



A novel bimediator amperometric sensor for electrocatalytic oxidation of gallic acid and reduction of hydrogen peroxide



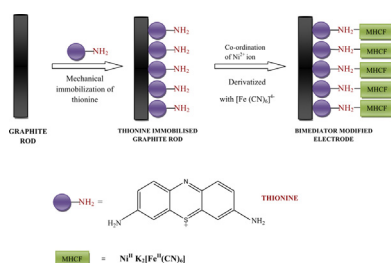
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HIGHLIGHTS

- Novel bimediator electrode was developed based on the TH and NiHCF.
- The bimediator electrode was characterized by cyclic voltammetry.
- TH/NiHCF bimediator electrode electrocatalytically oxidized GA and reduced H_2O_2 .
- The bimediator electrode exhibited good stability and reproducibility.
- GA and H_2O_2 in real samples were analyzed by TH/NiHCF bimediator electrode.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel bimediator amperometric sensor is fabricated for the first time by surface modification of graphite electrode with thionine (TH) and nickel hexacyanoferrate (NiHCF). The electrochemical behavior of the TH/NiHCF bimediator modified electrode was characterized by cyclic voltammetry, differential pulse voltammetry and chronoamperometry. The TH/NiHCF bimediator modified electrode exhibited a pair of distinct redox peaks for NiHCF and TH with formal potentials of 0.33 V and -0.27 V vs. SCE at a scan rate of 50 mV s^{-1} in 0.1 M NaNO_3 and $0.1 \text{ M NH}_4\text{NO}_3$ respectively. The electrocatalytic activity of the bimediator modified electrode towards oxidation of gallic acid with NiHCF and reduction of hydrogen peroxide with TH was evaluated and it was observed that the modified electrode showed an electrocatalytic activity towards the oxidation of gallic acid in the concentration range of 4.99×10^{-6} – $1.20 \times 10^{-3} \text{ M}$ with a detection limit of $1.66 \times 10^{-6} \text{ M}$ ($S/N=3$) and reduction of H_2O_2 in the concentration range of 1.67×10^{-6} – $1.11 \times 10^{-3} \text{ M}$ with a detection limit of $5.57 \times 10^{-7} \text{ M}$ ($S/N=3$). The bimediator modified electrode was found to exhibit good stability and reproducibility.

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1. Introduction

Gallic acid (GA) and its derivatives are naturally occurring polyphenolic compounds. GA is a strong antioxidant [1] and their biological properties include anti-inflammatory, antihistaminic

and antitumor activities, scavenging of free radicals and protection against cardiovascular diseases [2]. Over the years, various methods have been applied for the determination of gallic acid like flow injection analysis [3,4], resonance light scattering [5], thin layer chromatography [6] and electrochemical methods [7–10]. Due to the pharmacological importance of GA, there is a need for a better analytical method for its determination with good selectivity and sensitivity.

Hydrogen peroxide (H_2O_2) is a powerful oxidizing agent, which makes it extensively applied as a vital component in

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environmental, clinical and pharmaceutical analysis [11]. Recently many techniques have been employed for the determination of H_2O_2 including spectrophotometry, chromatography, flow injection etc. [12–14]. Among these the electrochemical methods have gained prominence owing to their advantages of easy preparation, fast detection, high selectivity and sensitivity [15–17]. Recently, many unique materials have attracted much attention for the development of H_2O_2 sensors and biosensors [18–22]. Generally, the direct electrochemical reduction or oxidation of H_2O_2 at bare electrodes requires a large over potential. To overcome this barrier and also to enhance the electron transfer reaction between the electrode and H_2O_2 , it has become imperative to develop chemically modified electrodes with remarkable operational stability and sensitivity.

Chemically modified electrodes (CMEs) have become relatively distinguished among various sensors due to their simplicity, enhanced selectivity and sensitivity towards analyte detection [23,24]. A wide variety of compounds like metal hexacyanoferrates [25], metal oxides [26], metal phthalocyanins [27], zeolites [28] and polymers [29] have been used as redox mediators for the development of chemically modified electrodes. Metal hexacyanoferrates (MHCFs) are insoluble, mixed-valence, polynuclear compounds with excellent redox characteristics. They have rendered tremendous applications in the areas like electrocatalysis [30], electrochromic devices [31], interfacial charge and electron transfer processes [32]. The pioneering works by Neff et al. [33] and Itaya et al. [34] have led to the development of chemically modified electrodes with Prussian Blue (PB) and its analogues such as cobalt, copper, nickel, indium and hybrid metal hexacyanoferrates [35–37]. Among these coordination compounds, nickel hexacyanoferrate (NiHCF) has been well-recognized for its unique electrochemical property. NiHCF has been widely used as an electron transfer mediator for fabrication of electrochemical sensors and biosensors [38,39] giving enhanced stability and with low detection limits of analytes. Several organic redox dye molecules like thionine [40], methylene blue [41], Azure A [42] and neutral red [43] due to their high electron transfer efficiency have also received considerable attention in the fabrication of CMEs. Thionine (TH), a phenothiazine dye exhibits excellent electroactive and photoactive properties. Number of methods have been developed for the modification of electrodes with thionine including electropolymerization [44], carbon nanotubes [45,46], Au nanoparticles [47], Au– SiO_2 nanocomposite [48], nano- TiO_2 [49] and covalent attachment [50].

Our previous reports includes the development of CMEs using metal hexacyanoferrates [51] and dyes [42,52] for surface as well as bulk modifications for the determination of several analytes. We were successful in the fabrication of stable CMEs by anchoring the metal hexacyanoferrate on aniline adsorbed graphite electrode [53] and on gold electrode modified with self assembled monolayer of cysteamine through amine linkage [54] based on the reported interaction of metal ion with amine group of organic compounds [55].

In the present work, for the first time we have developed an innovative method of immobilizing NiHCF with another redox mediator namely TH through amine linkage on to the graphite electrode. This modification was achieved by co-ordination of nickel on the amine group of TH mechanically immobilized on the graphite surface followed by chemical derivatization of nickel to the NiHCF film. The fabricated electrode exhibited the redox characteristics of both the TH and the NiHCF. The proposed modified electrode has been used for the electrocatalytic oxidation of GA and electrocatalytic reduction of H_2O_2 . Similar to bienzyme electrode [56], the fabricated modified electrode is termed as “bimediator modified electrode” as it is a single electrode exhibiting the redox properties of both the

mediators for electrocatalytic oxidation and reduction reactions. The immobilization of the bimediator on the graphite electrode was characterized by scanning electron microscopy (SEM). The TH/NiHCF bimediator modified electrode was electrochemically characterized by cyclic voltammetry, differential pulse voltammetry and chronoamperometric techniques. The TH/NiHCF bimediator modified electrode showed an enhanced electrocatalytic activity with high sensitivity towards the determination of GA and H_2O_2 even in commercial green tea and milk samples.

2. Experimental

2.1. Instruments and chemicals

The SEM images and EDS data were obtained on a S3400N scanning electron microscope (Hitachi, Japan), equipped with an energy-dispersive X-ray analyzer at an accelerating voltage of 15 kV. The XPS analysis was performed using a monochromatic 300 W Al $\text{K}\alpha$ X-ray radiation as the X-ray source for excitation (Model XM 1000, Omicron Nanotechnology, Germany). The UV–vis spectra were recorded using a PerkinElmer (Lambda 650) spectrophotometer.

All electrochemical experiments were carried out with CHI 660B electrochemical analyzer with standard three electrode system. The standard calomel electrode and the platinum wire served as the reference and counter electrode respectively. The bimediator modified electrode was used as the working electrode. Paraffin wax impregnated graphite electrodes were used for the modification. Thionine and potassium ferrocyanide were purchased from Himedia laboratories, India. Gallic acid, hydrogen peroxide and nickel chloride were from Merck, India. All other chemicals and reagents used were of analytical grade. All the solutions were prepared using double distilled water. The electrolyte solutions were purged with pure nitrogen to remove free oxygen before the experiment. The pH of the electrolyte solutions used was maintained at 7 using PBS buffer solution.

2.2. Fabrication of modified electrode

The fabrication of TH/NiHCF bimediator modified electrode involves three steps. In the first step, the TH was mechanically immobilized on the surface of paraffin wax impregnated graphite electrode by pressing and uniform rubbing similar to the method developed by Scholz and Lange [57]. Secondly, the TH electrode was dipped in a solution of NiCl_2 (0.01 M) in ethanol for 10 min for the coordination of metal ion (Ni^{2+}) to the free amine group of TH. Finally, the Ni^{2+} on the electrode surface was derivatized by cycling between -0.2 and 1.0 V (20 cycles) in KNO_3 (0.1 M) solution containing 0.02 M potassium ferrocyanide to form a stable and insoluble NiHCF film. The resulting TH/NiHCF bimediator modified electrode was used for further studies. The fabrication of the TH/NiHCF electrode is illustrated in Scheme 1.

The electrochemical behavior of the TH/NiHCF bimediator modified electrode towards the oxidation of GA and reduction of H_2O_2 was studied by cyclic voltammetry. In the determination of GA, cyclic voltammogram for the TH/NiHCF bimediator modified electrode was recorded in the potential range from 0.1 to 0.8 V at the scan rate of 50 mV s^{-1} using 0.1 M NaNO_3 as the supporting electrolyte containing known amounts of GA. Similarly for the determination of H_2O_2 , cyclic voltammogram of the bimediator modified electrode was recorded in 0.1 M NH_4NO_3 containing a known amount of H_2O_2 in the potential range from 0 to -0.7 V. The applicability of the TH/NiHCF bimediator modified electrode for the determination of GA and H_2O_2 in flow systems was also studied by chronoamperometry by fixing the potential at $+0.45$ V and

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