006), pp. 139–143.
[2] D. Philip, *Rapid green synthesis of spherical gold nanoparticles using* Mangifera indica *leaf*, Spectrochim. Acta A 77 (2010), pp. 807–810.
[3] S.P. Dubey, M. Lahtinen, and M. Sillanpaa, *Tansy fruit mediated greener synthesis of silver and gold nanoparticles*, Process Biochem. 45 (2010), pp. 1065–1071.
[4] D. Philip, C. Unni, S.A. Aromala, and V.K. Vidhu, *Murraya Koenigii leaf-assisted rapid green synthesis of silver and gold nanoparticle*, Spectrochim. Acta A 78 (2011), pp. 899–904.
[5] J. Kasthuri, S. Veerapandian, and N. Rajendiran, *Biological synthesis of silver and gold nanoparticles using apiin as reducing agent*, Colloids Surf. B 68 (2009), pp. 55–60.
[6] A.M. Fayaz, M. Girilal, R. Venkatesan, and P.T. Kalaichelvan, *Biosynthesis of anisotropic gold nanoparticles using* Maduca longifolia *extract and their potential in infrared absorption*, Colloids Surf. B 88 (2011), pp. 287–291.
[7] R.K. Das, P. Sharma, P. Nahar, and U. Bora, *Synthesis of gold nanoparticles using aqueous extract of* Calotropis procera *latex*, Mater. Lett. 65 (2011), pp. 610–613.
[8] V.G. Kumar, S.D. Gokavarapu, A. Rajeswari, T.S. Dhas, V. Karthick, Z. Kapadia, T. Shrestha, I.A. Barathy, A. Roy, and S. Sinha, *Facile green synthesis of gold nanoparticles using leaf extract of antidiabetic potent* Cassia auriculata, Colloid Surf. B 87 (2011), pp. 159–163.
[9] R.K. Das, B.B. Borthakur, and U. Bora, *Green synthesis of gold nanoparticles using ethanolic leaf extract of* Centella asiatica, Mater. Lett. 64 (2010), pp. 1445–1447.
[10] L. Castro, M. Luisa Blazquez, J.A. Munoz, F. Gonzalez, C. Garcia-Balboa, and A. Ballester, *Biosynthesis of gold nanowires using sugar beet pulp*, Process Biochem. 46 (2011), pp. 1076–1082.
[11] K. Mohan Kumar, B.K. Mandal, M. Sinha, and V. Krishnakumar, *Terminalia chebula mediated green and rapid synthesis of gold nanoparticles*, Spectrochim. Acta A 86 (2012), pp. 490–494.
[12] S. Surveswaran, Y.Z. Cai, H. Corke, and M. Sun, *Systematic evaluation of natural phenolic antioxidants from 133 Indian medicinal plants*, Food Chem. 102 (2007), pp. 938–953.
[13] B.N. Meyer, N.R. Ferrigni, J.E. Putnam, L.B. Jacobsen, D.E. Nichols, and J.L. McLaughlin, *Brine shrimp: A convenient general bioassay for active plant constituents*, Planta Med. 45 (1982), pp. 31–34.
[14] L.M. Liz Marzan, *Tailoring surface plasmons through the morphology and assembly of metal nanoparticles*, Langmuir 22 (2006), pp. 32–41.
[15] S.L. Smitha, D. Philip, and K.G. Gopchandran, *Green synthesis of gold nanoparticles using* Cinnamomum zeylanicum *leaf broth*, Spectrochim. Acta A 74 (2009), pp. 735–739.
[16] A.G. Skirtach, C. Dejugnat, D. Braun, A.S. Susha, A.L. Rogach, W.J. Parak, H. Mohwald, and G.B. Sukhorukov, *The role of metal nanoparticles in remote release of encapsulated materials*, Nano Lett. 5 (2005), pp. 1371–1377.
[17] X. Xu, M. Stevens, and M. Cortie, *In situ precipitation of gold nanoparticles onto glass for potential architectural applications*, Chem. Mater. 16 (2004), pp. 2259–2266.
[18] K.B. Narayanan and N. Sakthivel, *Phytosynthesis of gold nanoparticles using leaf extract of* Coleus amboinicus *Lour*, Mater. Charact. 61 (2010), pp. 1232–1238.

[19] J. Huang, Q. Li, D. Sun, Y. Lu, Y. Su, X. Yang, H. Wang, Y. Wang, W. Shao, N. He, J. Hong, and C. Chen, *Biosynthesis of silver and gold nanoparticles by novel sundried* Cinnamomum camphora *leaf*, Nanotechnology 18 (2007), pp. 105104–105114.

[20] M. Zhou, B. Wang, Z. Rozynek, Z. Xie, J.O. Fossum, X. Yu, and S. Raaen, *Minute synthesis of extremely stable gold nanoparticles*, Nanotechnology 20 (2009), pp. 505606–505615.

[21] D.M. Ali, N. Thajuddin, K. Jeganathan, and M. Gunasekaran, *Plant extract mediated synthesis of silver and gold nanoparticles and its antibacterial activity against clinically isolated pathogens*, Colloids Surf. B 85(2) (2011), pp. 360–365.

[22] P.P. Gan, S.H. Ng, Y. Huang, and S.F.Y. Li, *Green synthesis of gold nanoparticles using palm oil mill effluent (POME): A low-cost and eco-friendly viable approach*, Bioresource Technol. 113 (2012), pp. 132–135.

[23] L. Castro, M.L. Blázquez, F. González, J.A. Muñoz, and A. Ballester, *Extracellular biosynthesis of gold nanoparticles using sugar beet pulp*, Chem. Eng. J. 164(1) (2010), pp. 92–97.

[24] K.P. Kumar, W. Paul, and C.P. Sharma, *Green synthesis of gold nanoparticles with* Zingiber officinale *extract: Characterization and blood compatibility*, Process Biochem. 46(10) (2011), pp. 2007–2013.