Poly(2,5-dimethoxyaniline) based pH sensors

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ABSTRACT

Poly(2,5-dimethoxyaniline) (PDMA) has been prepared on stainless steel supported electrode through an electrochemical polymerization of 2,5-dimethoxyaniline. Oxalic acid was chosen as a dopant. pH sensitivity of the PDMA-modified electrode has been investigated with a combination of X-ray photoelectron spectroscopy (XPS) and potentiometry. The potentiometric responses to pH change of the PDMA-modified electrode appeared reversible and linear in the range from pH 2 to pH 8 with a sub-Nernstian potentiometric response slope of 49.31 ± 6.1 mV/pH (28°C). The PDMA-modified electrode readily responded to pH change and was stable in time over a period of a month. The selectivity of hydrogen ion was also studied using a fixed interfering method. XPS revealed that the potentiometric responses to pH change were related to the protonation and deprotonation of the nitrogen atoms contained in the PDMA structure. The advantage of this approach is that the proposed pH sensor can be easily fabricated on the available stainless steel supported electrode. Surface modification of the PDMA-modified electrode possibly improves the potentiometric responding to pH change and it is the work in progress.

Keywords: Poly(2,5-dimethoxyaniline), Conducting polymer, Potentiometric sensor,
pH sensor

INTRODUCTION

Determination of pH values is one of the most important tasks in analytical chemistry. Among the different types of pH electrodes, a glass pH electrode has occupied a unique place because of its excellent electrode performances with respect to response slope, long-term stability, selectivity and straight forward operation. However, the conventional glass electrode with internal liquid system exhibits some drawbacks, such as mechanical fragility, high cost and limited miniaturization for the use in clinical or biological applications.

There has recently been much interest in the development of pH sensors based on intrinsically conducting polymers due to their easy preparation, high conductivity and stability. In the oxidized state of these polymers, the positive charges in the polymer are compensated by counter-ions from the solution, giving ion-exchange properties to the polymer films. Therefore the intrinsically conducting polymers are applicable in potentiometric hydrogen ion sensors (Bobacka *et al.*,

2008). Polypyrrole and polyaniline have attracted the most attention since the protonation-deprotonation processes of amino groups contained in the structures are expected to impart pH responses (Yuqing *et al*., 2005). The conducting polymer-based pH sensors, however, have suffered from long response time, non-reproducibility and salt effect (Prissanaroon *et al*., 2004; Lakard *et al*., 2007). Attempts to improve the potentiometric responses to pH changes of the conducting polymer-based pH sensors have been reported. Chemical incorporation of a quinhydrone functionality, a well-known molecular charge-transfer complex consisting of a combination of benzoquinone and hydroquinone, into a thin film of conducting polypyrrole has been reported by Aquino-Binag et al. (1996). The potentiometric characteristics of the hydroquinone-functionalized PPy film showed a sub-Nernstian response of 46 mV/pH at 25 ^{o}C and allowed fabrication reproducibility. Recently, Prissanaroon-Ouajai et al. (2008) have reported that the polypyrrole doped with hydroquinone monosulfonate, a functional dopant with quinhydrone-like structure, showed an improved potentiometric response of 50.54 mV/pH (28 ^{o}C) and a response time less than 100 seconds.

In the present study, poly(2,5-dimethoxyaniline) (PDMA) film have been electrochemically synthesized on the stainless steel supported electrode and used as a pH sensor. PDMA has been selected because PDMA is possibly converted to poly(2,5-dihydroxyaniline) through the demethylation of methoxy groups in the 2,5-dimethoxyaniline units, resulting in the redox activity which is analogous to that of quinhydrone in aqueous electrolyte (Morita *et al*., 1995) and this is on-going work. Oxalic acid has been used as a dopant as it able to passivate the stainless steel via the formation of iron oxalate layer, leading to strongly adherent and smooth polymer film onto a stainless steel electrode (Prissanaroon *et al*., 2006). The PDMA surfaces were characterization by X-ray photoelectron spectroscopy (XPS). The sensitivity of the PDMA-based pH sensor was investigated using a potentiometric technique.

EXPERIMENTAL

PDMA film has been synthesized via a potentiostatically electropolymerization. The supported electrodes were made of stainless steel rods (Grade 430) fitted into Teflon tubes with an active coating area of 0.078 cm^{2} and were as working and auxiliary electrodes. Prior each synthesis, the electrodes were mechanically polished thoroughly with alumina, rinsed with deionized water and subsequently cleaned in an ultrasonic bath for 3 minutes. The electrolyte solution contained 2,5-dimethoxyaniline (0.125 M) and oxalic acid (1.0 M). The electropolymerization was performed using a GW Instek Power Supply (Model GPC 3030D, Taiwan) in a one-compartment cell with a constant applied potential of 1.2 V for 10 minutes at room temperature (28 ^{o}C). The PDMA-coated electrode was then removed from solution and washed thoroughly with copious amounts of deionized water to eliminate any loosely bound species. The electrode was dried in a desiccator before further characterization and testing.

The PDMA surfaces before and after treated with different buffer solutions were investigated by XPS using a Kratos Axis Ultra DLD spectrometer with a monochromatised Al Kα radiation source ($h\nu = 1486.6$ eV) operating at 150 W.

Survey and high-resolution region spectra were recorded at analyzer pass energies of 160 eV and 20 eV, respectively. A low-energy electron flood source as used to counter surface charging during spectral acquisitions, and spectra were corrected for charge shifting by referencing to the C–C component of the C 1s peak (E_b = 285. eV).

Potentiometric measurements were conducted using a 2700 digital multimeter/data acquisition system (Keithley, USA). The PDMA-modified electrode was conditioned in 0.1M oxalic acid overnight and rinsed thoroughly with deionized water before use as an indicating electrode. Standard buffer solutions of different pH values were prepared with appropriate mixtures of citric acid (Ajax), boric acid (Ajax) and $Na_3PO_4.10H_2O$ (Sigma-Aldrich) (Perrin and Dempsey, 1974). The open-circuit potentials (E_{cell}) of the electrode were recorded against an Ag/AgCl reference electrode. A calibration curve was constructed by plotting the E_{cell} (mV), against the pH value of the buffer solution. Electrode selectivity was evaluated in the presence of various interfering ions following the IUPAC recommendation that the interfering ion concentration was kept constant at 0.01 M and the pH was varied. The selectivity coefficient (K_{ij}) was estimated using the extended Nernstian equation (Buck and Linder, 1994). The electrode stability was monitored by repeatedly introducing the electrode into the buffer solutions, measuring the potentials and storing the electrode in the conditioning solution.

RESULTS AND DISCUSSION

1. Surface Characterization of the PDMA-modified Electrodes

Typical XPS survey spectrum for the PDMA surface is presented in Figure 1 showing the expected elemental composition of PDMA including carbon, oxygen and nitrogen. No signal of stainless steel electrode could be detected indicating complete coverage of PDMA.
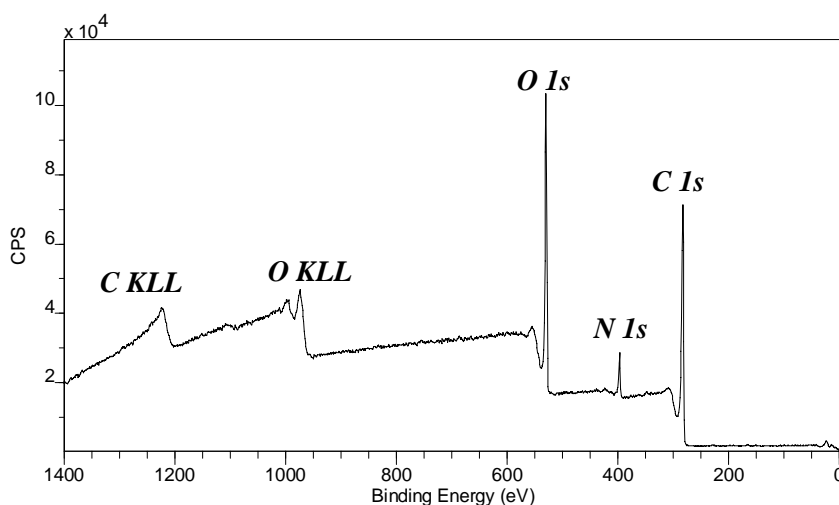

Figure 1 Typical XPS survey spectrum for PDMA surface

Response to pH change of the PDMA-modified electrodes was studied by immersing the PDMA films in different buffer solutions. Table 1 presents the elemental compositions derived from XPS survey spectra. The N 1s photoelectron spectra of the PDMA films before and after immersion in buffer solutions, together with their fitted peak components are illustrated in Figure 2 and the compositions of various nitrogen species are summarized in Table 1. For the as-prepared PDMA film (Figure 2a), the N 1s spectrum is deconvoluted into three components. A major component at 399.5 eV is attributed to the amine-like nitrogen (-NH-). Two other components with binding energies at 400.5 eV and 401.8 eV are associated with positively charged nitrogen species, N^+ and N^{2+} respectively, indicating that the as-prepared PDMA film is in the conducting state (Prissanaroon *et al.*, 2002). The similar fitting is observed for the PDMA film after immersing in acid (Figure 2b), however the positively nitrogen species appear to be more dominant suggesting a higher doping level.

A new peak located at 398.0 eV, attributed to imine-like nitrogen (-N=), is detected for the PDMA film after immersing in the solution of pH 7 (Figure 2c) (Prissanaroon *et al.*, 2004). When the PDMA film is treated with a base (Figure 2d), the intensity of the imine-like nitrogen increases, resulting in a 25% deprotonated PDMA base ([-N=] = 25%) which is considered to be a complete deprotonation (Su and Iroh, 1998). Therefore, it is proposed that the pH sensitivity of PDMA films involves protonation-deprotonation at the 2,5-dimethoxyaniline moieties contained in the PDMA chains of the polymer and hydrogen ion exchange processes in the polymer, represented by a proposed mechanism in Figure 3.

Table 1 Relative compositions of the PDMA surfaces evaluated from survey XPS spectra and   high-resolution N 1s photoelectron spectra

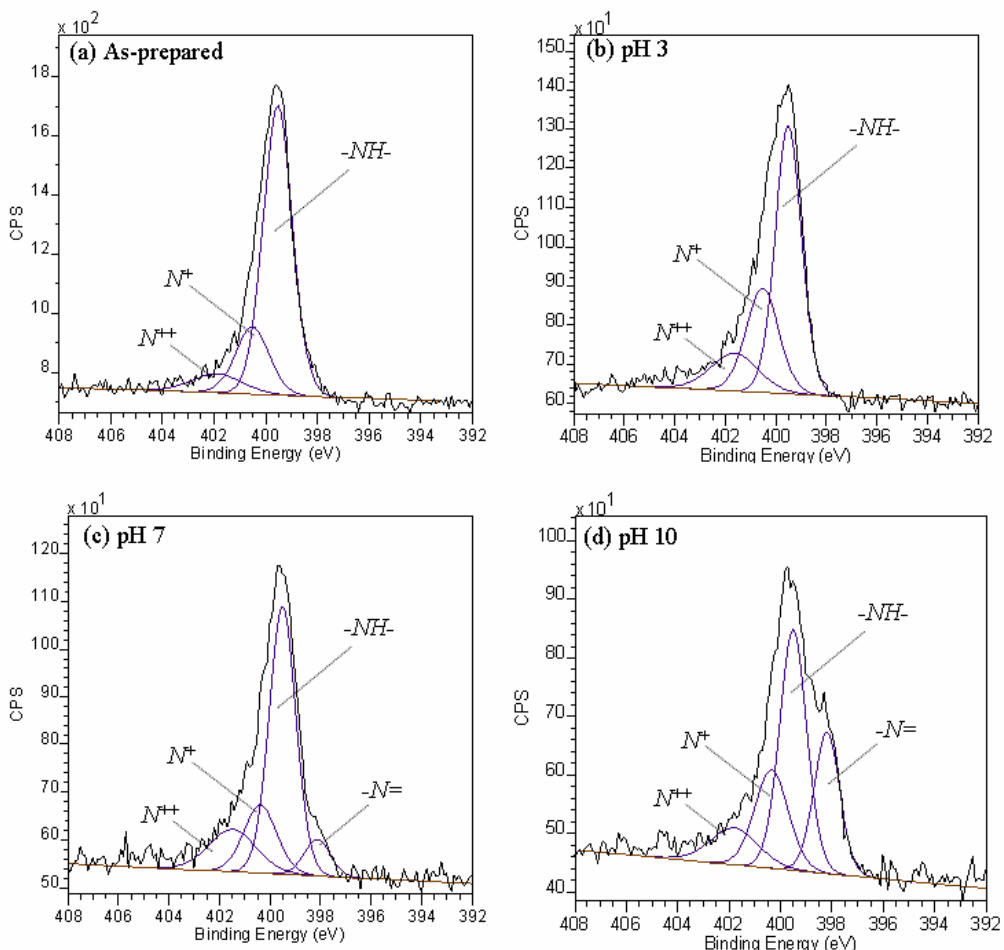| Sample	XPS survey spectra (Atomic %)			High-resolution N 1s spectra (Atomic %)			
	O 1s	N 1s	C 1s	-N=	-NH-	N^+	N^{++}
PDMA as-prepared	25.6	5.9	68.6	-	64.8	25.6	9.6
PDMA treated with pH 3	29.0	5.5	65.5	-	57.7	27.8	14.5
PDMA treated with pH 7	25.4	6.4	68.2	7.8	57.6	18.2	16.4
PDMA treated with pH 10	21.6	8.1	70.3	24.8	42.6	20.9	11.7

Figure 2 High-resolution N 1s photoelectron spectra of PDMA surfaces; (a) as-
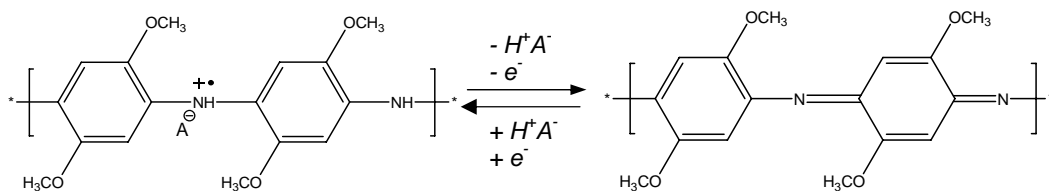prepared and after immersed in different buffer solutions of (b) pH 3, (c)
pH 7 and (d) pH 10

Figure 3 A proposed mechanism of acid-base treatment of PDMA involving a
protonation-deprotonation process

2. Potentiometric Measurements of PDMA-modified Electrodes

2.1 Potentiometric Responses to pH Change

Figure 4 presents the calibration plot of the PDMA-modified electrode. A response slope was found to be a sub-Nernstian slope of 49.31 ± 6.1 mV/pH (28°C) with the linear regression correlation coefficients greater than 0.997 over the pH range of 2 to 8. The evolution of potential as a function of measuring time for the PDMA-modified electrode in buffer solutions revealed that approximately 98% of the steady response occurred in less than 10 seconds indicating a short response time of the PDMA-modified electrode. As seen in Figure 4, however, a large deviation is observed above pH 8. This suggests that the PDMA-modified electrode may not be an effective pH sensor for basic solutions.
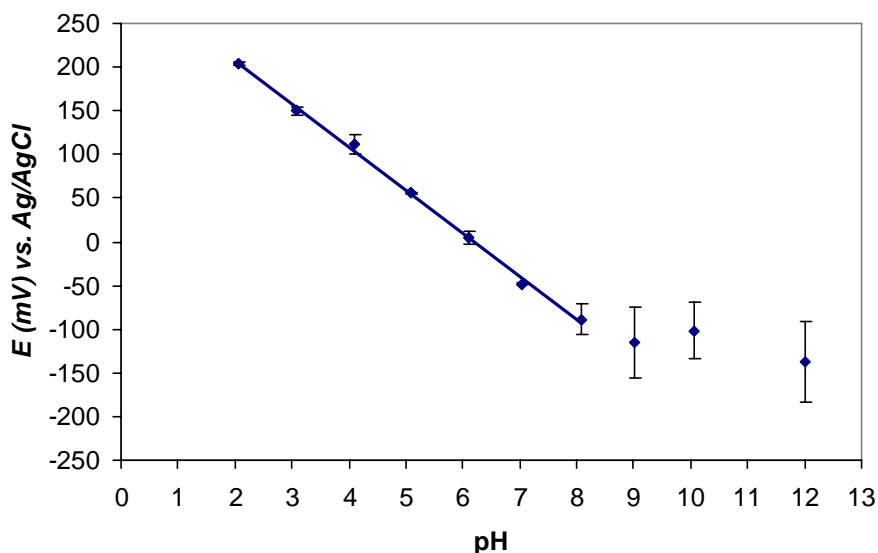

Figure 4 Potentiometric responses to pH change of the PDMA-modified electrodes

A comparison of pH measurements in various solutions, including buffer pH 4, buffer pH 7, Pepsi, Sponsor, orange juice and water, was performed using the PDMA-modified electrode and a commercial glass pH electrode. It can be seen in Table 2 that the PDMA-modified electrode shows an acceptable difference for all tested solutions, except water. It is important to note that the PDMA-modified electrode is not suitable for basic solution as mentioned earlier.

Table 2 pH values obtained for various solutions with the PDMA-modified
electrode and the glass pH electrode

Solution	pH value		pH difference
	Glass pH electrode	PDMA-modified electrode	
Pepsi	2.407	2.54	0.133
Sponsor	3.203	4.60	1.397
Orange juice	3.656	3.23	-0.426
Buffer pH 4	4.010	4.10	0.090
Buffer pH 7	7.000	5.50	-1.500
Water	7.922	5.00	-2.922

2.2 Electrode Selectivity

Selectivity of the PDMA-modified electrode was investigated by repeating the experiments with addition of some common interfering ions following the fixed interfering method (Buck and Linder, 1994). The calibration curves of the PDMA-modified electrodes in the presences of interfering ions are shown in Figure 5. The potentiometric selectivity coefficients (K_{ij}), quantified by evaluation of following the IUPAC recommendation, are summarized in Table 3. It is apparent that most interfering ions do not exhibit a large effect on the potentiometric response of the PDMA-modified electrode as selectivity coefficients are small. However, serious influences of pH sensitivity, including the large deviation from the calibration curve and relatively high selectivity coefficient, are observed for Zn^{2+}, Al^{3+} and SO_4^{2-}.
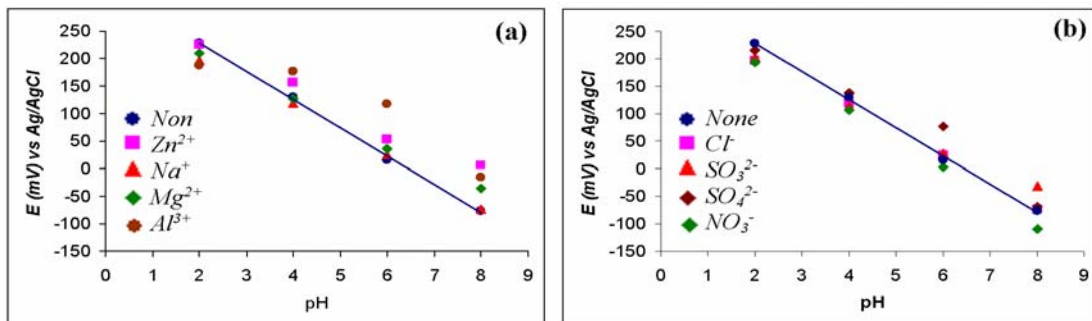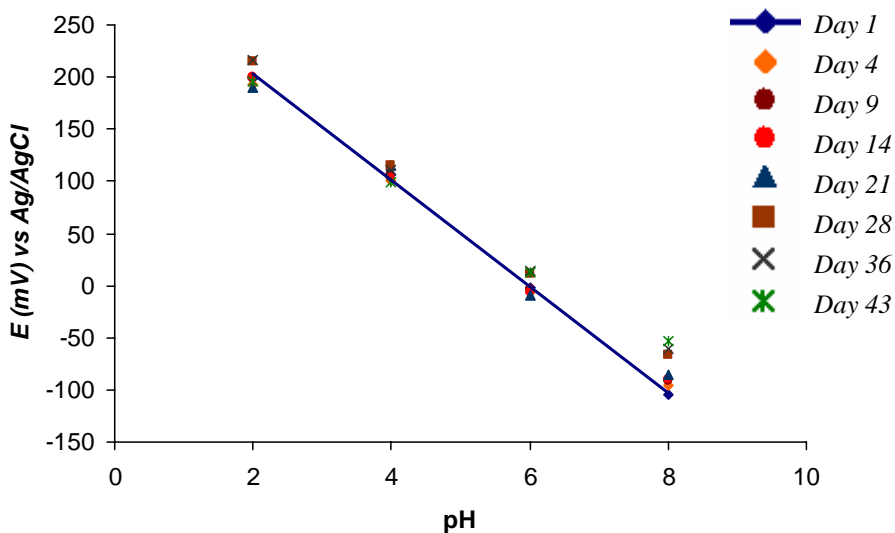

Figure 5 Influence of (a) cationic and (b) anionic interfering ions on the
potentiometric responses of the PDMA-modified electrodes.

Table 3   Selectivity coefficients of the PDMA-modified electrode in the presence of
various interfering ions

Interfering ions	Selectivity coefficient
None	-
Zn^{2+}	3.16×10^{-2}
Mg^{2+}	3.16×10^{-4}
Na^+	1.00×10^{-7}
Al^{3+}	3.33×10^{-3}
SO_3^{2-}	1.58×10^{-5}
SO_4^{2-}	1.58×10^{-3}
NO_3^-	1.00×10^{-9}
Cl^-	1.00×10^{-7}

2.3 Electrode Stability

Potentiometric response of the PDMA-modified electrode was examined
over a period of 43 days in order to study the stability of electrode. As seen in Figure
6, the calibration curves of the PDMA-modified electrodes remain linear and the
response slopes are close to the fresh electrode (1st day) even after repeatedly using
for 20 days. A significant decrease in response slope is observed for the PDMA-
modified electrode after 28 days of the first use. It is important to note that the
PDMA film was found to peel off the supported electrode and it is a possible reason
for the change of response slope.

Figure 6   Influence of aging time on the potentiometric responses of the PDMA-
modified electrodes

CONCLUSION

PDMA-modified electrode has been simply fabricated via a one-step electropolymerization of 2,5-dimethoxyaniline on stainless steel. The potentiometric sensitivity to pH change of the PDMA-modified electrode exhibits a response slope of 49.31 ± 6.10 mV/pH (28°C), a linearity range from pH 2 to 8 and the response time less than 10 seconds. The PDMA-modified electrode shows a small effect to several common interfering ions. The electrode lifetime is up to 20 days. XPS investigations reveal that the potentiometric responses to pH change were related to the protonation and deprotonation of the nitrogen atoms contained in the PDMA structure. Easy fabrication and low production cost of the PDMA-modified electrodes offer an alternative to polymer-based pH sensors. Further development has been focused on modification of the PDMA surfaces in order to improve the potentiometric responses to pH change which is the work in progress.

ACKNOWLEDGMENTS

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