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# One-step green synthesis of colloidal gold nano particles: A potential electrocatalyst towards high sensitive electrochemical detection of methyl parathion in food samples

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## ABSTRACT

A straightforward green fabrication of electrochemical assay for high sensitive quantitative detection of methyl parathion (organophosphate pesticide) via colloidal gold nanoparticles (AuNPs) modified glassy carbon electrode. Methyl parathion is widely known for its unpleasant functions in bio and ecological system. The synthesis utilizes tannic acid as a bi-functional reducing cum stabilizing agent under ambient temperature (25 °C). The colloidal TA@AuNPs were characterized through TEM, UV–vis, X-ray diffraction, and FT-IR spectroscopy. Fabricated TA@AuNPs/GCE assay has superior electrocatalytic activity toward MP in terms of a wide dynamic range (0.033–167.7 μM), and lower limit of detection (10.5 nM). In addition, the sensor displayed high selectivity, good reproducibility and stability. The practicality of fabricated electrode was verified through the determination of MP in various food and water samples.

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## 1. Introduction

Organophosphate (OP) are key neurotoxins that directly affects the eco system, aquatics, and human life. OPs are the major components of pesticides and insecticides in modern agriculture, added to this they also employed as chemical warfare agents in armed activities [1]. The annual global exposure of OPs, in food, and water supplies is about a billion pounds and became an ultimate thread to the ecosystem, and human life [2,3]. The acute toxicity of OPs is associated with their capacity of irreversible inhibition over acetylcholinesterase (AChE) activity, in the central and peripheral nervous system resulting in accumulation of the acetylcholine; consequently, led to organ failure, and eventual death [4]. According to the World Health Organization, 1.5 billion cases of diarrhea in children (leading to more than 3 million deaths) were caused by contamination of food and water resources each year [5]. Methyl parathion (MP) is an eminent member of OP pesticides. Exposure to MP will lead to eye and skin itching; whereas, the prolonged over exposure cause AChE inhibition, and potential

nerve damage. Consumption of food, and water contaminated with MP could cause nausea, vomiting, abdominal pain, diarrhea, headache, irregular heartbeat, and fasciculation [6]. Moreover, the presence of nitro-substitution on aromatic backbone with strong electron-pullers makes it poorly biodegradable. Therefore, there is an urgent demand for the rapid screening of MP in workplaces, food resources, water bodies and environment, to provide an early warning of MP contamination.

Constant efforts have been made over a decade to develop an efficient technique to determine pesticides in food and water. For instance, liquid/gas chromatography-mass spectrometry, [7,8] electrochemical analysis, [9,10] and enzyme-linked immunosorbent assays (ELISAs) [11] have been state of art platforms towards food and water analysis. However, these techniques are time-consuming, expensive, need expertized technician, sophisticated instrumentation, and not suitable for rapid analyses under field conditions. Among these, electrochemical sensors have received considerable attention due to their high sensitivity, extended dynamic range, cost effectiveness, and portability [12–14]. The redox active properties of nitroaromatic explosives and OPs also make the electrochemical determination as a feasible and preferable technique towards trace level detection of these hazardous substrates. Fabrication of sensor matrices using nano building blocks

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have become an emerging trend in electrochemical detection of OP pesticides [15–26]. In 2010, Kang et al. developed a simple electrochemical sensor for methyl parathion via gold nanoparticles, and nafion film modified glassy carbon electrodes [18]. Electro polymerized poly (p-aminothiophenol) membranes on a gold nanoparticles were proposed as potential electro catalyst towards the detection of MP by Xie et al. [23]. Anandhakumar et al. reported electrocatalytic sensing of methyl parathion using gold atomic cluster modified electrode [25]. Ma et al. developed a novel sensor for methyl parathion based on gold nanoparticle-coated multiwall carbon nanotube modified electrode [26]. Parallel to those earlier literatures it is obvious that the MPs are exhibit a good redox behavior at the gold nanoparticles modified electrode surface.

Gold nanoparticles (Au NPs) are still one of the most interesting nanomaterials because of their exceptional chemical stability, catalytic activity, high surface area, processability, and metallic nature, which provide them unique size-dependent optical and electronic properties. As a result, Au NPs are used in a wide variety of technologies including catalysis [27] nanoelectronics [28] biomedicine [29] and electrochemical sensor [30]. Owing to the high surface-to-volume ratio, Au NPs have outstanding catalytic performances for chemical reactions [31]. Among many chemical routes to synthesize gold NPs, the colloidal synthesis is advantageous due to their versatility and relative facileness. Most common strategies for the synthesis of gold nanoparticles based on the use of harsh reagents such as sodium citrate [32], hydrazine [33], lithium(triethyl)borohydrate [34], and sodium borohydride [35]. Enclosure of naturally derived polyphenols as green reducing agents towards the synthesis of metal nanoparticles could be a best alternant to avoid the inclusion aforementioned hazardous reducing agents. In the hunt of green reducing agent tannic acid (TA) has driven considerable attention, as it is a water-soluble poly phenol; naturally derived from oak, walnut and mahogany and used widely as common mordant in industry. Aromal et al. reported the synthesis of AuNPs using Tannic acid (TA) as reducing agent and stabilizing agent. However, at the end of the synthesis, the particle size and surface were distressed by high temperature [36]. Recently, Piella et al. introduced an efficient well-established protocol to AuNPs (<10 nm) by the combination of two competing reducing agents: TA and sodium citrate [37]. Here, as in the case of the excellent size control provided by this method, they using non-biocompatible reagent which prevents their further biological application. There is need of serious efforts to integrate engineering design rules and principles of green chemistry to provide alternatives to the high-temperature and energy-intensive nanoparticle synthesis procedures. High reducing activity of TA made this method suitable to perform synthesis of AuNPs at ambient temperature, thus likely to save energy about 80–90% over the conventional protocols. However, the synthesis of AuNPs using TA as reducing cum stabilizing agent under ambient temperature has not yet succeeded to produce average sized Au NPs.

In this strategy, we have reported that the TA mediated synthesis of AuNPs carried out through classical nucleation and growth mechanism using the TA as a bi-functional green reducing and stabilizing agent at ambient temperature (25 °C). We further constructed a methyl parathion sensor utilizing TA@AuNPs as electrocatalyst for the first time. The TA@AuNPs showed a high adsorption and strong affinity toward MP over metal ions and other nitro aromatic compounds, which presumably available in eco system. The detection of MP for TA@AuNPs was performed rapidly with a broad linear range and low detection limit, which was better than that of many traditional materials, and AuNPs synthesized via conventional techniques. These merits made TA@AuNPs as potential electrocatalyst for high sensitive quantitative determination MP contamination in food and water samples.

## 2. Materials and methods

### 2.1. Chemicals and characterization

Tannic acid ( $C_{76}H_{52}O_{46}$ ), Gold (III) chloride trihydrate ( $HAuCl_4 \cdot 3H_2O$ ), disodium hydrogen phosphate ( $Na_2HPO_4$ ), and sodium dihydrogen phosphate ( $NaH_2PO_4$ ) were obtained from sigma Aldrich. All chemicals and reagents were analytical grade and used as received without further purification. All the electrochemical experiments were performed in CHI 900 work station. The UV absorption spectra were recorded in a JASCO V-771 spectrophotometer. Fourier transform infrared (FTIR) spectra were taken using a KBr window on a JASCO FT/IR-6600 spectrophotometer. The morphology of the TA@AuNPs was observed via transmission electron microscopy (TEM) on a TECNAI G<sup>2</sup> under an accelerating voltage of 200 kV. X-ray diffraction studies were carried out in XPERT-PRO diffractometer using Cu K $\alpha$  radiation ( $k = 1.54 \text{ \AA}$ ) and Perkin-Elmer IR spectrometer. A Clean pH meter (pH500) with a combined pH glass electrode was utilized for pH measurements. The conventional three electrode system was used for the electrochemical studies, with the modified glassy carbon electrode as a working electrode (electrode surface area: 0.071 cm<sup>2</sup>), saturated Ag/AgCl as a reference electrode, and a platinum wire act as a counter electrode.

### 2.2. Green synthesis of gold nanoparticles (TA@AuNPs)

In a typical synthesis, 10 ml of 0.01 M gold chloride ( $HAuCl_4 \cdot H_2O$ ) were mixed with 20 mL of 0.1 M phosphate buffer (pH 7), and stirred to obtain a homogenous solution. The solution was coupled with 20 mL of freshly prepared 0.05 M tannic acid, and the mixture was stirred vigorously under room temperature for 1 h. The change in the color of solution from yellow to deep wine red postulating the formation of TA@AuNPs. The mixture kept stirred for extra 15 min to ensure complete reaction. In conclusion, quantitative yield of tannic acid capped AuNPs was obtained under ambient conditions without the incorporation of any harsh reagent, and following simple classical nucleation and growth mechanism. A schematic illustration of synthesis and mechanism of electrocatalysis towards MP is shown in Scheme 1.

### 2.3. Fabrication of TA@AuNPs/GCE electrode

The electrodes were fabricated via a simple drop casting method. Prior to the surface modification, the GCE was polished with 1.0 and 0.3 m alumina powder, and rinsed with double distilled water, followed by sonication in ethanol and double distilled water successively. Prior to the electrochemical studies a pre-cleaned GCE was drop casted with 6  $\mu$ L (optimized) of the tannic acid capped AuNPs and dried in room temperature further referred as TA@AuNPs/GCE.

## 3. Results and discussion

### 3.1. Surface portrayal of colloidal TA@AuNPs

In the field of material science synthetic rout of nano materials plays a vital role in the controlling the dimension and surface morphology of the product. In our synthesis the addition of TA into the gold chloride initiate the chemical absorption of TA on the surface of Au<sup>+</sup>. Where the phenolic hydroxyls of TA act as a surfactant, which could later allow the nucleation process towards formation of AuNPs without any supplementary reducing agents. The aggregation of reduced AuNPs particles were prevented by the surfactant nature of TA. Thus, tannic acid act as an amphibian reductant

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