

Surface and Electrochemical Characteristics of Poly(*o*-phenylenediamine)-Based pH Sensor

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A potentiometric pH sensor device was fabricated using galvanostatic electrochemical polymerization of *o*-phenylenediamine (oPD) onto a platinum wire from a suitable buffer solution containing the doubly crystallized oPD monomer and the dopant bovine serum albumin (BSA). This paper describes a robust pH transducer for biosensing. Electrochemical characteristics of the sensor were optimized against a Ag/AgCl reference electrode using universal buffer solutions with pH of 3 to 10. The poly(*o*-phenylenediamine) (PoPD)-coated pH sensor exhibited a nearly Nernstian response ($m = -50.7$ mV/pH), good linearity ($r = -0.997$) and high selectivity to hydrogen ions ($k_{ij} > 10^{-8}$). The sensor response was highly reproducible (RSD = 3%) and showed minimum hysteresis ($\Delta m = 1.06$ mV/pH) and very low electrode drift of 0.1 mV/min (RSD < 2%). Surface characteristics of PoPD were likewise investigated using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and time-of-flight secondary ion mass spectrometry (TOFSIMS).

Key words: poly(*o*-phenylenediamine), conductive polymer, pH sensor, surface analyses

INTRODUCTION

The past decade had shown a remarkable outpouring of research activities in the field of chemically modified electrodes. This area of research has attracted such a considerable interest because of potential applications to electrocatalysis [1], electrosynthesis, and photosensitization [2]. Chemically modified electrodes have also been introduced for stabilization of semiconductors [3], in fuel research [4] and for amperometric and voltammetric determinations [5-7]. Relatively few applications have employed chemically modified electrodes as potentiometric sensors [2].

The most common method for electrode modification involved covalent linking of suitable groups to electrode surface. In addition to covalent attachment, a more practical

approach is coating the electrode surface with polymeric films. These polymeric films have been formed by casting the film on an electrode surface using radio frequency plasmas and electropolymerization [2].

The development of a PoPD-modified platinum electrode would provide a miniature alternative to the conventional glass pH electrode. The pH sensitivity of the PoPD-based pH sensor has been attributed to protonation and deprotonation of amine linkages in the polymer [2] and to the permselectivity of PoPD to hydrogen ions [1,8,9]. The latter enhances the potentiometric response of the sensor because of its high selectivity to hydrogen ions. Furthermore, the nature of PoPD-based pH sensor offers the advantage of simple fabrication procedure, robustness, durability, and a possible pH transducer for enzyme biosensors. From previous studies [10-12], the use of surface analytical techniques such as XPS and TOFSIMS to examine the surface composition of the film is of great importance because it

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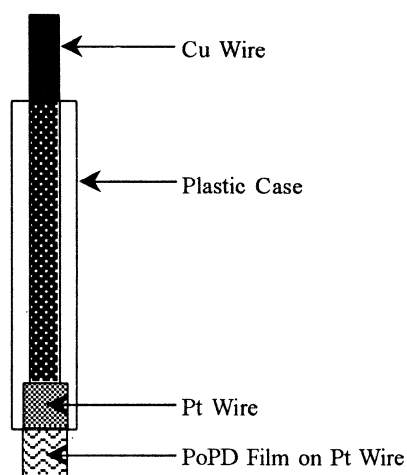


Fig. 1. Diagram of a fabricated PoPD-based pH sensor.

reveals the characteristics of the site where electrochemistry ultimately takes place. Surface analysis facilitates the understanding of sensor performance and rapidly optimizes the processing of such polymeric films. This is the first study done on both the electrochemical and surface (*e.g.*, SEM, XPS, TOFSIMS) characterization of the PoPD/BSA-based pH sensor.

EXPERIMENTAL

Materials and Reagents. All reagents used were analytical grade, and all solutions were prepared using deionized water (ca. 18 M Ω cm) unless otherwise indicated. The monomer, oPD was doubly crystallized using dichloromethane (Merck Chem. Co.) as solvent and decolorized with activated charcoal (ca. 0.1g/L) during the first crystallization. The buffer solutions, the purified monomer, and the dopant, BSA were refrigerated prior to use.

Fabrication of PoPD-pH Electrode. A 1.5 cm long platinum wire (99.99%, 0.1 mm diameter) was soldered to a copper wire and housed in an 8-cm long plastic case (4 mm diameter) as shown in Figure 1. Galvanostatic electrochemi-

cal polymerization of oPD monomer was carried out in a cylindrical glass compartment (ca. 5 cm in height x 2.5 cm in o.d.) provided with a removable cap where the platinum wire anode (0.20 cm²) and carbon black cathode (140 cm²) were fitted (Fig. 2). The Pt anode and the carbon black cathode were positioned parallel to each other 1 cm apart. A current limiting (IC LM334) device which provides a constant current through the cell was placed in series with the voltage source (< 30V) and the electrochemical cell [13]. The polymerization solution was composed of 0.10 M oPD monomer, 30 mg BSA dopant, and 0.10M phosphate buffer (pH 7.0).

Instrumentation and Measurement Procedure. A schematic diagram of the instrumentation set-up is shown in Figure 3. The PoPD-coated Pt wire working electrode and the Ag/AgCl (Orion 900200) reference electrode were connected to the pH/mV meter (Metrohm) and were immersed in a suitable vessel containing the test solution and a magnetic bar for constant stirring of the solution at room temperature (25 $\pm$ 2°C). The test solutions were derived from a 0.04 M Britton-Robinson universal buffer solution. The pH values were adjusted to the desired pH values (pH 3 to 10) by addition of 3.0 M NaOH solution.

The response (in mV) of the fabricated pH sensor was monitored against the Ag/AgCl reference electrode. Data acquisition was done by interfacing the measurement set-up to a computer through an 8-channel, 12-bit ADC card (Innovatrix Inc.). The sensor signal at a particular pH was read every 2 minutes until a steady state value was obtained for at least 2 minutes. A change of less than or equal to ± 1 mV/min was accepted.

Electrode Surface Characterization. XPS was used to analyze PoPD films grown on platinum wire electrodes. Experiments were performed using a Kratos AXIS surface analysis system. An Al anode X-ray source was operated at 190 W. The maximum energy resolution of the concentric hemispherical analyzer (CHA) was 0.50 eV operated for XPS analysis in the constant analyzer energy (CAE) mode with a pass energy of 20 eV for the Ag3d_{5/2} emission [14]. The

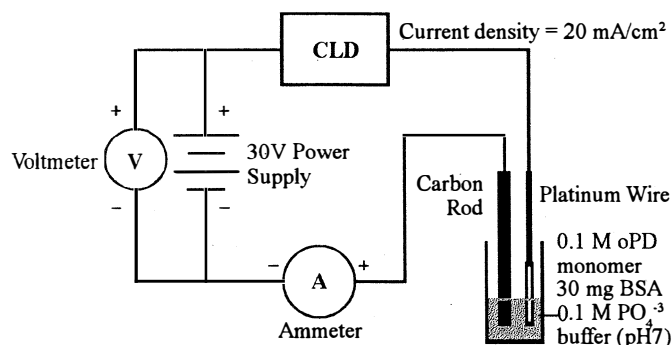


Fig. 2. Electrochemical polymerization of oPD monomer at constant current.

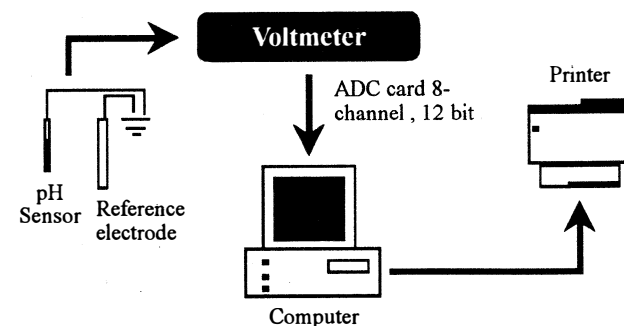


Fig. 3. Instrumentation and data-acquisition set-up for potentiometric characterization.

electron binding energies (E_b) were calibrated relative to a saturated hydrocarbon C 1s component peak at $E_b=285.0$ eV [15]. Peak areas were quantified using appropriate sensitivity factors.

Secondary ion mass spectra were obtained using a Kratos PRISM TOFSIMS. A monoisotopic ^{69}Ga ion source (25 keV energy, 10^{-3} nA beam current) was rastered over an area $\sim 200 \mu\text{m} \times 200 \mu\text{m}$. Static positive ion mass spectra were collected using 10^6 cycles and a 100 ns pulse width cycle $^{-1}$.

The surface morphology of the freshly prepared PoPD film samples was characterized using the JSM-840 SEM (JEOL). The selected sample was mounted on a copper stub, gold sputtered to improve conductivity, and held by silver paste. The SEM filament voltage was operated at 25 kV and a current of 10^{-4} A, with magnifications of 100x, 1000x, and 2000x.

RESULTS AND DISCUSSION

Electrochemical Polymerization. Galvanostatic polymerization of oPD was done in a conventional electrochemical cell containing the platinum anode and carbon black cathode. Under galvanostatic conditions, a current limiting device was connected in series with the voltage source and the cell. This arrangement allowed the control of the amount of current passing through the cell at 1.0, 2.5, and 4.0 mA values depending on the electrode area used. Electropolymerization of oPD (Fig. 4a) yielded a smooth and uniform yellow-brown polymeric film of PoPD coated on the platinum wire anode with conductivity ranging from 10^{-4} – 10^1 Scm^{-1} [16]. The PoPD film contains phenazine rings which was identified as 2,3-diaminophenazine [17] (Fig. 4b and c).

Optimized Electrode Fabrication. The effects of several electropolymerization parameters were investigated and optimized. The first parameter to be optimized was the current density (I_p). Three current densities were investigated, namely, 5.0, 12.5, and 20.0 mAcm^{-2} . There was no significant difference among the electrode responses, however the I_p at 20.0 mAcm^{-2} yielded the most repeatable responses (RSD < 6%, $n = 3$).

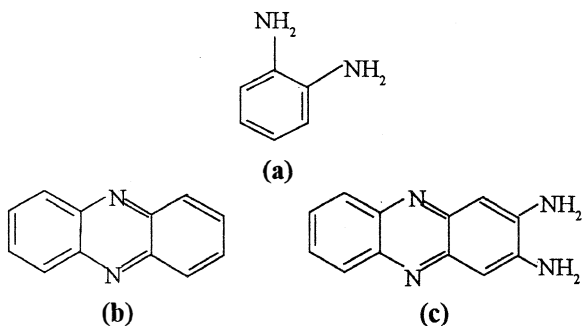


Fig. 4. Structures of (a) o-phenylenediamine (1,2-diaminobenzene); (b) phenazine; and, (c) 2,3-diaminophenazine.

The effect of different solid supports such as Pt, Ti, and Zr wires on the polymerization of oPD was evaluated through the electrochemical response and through visual inspection of the electrode film surface. The PoPD film formed on Ti was smooth, uniform, and black, while that grown on Zr was rough and non-uniform gray. The film grown on Pt was smooth, uniform, and brown and exhibited the best response, highest linearity and the least RSD (< 6%). The total pH response of the PoPD-based pH sensor could be accounted for by the electrode material itself, aside from the protonation-deprotonation properties of PoPD [8].

The electrolyte buffer system for polymerization was investigated using three buffer compositions, namely, phosphate, Tris and KHP at acidic (pH 5.0), neutral (pH 7.0) and basic (pH 9.0) solutions. Phosphate buffer was found to be the best buffer system for polymerization. It yielded the highest electrode response slope at pH 7.0. The sensitivity of the PoPD electrode was affected by the concentration of the phosphate buffer solution. Increasing the phosphate buffer concentration from 0.01 to 0.10 M increased the sensitivity of the sensor from -37.09 mVpH^{-1} to -47.27 mVpH^{-1} . However, increasing further to 0.20 M caused a remarkable decrease in the sensor sensitivity (-38.35 mVpH^{-1}). The optimum phosphate buffer concentration was therefore 0.10 M.

The concentration of the oPD monomer also had a significant effect on the polymerization. Increasing the concentration of the oPD monomer from 0.01 to 0.10 M increased the electrode sensitivity, from -39.65 mVpH^{-1} to -47.27 mVpH^{-1} . Increasing the concentration further to 0.20 M led to a decrease in sensitivity (-42.75 mVpH^{-1}). The best oPD monomer concentration was therefore 0.10M.

The counterion or dopant stabilizes the charge on the polymer but is not very mobile within the dry material [18]. Doping the polymer improves the electrical properties and processability of polymers [19]. The effect of a dopant was investigated by comparing the electrode response of the PoPD polymer in the absence and in the presence of BSA as dopant. There was a significant difference between the sensitivity of the doped PoPD-based pH sensor and that of the undoped sensor. The potentiometric characteristic improved as doping was done. Varying the amount of BSA dopant led to a significant difference in the electrode response slopes. The slope at 30 mg BSA was -47.27 mVpH^{-1} and that at 10 mg and 20 mg. BSA were -42.89 and -37.86 mVpH^{-1} , respectively. From these observations, 30 mg BSA dopant was inferred to be the optimum amount of dopant.

Stirring the polymerization solution hindered film formation, implying that electrodeposition of oPD onto Pt wire was not diffusion controlled. The plausible mechanism for the electropolymerization of oPD is believed to proceed via oxidation of oPD to the monocation radical and the subsequent dimerization $[\text{oPD}]^+$ by either C-N coupling or C-C coupling [20]; but the former coupling is proven to be domi-

Table 1. Summary of optimized electropolymerization parameters.

Electrochemical Polymerization Parameters	Optimized Conditions
Current density	20 mA/cm ²
Solid Support	Platinum
Electrolyte	0.10 M PO ₄ ⁻³ buffer (pH 7.0)
oPD monomer concentration	0.10 M
BSA dopant concentration	30 mg
Stirring	None
Polymerization time	40 min

nant. Further oxidation of oPD to the monocation radical and the C-N coupling of this type resulted in the formation of PoPD with a phenazine backbone [16,17,20]. If the polymerization solution is stirred, it is likely that the rate of migration of oPD monomer or monocation radical toward the Pt anode becomes too slow because they are carried away from the electrode surface. Thus, forced convection, such as stirring or agitation, will tend to decrease polymeric film formation, as manifested by the thinness and non-uniformity of the polymeric film formed.

It was also observed that increasing the polymerization time caused an increase of the response time of the sensor. This behavior can be attributed to the thicker films formed. A polymerization time of 40 minutes was chosen as the optimum on the basis not only of high sensitivity of the sensor but also of the uniformity of film grown. Electropolymerization of oPD was best done using the conditions presented in Table 1.

Potentiometric Characterization of the PoPD-Based pH Sensor. Figure 5 shows the calibration curve of the sensor. It exhibited a near-Nernstian response of -50.74 mV/pH unit, and a Pearson's correlation coefficient, r , of -0.997 and an average response time of less than 7 minutes. The electrode gave favorable repeatability with an RSD less than 4% for 3 replicates

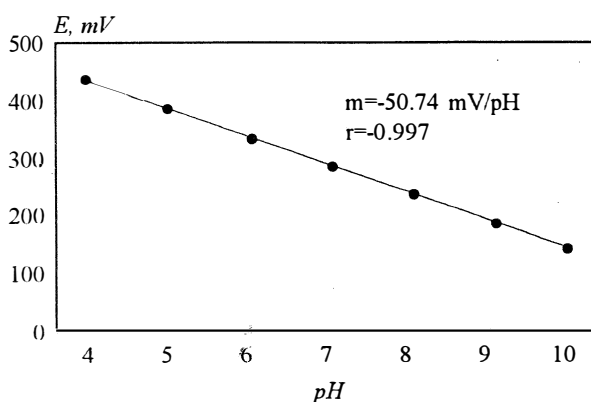


Fig. 5. Plot of E (mV) vs. pH based on the mean of three replicate measurements.

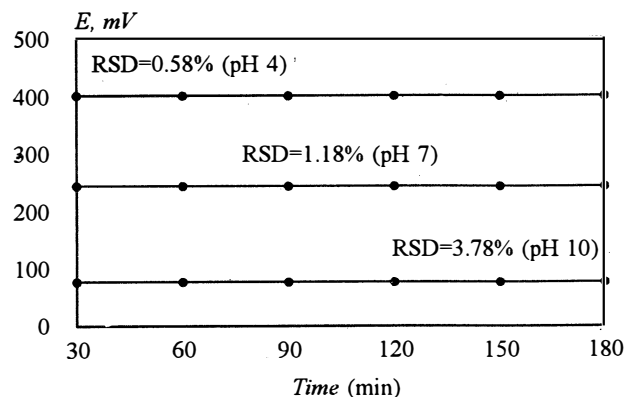


Fig. 6. Potential measurements taken every 30 min for a period of 3 hr at three different pH values.

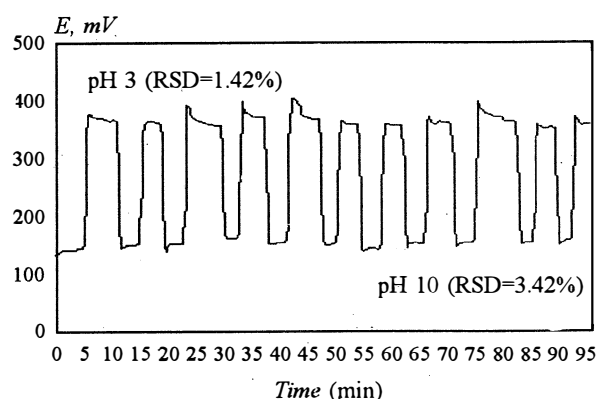


Fig. 7. Reproducibility of the sensor response.

Figure 6 illustrates the electrode drift of the sensor. Drift is the slow non-random change with time in the potential of an ion-selective electrode assembly maintained in a solution of constant composition and temperature [21]. It shows minimum drift at the three pH conditions studied.

The reproducibility profile of the sensor is presented in Figure 7. Reproducibility is an expression of precision in long term conditions [22]. The sensor response was highly reproducible, with RSD of 1.42% at pH 3 and 3.42% at pH 10 or less than 3% on the average.

Figure 8 shows the electrode memory effect or hysteresis. Electrodes are said to have suffered hysteresis if a different potential is observed when the concentration of the solution to which the electrode is exposed is changed and then restored to its original value [21]. The reproducibility of such an electrode will be poor. As depicted in Figure 8, the sensor exhibited a low hysteresis with a change in slope of 1.06 mV/pH unit at pH 3 to 10 and vice versa.

Electrode interferences arise when the electrode responds also to ions other than the test ion. The effect of interfering ions in the sensor response was determined by the addition of 0.01 M and 0.10 M of Na⁺ and K⁺ ions to the test solu-

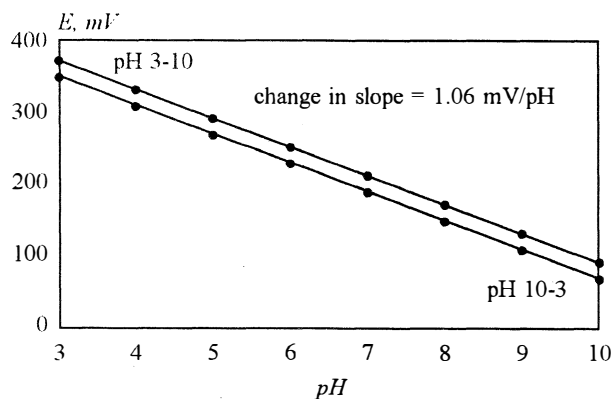


Fig. 8. Hysteresis of sensor response.

tions. The ionic strength of the test solution was increased by the addition of 0.10 M Li^+ . There was a shift to a lower potential in the presence of interfering ions. But the sensor still exhibited high selectivity to hydrogen ions with $k_{ij} > 10^8$. The high selectivity of the PoPD-based pH sensor is attributed to the permselectivity property of PoPD [23]. Ohnuki and co-workers [23] had established correlation between selective permeability of the swollen PoPD to various oxidation-reduction species and the Stoke radii of these species dissolved in aqueous solution. It is apparent that Na^+ ions, particularly at high concentration have relatively smaller Stokes radii than K^+ ions. This means that 0.10 M Na^+ can possibly permeate through the polymer matrix, thus affecting the sensor's selectivity.

Table 2 presents the summary of the potentiometric characterization of the optimized PoPD-based pH sensor. These are the figure of merits for the fabricated polymeric sensor.

Surface Properties of the PoPD Films

SEM Analysis. SEM studies of the surface morphology of the PoPD films (Fig. 9a and b) show that the PoPD film has a uniform, rough globular, fluffy surface. Figure 9a shows the black patches on the film that look like uncoated parts, but at high magnification (2000x) as shown in Figure 9b, these are also coated portions. From the surface morphol-

ogy, it could be suggested that the uniformity and roughness of the PoPD coating enhances the potentiometric property of the PoPD-coated pH sensor, that the electrode response is solely due to the polymer itself.

XPS Analysis. The PoPD coated Pt wire was excited with soft X-rays causing photoionization of atoms in the polymer. The binding energy is characteristic of the elements and compositional chemistry of the polymer surface of less than 10 nm. The BSA dopant is a carbohydrate-free polypeptide chain stabilized with 17 S-S bridges or disulfide linkages. The wide scan of the PoPD film (Fig. 10) revealed the C 1s, O 1s and the S 2p peaks which are due to the BSA dopant, and the C 1s and N 1s peaks which are characteristic of the PoPD polymer. The C 1s core level spectra (Fig. 11) of the PoPD grown on Pt wire showed three component peaks. The component peak centered at a binding energy of ~ 284.8 eV with FWHM 1.39 corresponds to the aromatic carbons of the phenazine ring systems. The left broad shoulder structure is due to contributions from the C-N of the phenazine rings at $E_B \sim 286.1$ eV (FWHM 1.67) and the carbonyl carbon (C=O) of the BSA dopant at $E_B \sim 288.3$ eV (FWHM 1.80).

Table 2. Figures of merit of the fabricated PoPD-based pH sensor.

Electrochemical Properties	Characteristics
Slope	-50.7 mVpH^{-1}
Linearity	-0.997
Response time	<7 min (pH 4 to 10)
Repeatability	RSD <4% (pH 4 to 10 at 3 replicates)
Reproducibility	RSD <%(at 11 replicate and alternate measurements at pH 3 to 10 for a period of <2h)
Hysteresis	$\Delta m = 1.06 \text{ mVpH}^{-1}$
Electrode drift	0.10 mVmin^{-1} with RSD <2% (pH 4, 7 and 10 for 3 h)
Selectivity to H^+ ions	$k_{ij} > 10^8$

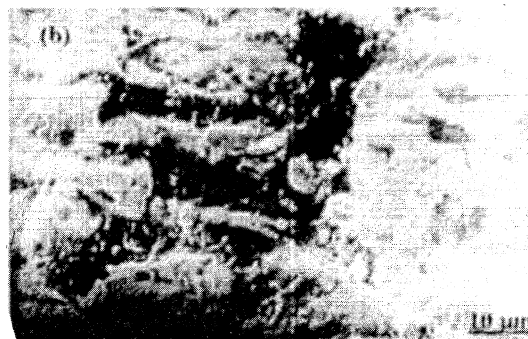
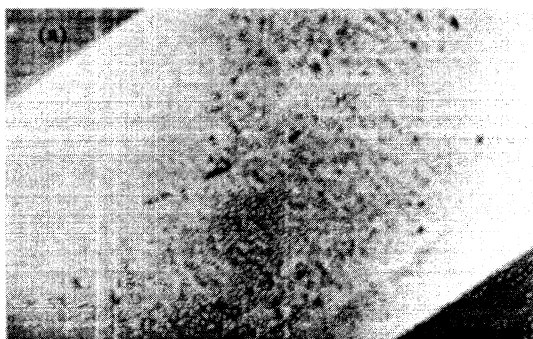


Fig. 9. Micrograph images of PoPD-coated Pt wire at (a) low magnification (100x) and (b) high magnification (2000x).

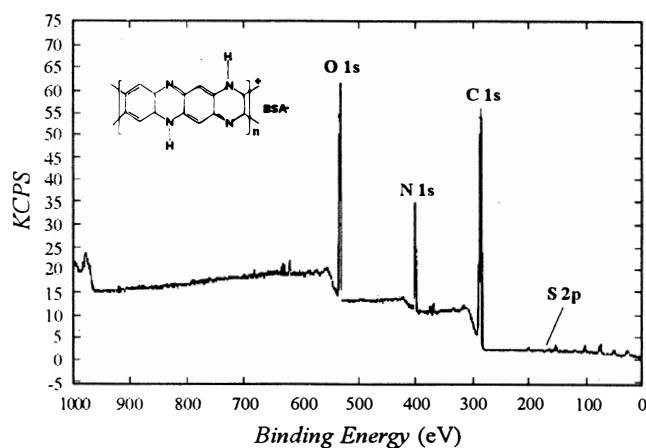


Fig. 10. XPS wide scan spectrum of PoPD/BSA over binding energy range 1000 to 0 eV.

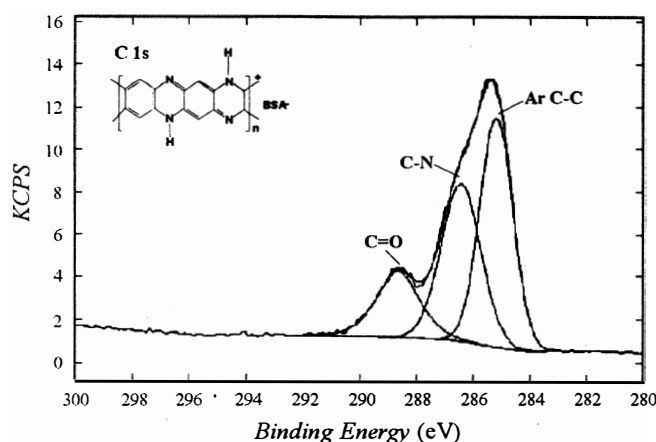


Fig. 11. C 1s XPS core level spectrum of PoPD/BSA with contributions from aromatic C-C, C-N and C=O carbon atoms.

The oxygen photoelectron spectrum is basically from the BSA dopant (Fig. 12). The oxygen of the BSA species centered at $E_B \sim 531.9$ eV (FWHM 2.14) for carbonyl oxygen ($\text{C}=\text{O}$) and $E_B \sim 533.0$ eV for C-O-H (FWHM 1.69).

The highly symmetrical and narrow N 1s photoelectron peak (Fig. 13) indicates that the two different states of nitrogen in the phenazine rings of the PoPD, namely, $\text{C}-\text{N}=\text{C}$ and $\text{C}-\text{NH}-\text{C}$ appear very closely at $E_B \sim 400.0$ eV.

TOFSIMS Analysis. The mass of ions ejected from the polymer surface following the bombardment of the film by high energy primary ions are collected and mass filtered. The ejected ions carry information both about the elements present in the sample and the atomic structure of the sample. The TOFSIMS spectra of the PoPD film (Fig. 14a and b) confirmed the structure of the polymeric film with N-containing fragments. These are at m/z 28, 56, 58, 81, 107 and 131 a.m.u. The rest of the spectra are the hydrocarbon fragmentations of the polymer backbone. These masses of ions ejected

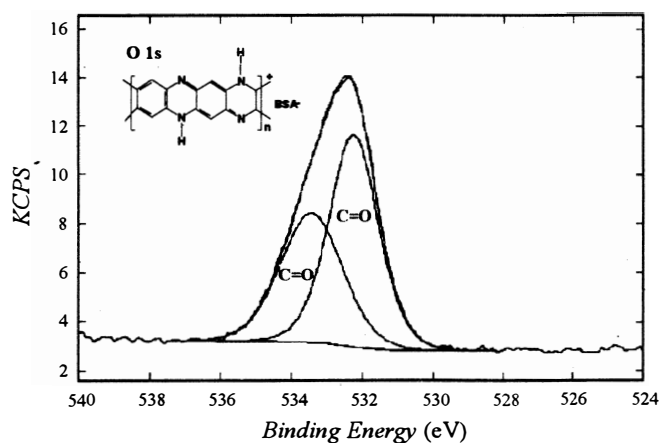


Fig. 12. O 1s XPS core level spectrum curve fit with contributing oxygen species of C-O and $\text{C}=\text{O}$ oxygen atoms for PoPD/BSA film.

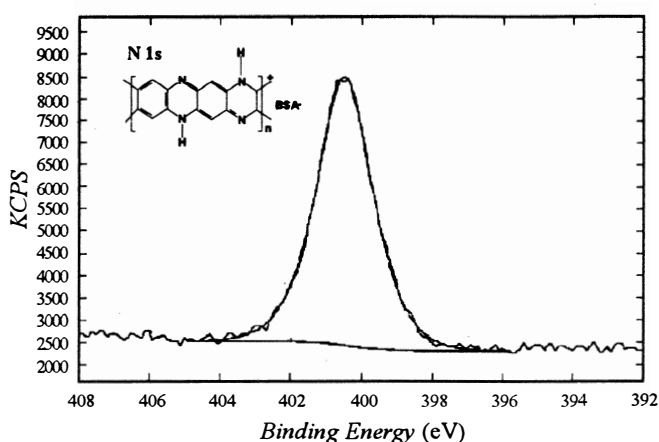


Fig. 13. N 1s XPS core level spectra for PoPD/BSA polymeric sensor.

from the PoPD polymeric film have very short range within the film thus, this technique is highly surface specific, information coming from only the first two or three monolayers of the polymer sample.

CONCLUSION

A novel potentiometric pH sensor device based on PoPD was developed using galvanostatic electrochemical polymerization of oPD monomer. The pH sensitivity of the PoPD-based pH sensor was attributed to the reversible protonation-deprotonation of the amine linkages in the polymer matrix as pH of buffer solution changes and to the permselectivity property of PoPD. The latter enhances the potentiometric property of the sensor because of its high selectivity to hydrogen ions.

Potentiometric studies showed the feasibility of PoPD as a promising alternative to the conventional glass pH electrode. Investigation of the sensor surface revealed the elemental

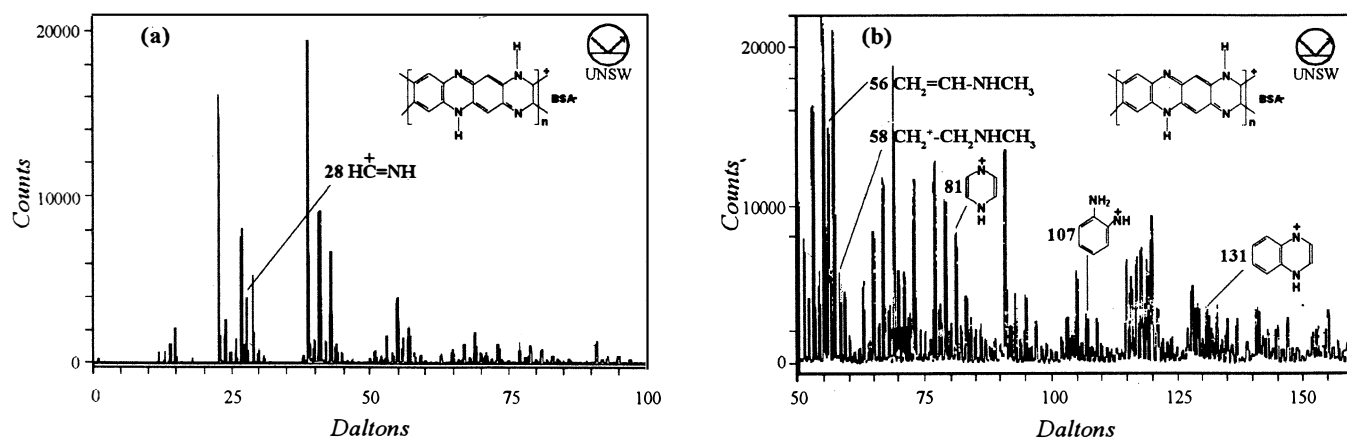


Fig. 14. Positive ion mass spectra of PoPD/BSA conductive polymer on platinum wire (TOFSIMS) over atomic mass units of (a) 0 to 100 a.m.u. and (b) 50 to 160 a.m.u.

composition of interest. All reactions occur on at the surface, and surface analyses gave the picture of what and how the electrode surface looks like.

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