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# Phyto mediated biogenic synthesis of gold nanoparticles using *Cerasus serrulata* and its utility in detecting hydrazine, microbial activity and DFT studies

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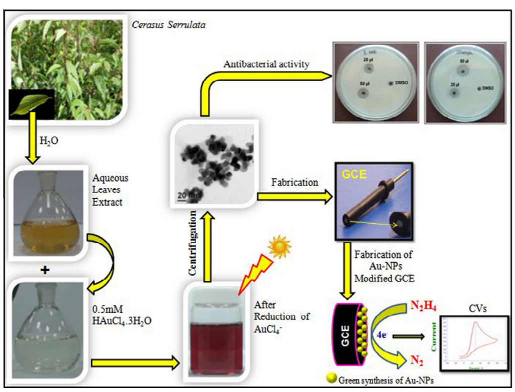
## GRAPHICAL ABSTRACT

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## ABSTRACT

Green synthesis of Au-NPs using *Cerasus serrulata* (*C. serrulata*) leaves extract has emerged as a nontoxic and ecofriendly option, as compared to currently available chemical and/or physical methods and also Au-NPs act as both reducing and stabilizing agent. The developed Au-NPs were characterized with XRD, UV–visible spectroscopy, FTIR, SEM, TEM and chemical constituents of *C. serrulata* leaves extract after and before reduction of Au-NPs have been identified through GC–MS. TEM images confirmed that biosynthesized Au-NPs were spherical in shape and approximately in the range of 5–25 nm. The electrochemical results showed remarkable electrocatalytic activity of the Au-NPs-modified GC electrode in the detection of environmentally hazardous pollutant like hydrazine. The modified electrode exhibits a wide linear range 5 nM to 272 μM with low detection limit 0.05 μM. The fabricated sensor shows good selectivity towards other electroactive species as well. Thus the proposed sensor seems to be a potential candidate for developing a simple, rapid and cost-effective electrochemical sensor. The synthesized Au-NPs exhibited higher antibacterial activity against gram negative (*Escherichia coli*) than gram positive (*Staphylococcus aureus*) bacteria. DFT studies revealed that the coumarin (CM) present in the *C. serrulata* leaves extract demonstrated greater reducing and stabilizing properties compared to the properties of other compounds like butylhydroxytoluene (BHT) and hydrocoumarin (HCM) present in the extract.


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## 1. Introduction

Hydrazine or its derivatives generally used in plant growth regulators, insecticides, rocket propellants, corrosion inhibitors, agricultural, as fuel cells, explosives and industrial application [1,2]. Hydrazine is also recognized to be very harmful to human life and environment pollutants because of its high toxicity and irritation effect of the eyes, nose, and throat, dizziness, headache, nausea, pulmonary edema, seizures, coma in humans. Further, hydrazine shows neurotoxin, hepatotoxic substance [3], mutagenic and carcinogenic effects, and can cause damages to liver, lungs, kidney and central nervous system of living organism if hydrazine is inhaled or introduced to the skin. Serious effects on the reproductive system are observed in animals after hydrazine inhalation. These effects have included reduced ovary and testes size and decreased sperm production [4,5]. Therefore, the precise and sensitive detection of hydrazine is of great importance. Compared with the other previews methods for the detection of hydrazine such as fluorescence, spectrophotometry, chromatography and titration [6–11], the electrochemical method provides more comprehensible advantages including low cost, rapid response, wide linear range, portability, high sensitivity, selectivity and operating procedure [12–14]. Regrettably, hydrazine exhibits irreversible oxidation effectively higher overpotential at conventional electrodes. A variety of organic and inorganic resources have been used to fabricate chemically modified electrodes for the detection of hydrazine, which can considerably lower over potential and improve the electron transfer rate [15–19].

Interestingly, in recent years, the metal nanomaterials especially noble metals such as Pd, Pt, Au, Ag, and Ru [20] are used in many applications for electrocatalyst because they demonstrate a high surface to volume ratio, exhibit high stability, excellent electrocatalytic properties, optical, unique electronic, and chemical properties. Furthermore, they are commonly available and give rapid electron transfer rates [21–24]. Noble metal nanoparticles have also been used mostly in biosensor and electrochemical sensor for the fabrication, in specifically; the green synthesized gold nanoparticles (Au-NPs) is a growing research area due to the potential application for the development of novel technologies [25]. Eco-friendly, simple, reproducible and cost-effective procedures for the synthesis of nanoparticles are of interest to biologists, chemists and materials scientists alike, especially in light of efforts to find "greener" methods of inorganic material synthesis and much faster as compared to microorganisms, glucose, chitosan, starch and stable formation of metal nanoparticles [26–33]. In the past decades green nanoparticle synthesis has evolved into an important branch of nanotechnology because of its potential application in the biomedical, magnetic, energy science and aerospace industries. Large amounts of nanoparticles can be easily synthesized from plants and the majority of these are nontoxic [34–37]. Most of the metal nanoparticles have oxidation and catalytic properties [38]. In addition, the Au-NPs generally known as an excellent electrocatalytic and very active material for the hydrazine oxidation [39]. The previously demonstrated hydrazine sensor shows low sensitivity, high linear range and high detection limits. Therefore, still there is a need to develop a highly sensitive, robust and reliable hydrazine electrochemical sensor based on green synthesis of nanomaterials. The easy and low cost novel nanomaterials with superior properties for the detection of hydrazine will surely get more attention to the readers of analytical chemistry and nano science.

The genus Cerasus belongs to the subfamily *Prunoideae* within the family *Rosaceae*, and comprises about 150 species mainly distributed in the temperate northern hemisphere, especially in China, Japan and Korea. More often it is treated as the subgeneric or sectional level within the genus Prunus. Cerasus species are widely cultivated in China for their edible fruits or as garden ornamentals. *Cerasus serrulata* is a deciduous tree of 3–8 m tall and bears white or rarely pink petals during the blooming period from April to May. It is mainly growing in mountain forests, and is also planted throughout China. This species are popular ornamentals [40]. Essential oils of flowering cherries in China are used as perfumes due to their superior aroma quality, and in aromatherapy for relaxation and stress reduction.

This present study envisages easy and innovative method for greener synthesis of Au-NPs on the glassy carbon electrode (GCE) and it's used for the detection of hydrazine by using sensitive amperometric method. The fabrication of Au-NPs modified GCE involves a simple electrochemical method. The optimization of green synthesized of Au-NPs has also been discussed elaborately, and the possible compounds as reducing agents present in the leaves extracts of *C. serrulata* can be identified by using gas chromatography mass spectrometry analysis (GC–MS) and quantum chemical studies. The fabricated hydrazine sensor based on Au-NPs shows a good electrocatalytic activity to toward electrochemical oxidation of hydrazine. The sensor proves its superior selectivity even in the presence of 1000 and 150 folds of common metal ions and biologically co-active interfering species. A good linear range, sensitivity and low detection limit have been achieved from the fabricated hydrazine sensor. Furthermore, their antibacterial activity beside representatives of human pathogenic microorganisms was also investigated. To the best of our knowledge, this is the first report in which green synthesized Au-NPs derived from *C. serrulata* plant leaves extract on the modified GCE utilized as electrochemical sensor for the detection of hydrazine.

## 2. Experimental

### 2.1. Preparation of C. serrulata leaves extract

Leaves of *C. serrulata* have been collected from National Taipei University of Technology, Taiwan. They were washed to remove adhering mud particles and possible impurities, then spread over on filter paper to remove the wetness of leaf and dried at room temperature for an hour. This cleaned and dried leaves of about 0.3 g was weighed and sliced in tiny size and then boiled in 300 ml of sterile distilled water in Erlenmeyer flask for 15 min. It is then allowed to cool at room temperature and then filtered twice using Whatman No. 1 filter paper. Finally, the fresh, clean and pale yellow colored extract was obtained.

### 2.2. Synthesis of Au-NPs

30 ml of *C. serrulata* leaves extract was mixed with the 150 ml of aqueous solution of 0.5 mM $HAuCl_4$ in 250 ml Erlenmeyer flask at room temperature. The yellow color solution becomes ruby red color and then there was no further noticeable difference in the color within an hour after $HAuCl_4$ added, which indicates that the bio-reduction process is over within an hour. The color changes demonstrate the formation of Au-NPs in aqueous solution due to excitation of surface plasmon vibration (SPR) in the metal nanoparticles. The general reduction mechanism of metal ions to metal nanoparticles were previously reported [41,42]. The above stages of the experiment have been repeated thrice to confirm the reduction process. The synthesized Au-NPs were collected by centrifugation (5000 rpm, 20 min) and it was cleansed by washing several times with sterile double distilled water and air-dried. Then the air-dried Au-NPs could be lyophilized at −160 to −186 °C in