



A novel potentiometric hydrogen peroxide sensor based on pK_a changes of vinylphenylboronic acid membranes

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ABSTRACT

A potentiometric hydrogen peroxide (H_2O_2) sensing scheme was developed using arylboronic acid as the electrode modifier. It is well-known that both aliphatic and aryl boronic acid undergo electrophilic displacement reaction with H_2O_2 . This reaction involves replacement of boronic acid by the hydroxyl group of peroxide resulting in a change in pK_a value that can be exploited for sensing of H_2O_2 . Vinylphenylboronic acid (VPBA) ink was prepared using Nafion as the binder and it was drop cast on an electrode surface. Morphology of the modified electrode was analysed using scanning electron microscopy (SEM). The present modifier exhibited a linear relationship between the difference in electrode potential (ΔE_p) vs. $[H_2O_2]$ with a Nernstian slope of 26 ± 2 mV in the concentration range of 10^{-1} – 10^{-5} M. Application of the VPBA modified electrode for hydrogen peroxide sensing was studied in an industrial dye-bleach effluent.

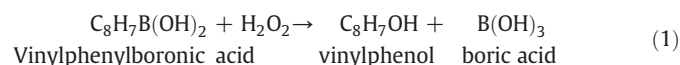
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1. Introduction

The determination of hydrogen peroxide has become an important task in the field of food, biomedical and environmental protection [1,2]. It is an intermediate product in the enzymatic reaction of glucose, uric acid, cholesterol and lactate determination. Atmospheric gases such as ozone and volatile organic compounds undergo photochemical reactions which increase the concentration of H_2O_2 in drinking, sea and rain water that affects the eco-system. Several analytical detection methods have been reported for the determination of H_2O_2 , including titrimetry spectrometry, chemiluminescence, fluorescence [3] and electrochemistry [4]. Amongst these, electrochemical methods have become popular because of their high sensitivity, selectivity and fast response [5]. However, amperometric technique requires high overpotential for hydrogen peroxide oxidation or it needs a redox mediator for precise determination since H_2O_2 is an unstable molecule, which obstructs the broad spectrum of usage of this technique [6]. Most of the reported H_2O_2 determination involves enzyme as the mediating layer, whereas enzymes can easily be affected by temperature, pH, humidity and toxic chemicals [7]. For an enzyme electrode one or more enzyme layers should be placed on the bare electrode through carefully optimised processes and enzyme electrodes [1]. Alternatively, electrochemical determination of hydrogen peroxide without employing redox mediators is one of the areas of increasing research activity. However only a few attempts have been reported with respect to the potentiometric H_2O_2 sensor without

using enzyme, i.e., simultaneous detection of peracetic acid and hydrogen peroxide based on transient change of electrode potential for I_3^-/I^- as a result of the oxidation of I^- by peracetic acid and H_2O_2 [8].

Interactions of boronic acid with a range of analyte molecules have earlier been exploited for the development of various sensors [9]. It is reported that the reaction between aryl boronic acid with hydrogen peroxide leads to the lowering of pK_a value (Eq. (1)). Kuivila reported that the arylboronate undergoes an electrophilic displacement reaction with hydrogen peroxide to yield phenol and boric acid as products in the pH range of 2 to 6 [10]. The fluctuation in the pH during the displacement reaction at electrode surface, results in a steady-state change in the electrochemical potential. In this work, we demonstrate the use of vinylphenylboronic acid to work as a sensitive and selective electrode-modifier with a detection limit down to micromolar level.



2. Experimental

2.1. Chemicals

4-vinylphenylboronic acid (VPBA), glucose and Nafion solution (wt.% in lower aliphatic alcohol) were purchased from Aldrich and used as received. Hydrogen peroxide (Merck) stock solution was prepared afresh in phosphate buffer of pH 7.4. Standard solutions of hydrogen peroxide were prepared by appropriate dilution of stock

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solution and stored in dark. All other chemicals were of analytical grade and were used as received. An ITO glass (Donnelly Corporation, USA) plate of 28 Ω cm sheet resistance was used for VPBA coating and FT-IR and SEM characterization.

2.2. Fabrication of VPBA-modified electrode

For electrode modification, 10 mg of VPBA was dispersed in 2% Nafion solution using ethanol. The above mixture was sonicated for 30 min to obtain a homogenous VPBA ink. 3 μ l of the ink was drop cast on the pre-polished glassy carbon electrode (BAS Inc., USA) and dried at room temperature for 1 h. The morphology of the VPBA modifier on the electrode surface was examined using SEM (Hitachi Model H-3000). FT-IR spectra in the transmittance mode were recorded using FT-IR spectrometer (Thermo Nicolet Model 670).

2.3. Potentiometric measurement

Potentiometric measurements were performed at 25 $^{\circ}$ C in a standard two electrode cell configuration. VPBA modified glassy carbon electrode was used as the working electrode and Ag/AgCl as the reference electrode. All open circuit measurements were carried out in a stirred 0.1 M KCl solution at pH 5.6. The electrode potential was allowed to reach a stable value in KCl solution prior to the measurement. After the VPBA modified electrode was stabilised, the change in open circuit potential was noted before and after the addition of H_2O_2 .

3. Results and discussion

3.1. Characterisation of unreacted and reacted VPBA-Nafion composite film

The displacement reaction between vinylphenylboronic acid and hydrogen peroxide yields vinylphenol and boric acid resulting in minor perturbation of the interfacial pH. This reaction could be evidenced by observing the molecular vibrational changes in an infrared radiation field. Fig. 1 presents the FTIR spectrum of the VPBA-Nafion film before and after its reaction with hydrogen peroxide. Unreacted VPBA shows broad and strong absorption band at 3200 cm^{-1} due to O–H stretching vibrations in the boronic acid moiety of VPBA. Intramolecular hydrogen bonding of the OH groups results in a strong and broad peak and it appears in the higher frequency range. The B–O

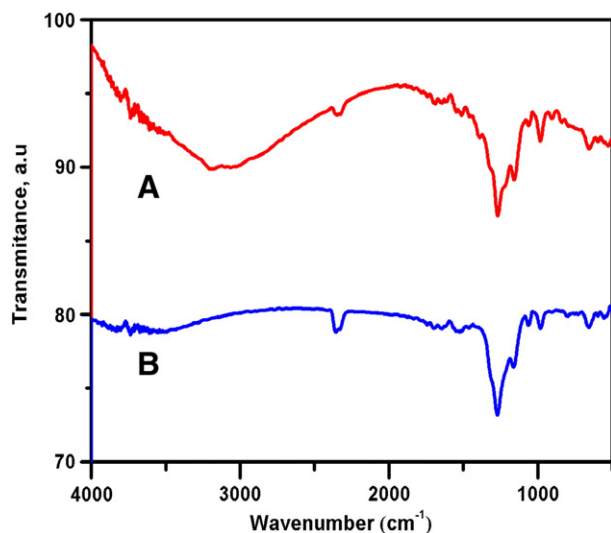


Fig. 1. (A) FT-IR spectrum of VPBA; as prepared (B) VPBA reacted with hydrogen peroxide.

asymmetric stretching vibration was observed at 1335 cm^{-1} , whereas in the case of phenylboronic acid and pentafluorophenylboronic acid it was observed at 1375 cm^{-1} and 1350 cm^{-1} respectively [11]. Thus the shift in the absorption may be attributed to the vinyl group substituted in the phenyl ring. The B–O–H deformation was observed at 982 cm^{-1} and the absorption band at 525 cm^{-1} is due to BO_2 deformations [12]. BO_2 rocking deformations observed at 458 cm^{-1} generally occur in the lower frequency region. When VPBA undergoes displacement reaction with H_2O_2 , the peaks appear at 449 cm^{-1} and 665 cm^{-1} that are assigned to O–B–O ring bending and B–OH out-of-plane bending, suggesting the formation of boric acid. The peak observed at 1271 cm^{-1} is due to the in-plane bending of B–OH [13]. The absence of broad absorption band at 3200 cm^{-1} for OH stretching and 1687 cm^{-1} for phenyl ring absorption clearly indicates the formation of vinylphenol as the by-product and it is leached out into the solution. All these observations indicate the formation of boric acid at the electrode interface that shifts the pK_a value at the electrode interface during the electrophilic displacement between hydrogen peroxide and vinylphenylboronic acid.

The surface morphology of VPBA-Nafion modification was investigated using SEM. Fig. 2 shows the SEM micrograph of the un-reacted and H_2O_2 reacted VPBA-Nafion composite film. Both micrographs show distinctly different morphology where the unreacted films show needle shaped segregations at the surface. When reacted with hydrogen peroxide, a close aggregation with bright spots indicates the leaching of vinyl phenol into the solution leaving boric acid at the

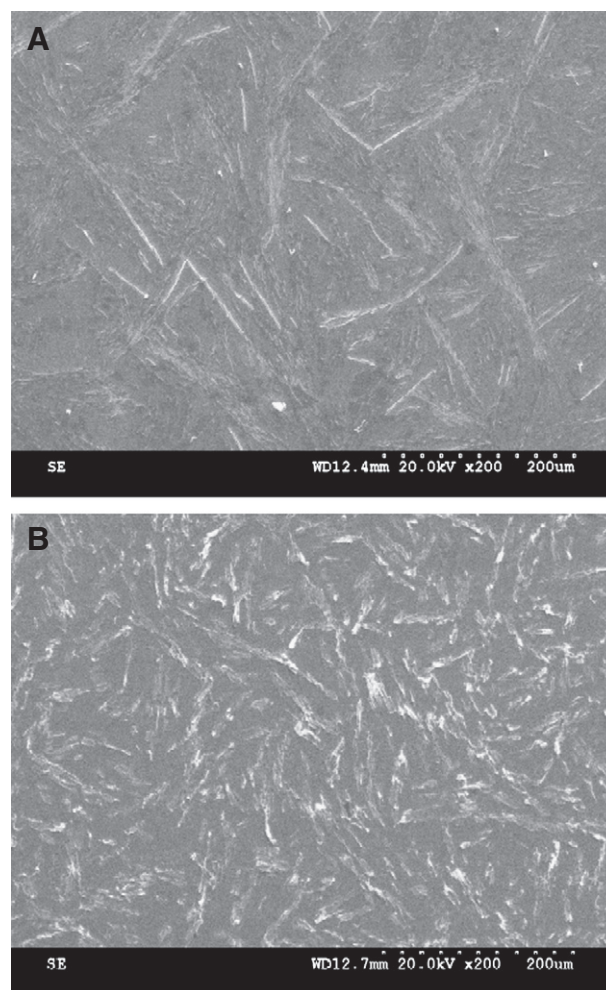


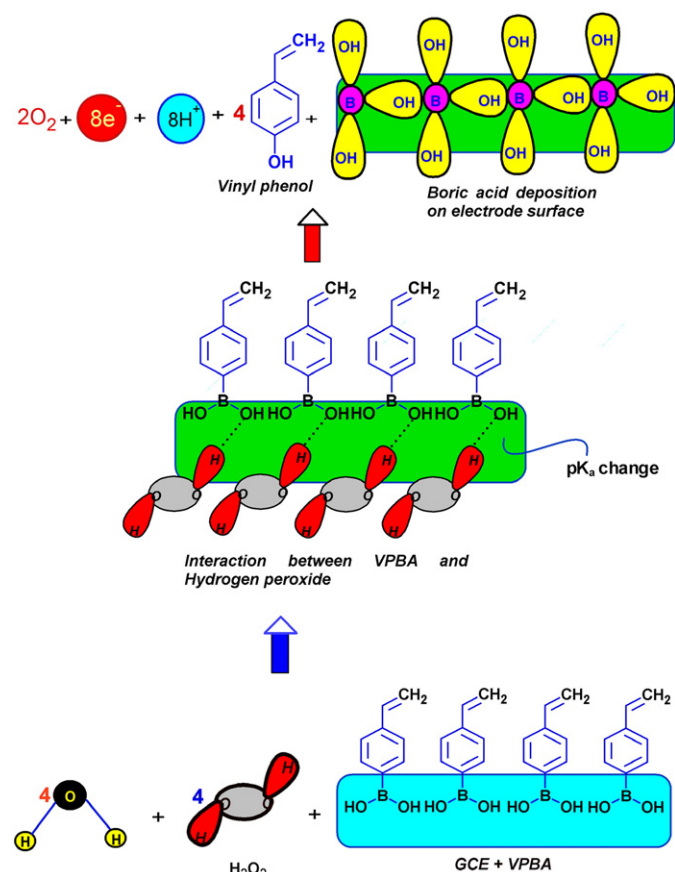
Fig. 2. (A) SEM image of the VPBA film as prepared (B) VPBA after reaction with hydrogen peroxide.

electrode surface, which is corroborated by the vibrational spectral information.

3.2. Sensor characterisation

The electrophilic displacement reaction between VPBA and hydrogen peroxide shifts the interface pH by lowering the pK_a value. The transient perturbation with short-lived pH changes associated with the steady state change in the electrochemical potential that is dominated by the pK_a value change at the electrode interface. These pK_a changes at an electrode surface can be directly correlated to the concentration of H_2O_2 . A schematic representation of pK_a changes of VPBA films on glassy carbon electrode due to electrophilic interaction with H_2O_2 is given in Scheme 1. The potentiometric calibration curve (Fig. 3) shows the potential response of the VPBA-Nafion modified electrode versus logarithm of H_2O_2 concentration, in solutions saturated with oxygen (or air) as linear over the concentration range of 1×10^{-5} to 1×10^{-1} M. The VPBA-Nafion modified electrode shows Nernst-like behaviour with respect to the H_2O_2 concentration. Maximum sensitivity was obtained at pH 5.6 with a slope of 26 ± 2 mV per decade. A potentiometric detection limit of $25 \mu\text{M}$ was obtained for H_2O_2 . The electrode retained its full activity for a month and the slopes of the calibration plots were reproducible within 1–2 mV per decade of H_2O_2 concentration. At higher pH values, the sensitivity of the VPBA modified electrode was affected due to the interference of OH^- ion.

In the present investigation it is observed that the low detection limit of hydrogen peroxide is $25 \mu\text{M}$, which is considered significant because in enzymatic glucose sensing the level of peroxide produced is of the concentration range. This VPBA-based potentiometric H_2O_2 sensor may find a practical application in analysing the concentration



Scheme 1. Schematic representations of pK_a changes on VPBA modified glassy carbon electrode due to electrophilic reaction with H_2O_2 .

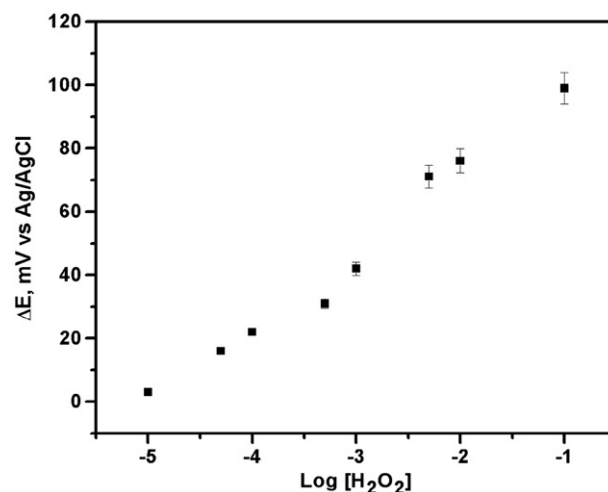


Fig. 3. Potentiometric calibration plot of VPBA modified electrode in 0.1 M KCl containing 10^{-5} – 10^{-1} M of H_2O_2 .

of H_2O_2 residue in the dye-bleach effluent which is collected from a nearby industry. A solution of 0.1 M KCl was chosen as supporting electrolyte for carrying out H_2O_2 analysis in the dye-bleach effluent. From the calibration plot, the concentration of H_2O_2 in the dye bleach effluent was determined to be in the range of 10^{-4} to 10^{-3} M which coincides with determination by titration.

4. Conclusion

The electrophilic displacement reaction of boronic acid group in VPBA with hydrogen peroxide resulting in a change of pK_a at an electrode surface is taken advantage of in developing a potentiometric hydrogen peroxide sensor. VPBA-Nafion modified glassy carbon electrode showed a sensitive and selective potentiometric response to hydrogen peroxide in a micromolar concentration range, which is considered significant for low level enzymatic glucose determination. The selective response of the present sensor matrix was found to be high compared to those of previously reported hydrogen peroxide since the negatively charged Nafion ionomer selectively allows permeation of H_2O_2 and blocks other interferences.

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