



# Gold nanoparticles decorated on cobalt porphyrin-modified glassy carbon electrode for the sensitive determination of nitrite ion



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## ABSTRACT

The present study reports the electrochemical determination of nitrite ion using citrate-gold nanoparticles (cit-AuNPs) decorated on *meso*-tetra(*para*-aminophenyl)porphyrinatocobalt(II) (Co(II)MTpAP) self-assembled glassy carbon electrode (GCE). The decoration of cit-AuNPs on Co(II)MTpAP was achieved with the aid of amine groups present on the surface of the self-assembled monolayer (SAM) of Co(II)MTpAP. The SEM image shows that the cit-AuNPs were densely packed on Co(II)MTpAP. The AuNPs decorated electrode was successfully used for the determination of nitrite ion. The cit-AuNPs decorated electrode not only shifted nitrite ion oxidation potential towards less positive potential but also greatly enhanced its current when compared to bare and Co(II)MTpAP SAM modified electrodes. The amperometric current increases linearly while increasing the concentration of nitrite ion ranging from  $0.5 \times 10^{-6}$  to  $4.7 \times 10^{-3}$  M and the detection limit was found to be 60 nM ( $S/N = 3$ ). Further, the modified electrode was successfully used to determine nitrite ion in the presence of 200-fold excess of common interferents such as  $\text{Na}^+$ ,  $\text{NO}_3^-$ ,  $\text{I}^-$ ,  $\text{K}^+$ ,  $\text{CO}_3^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$  and glucose. The practical application of the cit-AuNPs decorated electrode was demonstrated by determining nitrite ion in water samples.

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## 1. Introduction

Nitrite ions are widely used as corrosion inhibitor [1], food additive [2] and fertilizer [3]. Because of its more usage in domestic life, nitrite ion made negative impact in both environment and biological processes. According to World Health Organization, the maximum permissible amount of nitrite ion in drinking water is 50 mg/l [4]. Nitrite ion can oxidize haemoglobin to metahaemoglobin and hence the blood oxygen carrying capacity markedly reduced [5]. Further, it interacts with dietary compounds in stomach to form carcinogenic nitrosamines [6]. The major health issues caused by this ion are blue baby syndrome and gastric cancer [6]. Therefore, an accurate determination of nitrite ion is very essential.

Several techniques have been employed to determine nitrite ion which includes spectrophotometry [7–9], chromatography [10,11] and voltammetry [12–15]. The conventional spectrophotometric determination of nitrite ion is based on the absorbance of azo dye measured at 526 nm which is formed by the reaction of nitrite with sulphonamide and N-(1-naphthyl)ethylene diamine [7,8]. However, this method has serious limitations such as controlling

of acidity in each step, toxicity of reagents used, more time consumption and the possible interferents of strong oxidants in the sample [7,8,16]. Similarly, the chromatographic determination of nitrite ion has several disadvantages which include tedious sample preparation, requires trained personnel and derivatisation [10,11]. On the other hand, the electrochemical determination of nitrite ion is simple, faster, cheaper and safer when compared to the above two methods. The nitrite ion can be determined either by electrochemical oxidation or reduction [12–15]. The determination of nitrite ion by reduction leads to the interference of molecular oxygen and nitrate [14]. However, the determination of nitrite ion by oxidation often free from these two interferences. Although nitrite ion is electroactive at carbon electrodes, its oxidation needs high over-voltage and hence the oxidizable compounds interfere with the sample [16]. Thus, it is necessary to modify the electrode with suitable material to oxidize the nitrite ion at less overpotential.

It has been well-documented in the literature that the electrodes modified with metalloporphyrin and metallophthalocyanine complexes can be used as electrocatalysts [17–19]. The electrochemical oxidation of nitrite ion at metalloporphyrin and metallophthalocyanine modified electrodes has been studied using different strategies such as drop casting [20–23], electropolymerization [24–28], adsorbed on  $\text{SiO}_2/\text{SnO}_2$ /phosphate modified electrode [29] and layer by layer adsorption [22]. It is well known

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that self-assembly is a suitable method for the preparation of ordered layer on electrode surface [30]. The self-assembly of porphyrin molecule on electrode surface can be achieved by functionalizing them with suitable functional groups [31,32]. Recently, Gallardo et al. reported the spontaneous adsorption of aryl and alkyl amines on glassy carbon surface via the nucleophilic addition of amine with olefinic GCE surface [33]. Based on the knowledge grasped from this paper, very recently, we have successfully self-assembled *meso*-tetra(*para*-aminophenyl)porphyrinatocobalt(II) (Co(II)MTpAP) on GCE surface [34].

In recent years, the modification of electrode surface with gold nanoparticles (AuNPs) has been received much interest due to their greater electrocatalytic activity when compared to bulk gold [35]. Several strategies have been employed to immobilize the AuNPs including electrodeposition [36], self-assembly [37,38] and seed mediated growth technique [39]. The self-assembly of AuNPs can be achieved on the surface with suitable functional groups including thiol and amine [37,38]. Although the self-assembly method was successfully used for the immobilization of AuNPs, the complete surface coverage was not achieved due to the interparticle repulsion between the attached AuNPs and AuNPs in solution. For example, only 10% coverage of AuNPs was achieved at SAM terminated with alkyl amine functional group and 0.36% and 2.56% of particle coverage of AuNPs were obtained at alkanedithiol modified electrodes [37,38]. In order to achieve higher surface coverage, it is necessary to find out a suitable linker. In the present study, we have used Co(II)MTpAP as a linker for the immobilization of AuNPs on GCE. In Co(II)MTpAP, four amine groups are present in the *meso* phenyl ring. Based on the XPS and CV studies, we found that free amine groups were available on the surface of the SAM [34]. In the present study, we have attached AuNPs on the Co(II)MTpAP SAM with the aid of free amine groups. The attachment of AuNPs on Co(II)MTpAP was confirmed by UV–vis spectroscopy, SEM and cyclic voltammetry. The SEM image showed that cit-AuNPs were densely packed on the SAM modified electrode. Finally, the cit-AuNPs decorated Co(II)MTpAP SAM modified electrode was used for the determination of nitrite ion with wide range of concentration.

## 2. Materials and methods

### 2.1. Chemicals

Pyrrole, 4-nitrobenzaldehyde, boron trifluoride etherate complex (BF<sub>3</sub>-Et<sub>2</sub>O), HAuCl<sub>4</sub>·3H<sub>2</sub>O, NaBH<sub>4</sub> and trisodium citrate were purchased from Aldrich, India. CoCl<sub>2</sub>·6H<sub>2</sub>O, SnCl<sub>2</sub>·2H<sub>2</sub>O and NaNO<sub>2</sub> were purchased from Merck, India. All other chemicals used in this investigation were of analytical grade. Indium tin oxide (ITO) plates were purchased from Asahi Beer Optical Ltd., Japan. Millipore water was used for all the experiments. Phosphate buffer solution (PBS) (pH 7.2) was prepared by using NaH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub>.

### 2.2. Synthesis of *meso*-tetra(*para*-aminophenyl)porphyrinatocobalt(II) (Co(II)MTpAP)

*Meso*-tetra(*para*-aminophenyl)porphyrin (MTpAP) was synthesized by the reported procedure and purified by column chromatography on silica gel (60–120 mesh) using dichloromethane–methanol mixture as eluent [40]. The product was confirmed by <sup>1</sup>H NMR spectroscopy and ESI-Mass (Figs. S1 and S2). The Co(II)MTpAP was obtained by stirring CoCl<sub>2</sub>·6H<sub>2</sub>O with MTpAP in chloroform and methanol mixture at room temperature for 12 h. The metallated product was confirmed by UV–vis spectroscopy (Fig. S3).

### 2.3. Synthesis of citrate capped gold nanoparticles (cit-AuNPs)

All glassware was thoroughly cleaned with freshly prepared aqua regia and rinsed with double-distilled water before use. A colloidal solution of cit-AuNPs was prepared by the reported procedure [41]. Twenty-five milligram of HAuCl<sub>4</sub>·4H<sub>2</sub>O in 83 ml of Millipore water (0.83 mM) was boiled with vigorous stirring in a round-bottom flask fitted with reflux condenser and 8.75 ml of 1% (w/v) trisodium citrate solution was then added rapidly to the flask. The solution was boiled for another 15 min, during which the colour of the solution was changed from pale yellow to deep red. The solution was allowed to cool at room temperature with continuous stirring and stored at 4 °C. The formation of cit-AuNPs was confirmed by UV–vis spectroscopy and TEM (Figs. S4 and S5).

### 2.4. Preparation of the modified electrodes

The GC working electrode was polished with alumina slurry (0.5 μm) and sonicated in Millipore water for 10 min and the surface of the polished electrode was checked with 1 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>] in 0.1 M KCl. The SAM of Co(II)MTpAP formed by immersing the well cleaned GCE into the vials containing 1 mM of Co(II)MTpAP in dimethylformamide (DMF) for 6 h. The electrode was then removed from the solution and washed with DMF and Millipore water. For the decoration of cit-AuNPs, the Co(II)MTpAP SAM modified electrode was immersed into the colloidal solution of cit-AuNPs for 6 h. Then, the electrode was washed with Millipore water and used for the electrochemical measurements. The Co(II)MTpAP modified electrode is abbreviated as GCE/Co(II)MTpAP and cit-AuNPs decorated electrode as GCE/Co(II)MTpAP/cit-AuNPs.

### 2.5. Instrumentation

UV–vis spectra were recorded with a Perkin Elmer Lambda 35 spectrophotometer. The <sup>1</sup>H NMR was measured using BRUKER 300 MHz instrument. Electrochemical measurements were performed in a conventional two-compartment three-electrode cell with a GCE of 3 mm diameter (area = 0.07 cm<sup>2</sup>) as working electrode, a platinum wire as auxiliary electrode and a NaCl saturated Ag/AgCl as reference electrode. All the electrochemical measurements were carried out with CHI Model 650B (Austin, TX, USA) Electrochemical workstation. ESI-Mass analyses were recorded using THERMO-FINNIGAN LCQ ADVANTAGE MAX mass spectrometer. High resolution transmission electron microscopy (HR-TEM) images were measured from a JEOL JEM 3010 operating at 200 kV. The samples were prepared by dropping 2 μL of a colloidal solution onto a carbon-coated copper grid. SEM measurements were carried at VEGA3 TESCAN.

## 3. Results and discussion

### 3.1. Spectral and SEM characterization of cit-AuNPs decorated electrode

Fig. 1 shows the UV–vis spectra obtained for bare ITO, the SAM of Co(II)MTpAP and cit-AuNPs decorated ITO substrates. No characteristic band was observed for bare ITO (curve a) whereas Co(II)MTpAP SAM modified substrate shows a Soret band at 452 nm and two Q-bands at 554 and 598 nm (curve b). On the other hand, the cit-AuNPs decorated substrate shows an absorbance band at 562 nm in addition to a Soret band at 452 nm (curve c). The absorbance band at 562 nm corresponds to the surface plasmon resonance (SPR) band of cit-AuNPs. This confirms that the cit-AuNPs were successfully attached on the SAM of Co(II)MTpAP modified substrate. In contrary, the Soret band of Co(II)MTpAP in

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