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Carbon Paste Electrode based on Neutral Red Functionalized Graphite as an Amperometric Sensor for Hydrogen Peroxide

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Abstract: The determination of hydrogen peroxide at a new Neutral Red carbon paste electrode is reported in this work. The phenazine dye, neutral red which is electrochemically active has been used as the mediator and has been rendered leak free for the development of sensor by covalently immobilizing neutral red to the functionalized graphite powder which was then made into a carbon paste electrode. The sensor demonstrated good sensitivity towards hydrogen peroxide and the linear response range spanned from 1.91 x 10^{-5} M to 6.60 x 10^{-3} M of H_2O_2 with a detection limit of 1.15 x 10^{-5} M. The developed hydrogen peroxide sensor had excellent stability and reproducibility.

Keywords: Carbon paste electrode; neutral red; amperometric sensor; hydrogen peroxide.

Introduction and Experimental

Hydrogen peroxide (H_2O_2) plays a very crucial role in environmental, biological and industrial processes. Thus quantification of hydrogen peroxide using reliable, rapid and simple method has become very significant. Several techniques have been proposed for the detection of H_2O_2 such as titrimetry [1], spectrometry [2], chemiluminescence [3] and electrochemistry [4]. Determination based on electrochemistry has gained much preference over other techniques owing to the advantages of low detection limits and rapid response times. Electrochemical determination of H_2O_2 has been proposed by many researchers [5,6] whereas the need for improved sensing drives the thrust for development of new sensors.

Chemically modified electrodes have emerged as attractive analytical tools in different research fields owing to the variety of modifications offered during electrode manufacture [7]. Modified carbon paste electrodes (CPE) using graphite powder and paraffin oil as the gluing material are constructed either by adsorption, covalent binding, dissolution or direct mixing. In general, the modifiers used by direct mixing should be insoluble in the analytic solution, as well as should be adsorbed strongly by carbon paste in order to avoid dissolution of the molecules from the electrode surface during the measurements [8].

The organic mediators such as neutral red, toluidine blue, thionine, and Azure A have good electrochemical behaviour and proven electrocatalytic activity. But they are associated with the drawback of high solubility in aqueous solutions, hindering their use as mediator for electrocatalytic applications. The present work describes the new approach for the covalent immobilization of neutral red to the functionalized graphite through an amide linkage and developing it as an electrochemical sensor for hydrogen peroxide.

Chemicals and Apparatus

Neutral red was purchased from s.d fine Chemicals. Graphite powder (1-2 micron) was obtained from Aldrich and H_2O_2 (50%) from Merck. Electrochemical experiments were performed with a CHI 400A Electrochemical Analyzer. A platinum wire as auxiliary electrode, a saturated calomel electrode (SCE) as reference and Neutral red carbon paste electrode(NR-CPE) as working electrode were used for all electro chemical studies.

Functionalisation of graphite and construction of carbon paste electrode

For the covalent immobilization of the mediator, the graphite powder was first activated by functionalisation. 10 g of graphite was refluxed with 200 ml of 5 M nitric acid for 7 h. Then the oxidized graphite powder was washed thoroughly and dried at 150º C for 13 h [9]. The activation procedure provides free carboxyl groups on the surface of the graphite powder. The carboxyl groups were converted to acid chloride by refluxing 4.5 g of oxidized graphite powder with 15 ml of thionyl chloride (5 % in toluene) for 5 h and washed extensively with toluene and dried 150º C for 13 h [10]. 4 mg of NR in 100 ml of benzene was refluxed with 1 g of functionalised graphite for 12 h. The graphite powder was washed thoroughly with benzene, dried at room temperature for 4 h and used for further modification. Neutral red immobilized graphite powder was thoroughly mixed with appropriate amount of silicone oil to form a homogeneous paste. This paste was then packed into the cavity of a glass tube with 2 mm internal diameter and pressed tightly.

Results and Discussion

Electrochemical characterization of NR-CPE was carried out with cyclic voltammetry and the results are presented in **Fig. 1**. The cyclic voltammogram of the NR-CPE between the potential limits 0.1 V to –0.5 V in 0.1 M NH_4NO_3 exhibits a single reversible couple with the cathodic and anodic peak potentials at –0.296 and –0.230 V respectively at a scan rate of 20 mVs^{-1} **(curve b)**. The formal potential $E^{0'}$ of the redox couple is –0.263 V and the reversible couple is attributed to the redox reaction of the NR immobilized in the carbon paste electrode. The peak-to-peak separation for the reversible couple is 66 mV at 20 mVs^{-1}.

The NR-CPE was used to study the electrocatalytic reduction of H_2O_2. CVs for the modified electrode and the bare electrode in the presence and absence of H_2O_2 are shown in **Fig. 1**. The bare electrode shows negligible increase in current in the presence of H_2O_2 **(curve b)** while a higher current is observed with the modified electrode **(curve d)** for the same concentration of H_2O_2. A significant increase in the cathodic current with the addition of H_2O_2 at the peak potential of -0.3 V indicates the mediated electrocatalytic reduction of H_2O_2. Calibration graph for the determination of H_2O_2 was obtained and the linear range spans from 1.91 x 10^{-5} M to 6.60 x 10^{-3} M of H_2O_2 with a detection limit of 1.15 x 10^{-5} M.

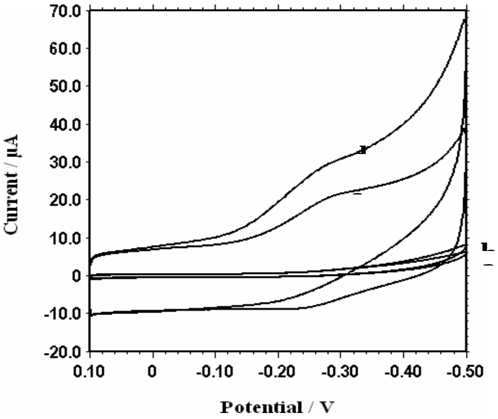

Fig. 1. CVs of (a) bare CPE (b) 1.05 x 10^{-4} M H_2O_2 at bare CPE (c) NR-CPE (d) 1.05 x 10^{-4} M H_2O_2 at NR-CPE in 0.1 M NH_4NO_3; (0.05 M Phosphate buffer, pH 7.0); Scan rate: 20 mVs^{-1}

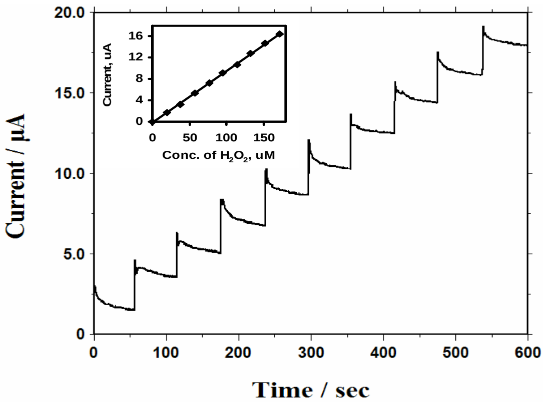

Fig. 2. Current-time response observed with the NR-CPE for successive addition of 0.5 ml of 3.44 mM H_2O_2 in 0.1 M NH_4NO_3 (0.05 M Phosphate buffer, pH 7.0); Stirring rate: 300 rpm; Potential: -0.3V. Inset: Calibration graph for H_2O_2 determination.

Amperometric determination of H_2O_2 was carried out using the modified electrode by fixing the working potential at –0.3 V. When an aliquot of H_2O_2 is added to the stirred buffer solution, the reduction current rises steeply (Fig. 2). The plot of current obtained against the concentration of H_2O_2 in the range of 1.91 x 10^{-5} M to 1.71 x 10^{-4} M H_2O_2 is shown in Fig. 2 (inset) and the linearity was observed upto a higher concentration of 4.72 x 10^{-3} M H_2O_2.

Conclusion

The highly water-soluble mediator, neutral red has been successfully immobilized to the graphite by covalent method. In the presence of H_2O_2 a remarkable electrocatalytic activity was observed at the NR-CPE at a very low potential of -0.3 V, which aided in interference free determination of the analyte. In addition to the simple surface renewability, the sensor has distinct advantages of low cost, fast response, good sensitivity and stability suggesting a promising tool for nitrite sensing.

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