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Fabrication and Characterization of a Hydroquinone-Functionalized Polypyrrole Thin-Film pH Sensor

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The physical and chemical properties of polypyrrole (PPy) derivatized at the 3-position with dimethoxybenzyl and dihydroxybenzyl functionalities via a novel high-yield pathway were evaluated for pH response. The monomers were electrochemically polymerized with perchlorate dopant in a propylene carbonate electrolyte solution. The potentiometric characteristics of the resulting films show a sub-Nernstian response of 46.0 mV pH^{-1} (25 °C); a detection limit of 1×10^{-10} mol dm^{-1}; potential drift of ±1.9 mV and a low hysteresis with Δslope = ±1.9 mV pH^{-1}. X-ray photoelectron spectroscopy (XPS) shows a reduction in the carbon 1s and chlorine 2p photoelectron peaks widths for functionalized PPy in comparison with the PPy indicating presence of β-carbon substituents. Time-of-flight secondary positive ion mass spectra showed peaks at m/z values of 107 and 109, indicating the presence of hydroquinone species at the outermost film surface of the functionalized PPy. The structure of the functionalized monomers was confirmed by C^{13} and H^1 NMR. Cyclic voltammetry (CV) showed the expected electrochemical response of the hydroquinone functionality incorporated into the PPy repeat unit. Functionalized polypyrrole offers potential for pH sensor devices with the electroactive species, conductive support, and mechanical support in an integrated form.

Introduction

Quinhydrone, a combination of hydroquinone and quinone has found wide application in pH sensing devices.[1−3] A thin-film pH sensor using quinhydrone (QH) as the electroactive species supported in an inert matrix of poly(vinyl chloride) (PVC) coated onto a carbon support has been reported previously.[4] This sensor has good potentiometric response with a slope of 44.0 mV pH^{-1} (25 °C). However, there is a significant deviation in the range of electrode response due to segregation and variability in the PVC-QH mix and nonreproducible fabrication steps. In this study, the key QH electroactive species is retained. The QH is chemically incorporated into a thin film of conductive polypyrrole (PPy) allowing enhancement of sensor structure and fabrication reproducibility.

Polypyrroles are ideally suited for sensor applications due to high conductivity and electroactivity. In addition, the pyrrole monomer can be modified by chemical substitution to produce functionalized forms of PPy. PPy can be used as a general matrix and further modified with other compounds in order to change selectivity. It has been shown that organic compounds can be introduced electrochemically into the bulk of the PPy film or that its surface can be derivatized.[5]

Derivatization of PPy has led to polymers with promising modified electrode behavior. The synthesis of 3-substituted PPy is not as straightforward as that of N-substituted forms. Hence, most derivatization of PPy focuses on the pyrrole nitrogen (the 1-position). N-substituted pyrrole polymers are, however, less conductive relative to the parent pyrrole due to loss of planarity,[6] loss of hydrogen, on the nitrogen or loss of conjugation[7] which represents a significant limitation. An alternative is to derivatize PPy in the 3-position. The 3-substituted pyrrole polymer films show highly reversible electrochemical behavior and are, therefore, useful over wider electrochemical ranges than the equivalent 1-substituted materials.[7,8] 3-(2,5-Dimethoxybenzyl)pyrrole (**2**) is an important pyrrole compound (Scheme 1) because the polymerized form can be demethylated to yield a hydroquinone substituted polypyrrole (**4**) (Scheme 2). Despite the simple structure and importance as a key starting material, no high-yielding synthesis of this compound has been reported. A new high-yield synthetic pathway is presented for attaching a redox hydroquinone functionality to pyrrole in the 3-position.

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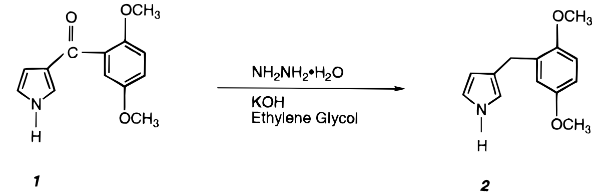
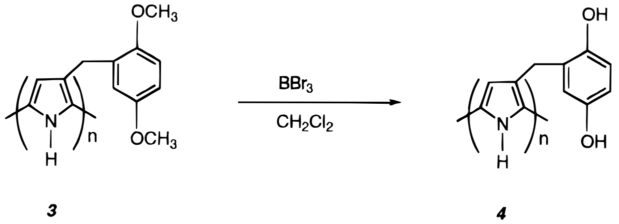
Scheme 1



Scheme 2



This paper describes the surface and potentiometric properties of the functionalized polypyrrole integrated sensor structure in which the polymer serves as the electroactive species and the conductive and mechanical support. Chemical linking of the matrix and electroactive species enhances reproducibility and processability of the sensor.

Experimental Section

Synthesis of Functionalized Monomers. 1-(Benzenesulfonyl)pyrrole[9] and 2,5-dimethoxy-1-benzoyl chloride are used as substrates in $AlCl_3$-catalyzed Friedel−Crafts acylation reactions in this regiospecific synthesis of 3-acylpyrroles. The benzenesulfonyl group is readily removed by subsequent alkaline hydrolysis to give 3-(2,5-dimethoxybenzoyl)pyrrole (**1**, Scheme 1) with excellent yield (90%). A standard Wolff−Kishner reduction of 3-(2,5-dimethoxybenzoyl)pyrrole using hydrazine hydrate and potassium hydroxide in ethylene glycol gives 3-(2,5-dimethoxybenzyl)pyrrole (**2**, 0.17 g, 0.78 mmol, 90%).[10,11] The synthetic aspects of this methodology have been reported previously in more detail.[12]

Polymer Formation and Characterization. Voltammetric experiments were used to monitor the growth of polymers and were performed in a conventional (Bioanalytical Systems, Inc. BAS 100B) three-electrode, one-compartment cell (50 × 25 mm) with 0.1 M $LiClO_4$ electrolyte and 0.007−0.03 M monomer under a nitrogen atmosphere. Electrochemical potentials were recorded vs a Ag/AgCl reference electrode (BAS) and platinum counter electrode scanning from +0.5 to +2.0 V with a 10 mV s^{-1} scan rate. Electrodes used were Teflon-coated or Kel-F-coated (BAS 100B) platinum and carbon disks, 0.15 mm i.d. (BAS) or platinum wire, 0.1 mm thick (99.99%). The polymer coated electrodes were evaluated in a fresh electrolyte solution with the appropriate dopant, free of monomer, by scanning from −1.0 to +1.0 V at 50 mV s^{-1} scan rate.

The polymer electrodes, **3**, were demethylated by immersion for 3 h in a 3.0 M solution of boron tribromide in dichloromethane[13] (Aldrich, Scheme 2). The electrodes were removed and washed with distilled water prior to characterization. Electrodes were evaluated by cyclic voltammetry before and after demethylation in 1.0 M H_2SO_4 solution vs Ag/AgCl reference electrode.

Electrode potentiometric characterisation and pH measurements were performed with a pH/mV meter (Activon Model 209) and a calomel reference electrode (Metrohm Model B-NS 14/15) at 25 ± 2 °C. Experimental procedures have been reported previously in more detail.[4]

Electrode Surface Characterization. X-ray photoelectron spectroscopy (XPS) was used to analyze PPy films grown on platinum wire electrodes. Experiments were performed using a Kratos AXIS surface analysis system. A Mg anode X-ray source was operated at 190 W. The maximum energy resolution of the concentric hemispherical analyzer (CHA) was 0.87 eV operated for XPS analysis in the fixed analyser transmission (FAT) mode with a pass energy of 20 eV for the Ag $3d_{5/2}$ emission.[14] The 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 time-of-flight secondary ion mass spectrometer (TOF-SIMS). A monoisotopic ^{69}Ga ion source (25 keV energy, 10^{-3} nA beam current) was rastered over an area ∼200 μm × 200 μm. Static positive ion and negative ion mass spectra were collected using 10^6 cycles and a 100 ns pulse width $cycle^{-1}$.

Results and Discussion

Functionalized Monomer Synthesis. Regiospecific synthesis of 3-acylpyrroles requires the use of indirect methods involving several steps. Skell and Bean[16] have prepared numerous 3-alkylpyrroles by the alkylation of pyrrolylmagnesium bromide. The 3-isomer obtained has low yield (5−18%). This route also requires the separation of the 3-isomer from relatively large amounts (10−32%) of the 2-isomer. Recently Foos et al.[8] reported the preparation of 3-(2,5-dimethoxybenzyl)pyrrole by reaction of pyrrolylmagnesium bromide with 2,5-dimethoxybenzyl bromide with a 3% yield. This yield is low and requires extensive chromatography to isolate the desired 3-isomer from 1- and 2-substituted pyrrole. Attempts in this study to improve the yield of 3-isomer by modifying the order of addition of benzyl bromide were unsuccessful.

Gram quantities of **2** are required as a starting material for the preparation of the polymer for chemical sensor applications. A synthetic route (Scheme 1) which gives a high yield of the 3-isomer has been devised based on the acylation and hydrolysis of 1-(benzenesulfonyl)pyrrole[10] and subsequent Wolff−Kishner reduction giving the 3-(2,5-dimethoxybenzyl)pyrrole (**2**). This is a high-yield and highly regioselective synthesis for the 3-isomer resulting in a yield of 80−90% or about 30 times greater yield than the previous route. The simplicity and high overall yield of this pathway have made this the method of choice for the synthesis of the dimethoxybenzyl and hydroquinone-functionalized PPy. Compound **2** was characterized by ^{1}H NMR, ^{13}C NMR, mass spectrometry (M^+, m/z 217), elemental analysis, and IR and UV−vis spectroscopies. The product of this synthetic route is incomplete as the functionalized pyrrole has methoxy groups as substituents. Polymer films are formed using dimethoxybenzylpyrrole. Boron tribromide is then used to demethylate the aryl methyl ethers completely[13] to generate a polypyrrole film with

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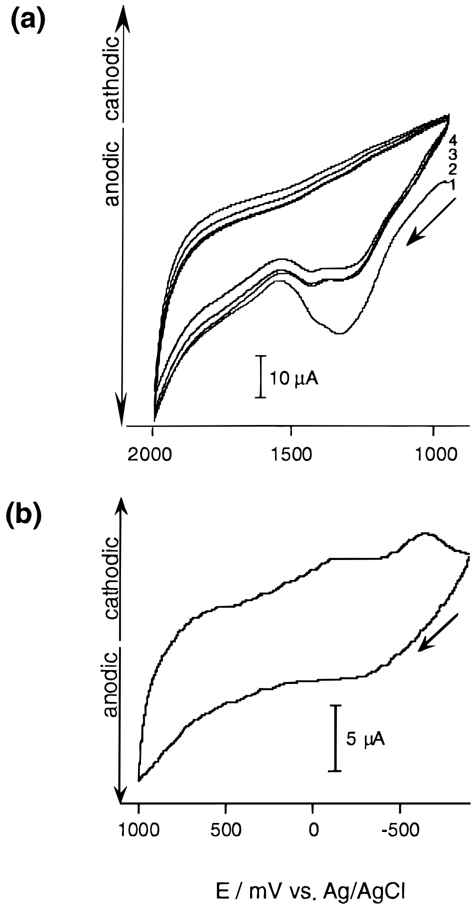

Figure 1. (a) Cyclic voltammogram growth of 3-(2,5-dimethoxybenzyl)pyrrole, **2**, on platinum wire electrode doped with perchlorate. (b) Evaluation of the polymer film, **3**, in fresh electrolyte and dopant solution.

a hydroquinone functionality (Scheme 2). The boron tribromide reacts specifically with the methyl groups and does not cause any change or disruption to the polypyrrole structure.

Removal of methyl groups with BBr_3 is an inconvenient process to adapt to production of sensor devices beyond the laboratory scale. Alternative methods were investigated unsuccessfully for the direct synthesis of a pyrrole monomer with a hydroquinone functionality, avoiding the demethylation step. One pathway involves the protection of phenolic groups using benzyl bromide. The key steps are esterification of dihydroxybenzoic acid, benzylation, hydrolysis, and then $AlCl_3$-catalyzed acylation of 1-(benzenesulfonyl)pyrrole with 2,5-benzyloxybenzoyl chloride. However, no 3-acyl-derivatized product was produced even at low temperature (0 °C). Acetic anhydride was also used to protect the phenolic groups but also failed to give the expected product after esterification.

Electrochemistry. The cyclic voltammogram in Figure 1a shows the film growth of 3-(2,5-dimethoxybenzyl)polypyrrole with oxidation potential greater than +1.0 V (vs an Ag/AgCl reference electrode) where voltammograms were scanned over the range +0.5 to +2.0 V. It shows the successive growth of the polymer film and the irreversible oxidation peaks at +1.3 V, electrolyte discharge at +2.0 V, and the gradual shifts to positive anodic potential as the film thickens.[17,18] During the cyclic voltammetric experiments, a brown-black, continuous film was deposited on the Pt electrode after the first scan. This implies that oxidized dimethoxybenzyl Ppy is formed readily during the early stages of electrodeposition. The inductive effect of the aryl group makes this monomer, **2**, more difficult to oxidize, resulting in a more positive or higher anodic potential[19] compared with the parent PPy which oxidizes at +0.81 to +1.0 V.[20] Film thicknesses were estimated to be ~20 μm using scanning electron microscopy. The use of a higher upper potential limit might be expected to degrade the conductivity of the film.[21] However, observed electrode potentiometric characteristics are still sensitive to pH changes, and thus the electrode remains an effective pH sensor. After removal of the polymer film, **3**, from the solution and replacement of the electrolyte solution, scanning of the system in the range −1.0 to +1.0 V showed anodic potential $E_{pa} \sim -0.25$ V and cathodic potential $E_{pc} \sim -0.55$ V. It is assumed that traces of water and oxygen were present as impurities in the solvent, and since the electrodes were very small, it is possible for thin metal oxide layers to envelope the electrodes completely.[22] Two reasons can be proposed for the formation of the metal oxide layers during the cyclic voltammetry experiments. First, when the microelectrode was transferred to the CV cell after cleaning, it was in contact with air resulting in oxide formation. Second, when a CV scan was first performed, the metal electrode was oxidized and hence passivated before the oxidation potential of the pyrrole monomer was reached.

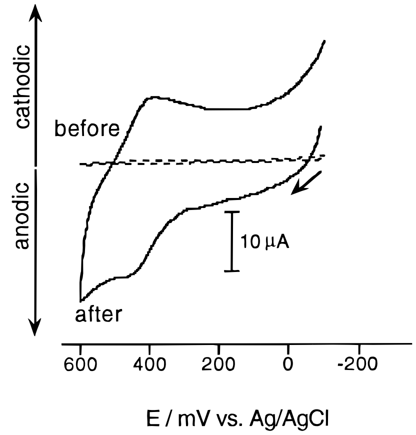

Figure 2. Voltammograms of **3** before (---) and after (—) demethylation (with BBr_3) in 1.0 M H_2SO_4 (vs Ag/AgCl).

Figure 2 shows a voltammogram comparing a dimethoxybenzyl PPy film (before demethylation) in 1.0 M H_2SO_4 supporting electrolyte and a dihydroxybenzyl PPy film (after demethylation) in the same electrolyte. In the dimethoxybenzyl PPy voltammogram only charging due to the polypyrrole backbone is observed, that is, a very small increase in current, in comparison the presence of the dihydroxybenzyl group. After demethy-

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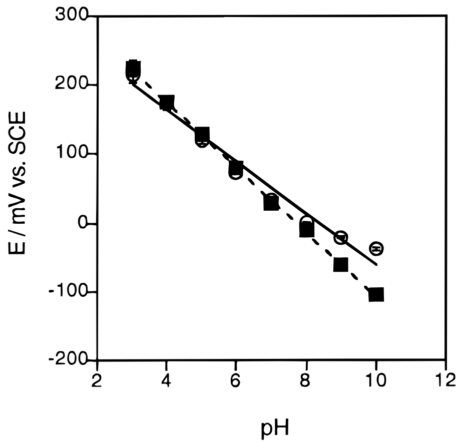

Figure 3. Comparative potentiometric response of parent polypyrrole (—) and 3-(2,5-dihydroxybenzyl)polypyrrole, **4**, (---).

Table 1. Electrode Characteristics of Parent Polypyrrole and Hydroquinone Functionalized Polypyrrole (4) (Values Are Averages of Four Calibrations of Individual Electrodes)

	parent polypyrrole	hydroquinone-functionalized polypyrrole
slope/mV pH^{-1}	35.0	46.0
hystresis Δslope/mV pH^{-1}	±8.7	±1.9
drift/mV	±4.1	±1.9
detection limit/ mol dm^{-3}	3.2×10^{-10}	1×10^{-10}

lation, the hydroquinone−quinone redox electrochemistry was observed at ∼+0.46 V anodic potential.[8] This confirms the successful removal of methyl groups from the conductive polymer using boron tribromide to give the hydroquinone functionality.

Figure 3 shows the comparative potentiometric response of electrodes coated with the parent PPy and with hydroquinone-functionalized PPy. The parent PPy has a non-Nernstian slope of 35.0 mV pH^{-1} while the functionalized PPy has a sub-Nernstian response 46.0 mV pH^{-1}. The functionalized PPy has minimal electrode hysteresis, and a lower detection limit and therefore better sensitivity, as shown in Table 1. Both types of film have a wide linear working pH range of 3−10. The potential drift of functionalized PPy electrode in basic, neutral, and acidic media showed minimal carryover of ±1.9 mV as seen in Figure 4. Significantly, the functionalized PPy showed stability toward basic media pH (pH 10) which is very unusual for conjugated polymers. Titrations done with the hydroquinone-functionalized PPy electrode in 0.1 M HCl with 0.1 M NaOH and phenolphthalein indicator gave a similar end-point with the pH glass electrode, as shown in Figure 5.

This hydroquinone-functionalized PPy pH sensor gave better response slope and smaller deviation in range of electrode response (46.0−42.0 mV pH^{-1}) than the PVC/QH pH sensor (44.0−22.0 mV pH^{-1}),[4] because of the highly reproducible fabrication steps and greater uniformity of QH in the matrix.

Surface Properties of the Functionalized Polypyrrole. *Time-of-Flight Secondary Ion Mass Spectrometric Analysis.* Positive ion mass spectra for the parent PPy and the hydroquinone-functionalized PPy grown on platinum wires are shown in Figure 6a,b, respectively. Peaks at *m/z* 28, 40, 42, 44, 56, and 58 are characteristic of fragmentation of the parent polypyrrole (Figure 6a).[23,24] Other groups of peaks with *m/z* 27, 39, 41, 57, 77, and 91 are attributed to $C_2H_3^+$, $C_3H_3^+$, $C_3H_5^+$, $CH_2OHCH{=}CH^+$, $C_6H_5^+$, and $C_7H_7^+$ hydrocarbon fragments respectively.[23,24] Figure 6b shows a series of peaks which are consistent with the hydrocarbon peaks from the parent polypyrrole, discussed above. Significantly, peaks are also observed at *m/z* of 107 and 109 corresponding to quinone and hydroquinone ions, respectively. This indicates the presence of the desired electroactive species at the outermost surface of the polymer. The mass spectra were collected under “static” conditions (low total ion dose) which results in the removal of <1% of the atoms from the surface monolayer.[25] This result also confirms the successful demethylation of the functionalized polypyrrole. Negative ion mass spectra showed several anionic species, for example, $^{16}O^-$, $^{35}Cl^-$, and $^{37}Cl^-$, but provided no additional molecular information.

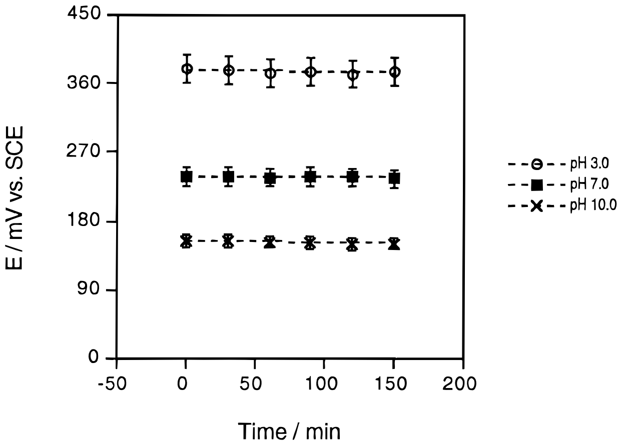

Figure 4. Electrode drift of hydroquinone functionalized PPy. Potential readings of buffer solutions with pH 3.0, 7.0, and 10.0 taken every 30 min over a period of 3 h.

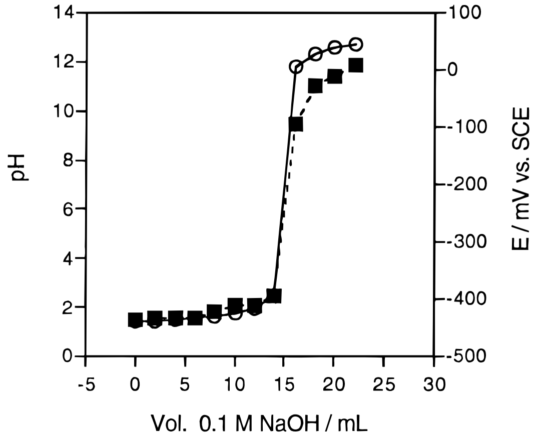

Figure 5. Titration of hydroquinone-functionalized PPy (---) in 0.1 M HCl with 0.1 M NaOH compared with pH glass electrode (—).

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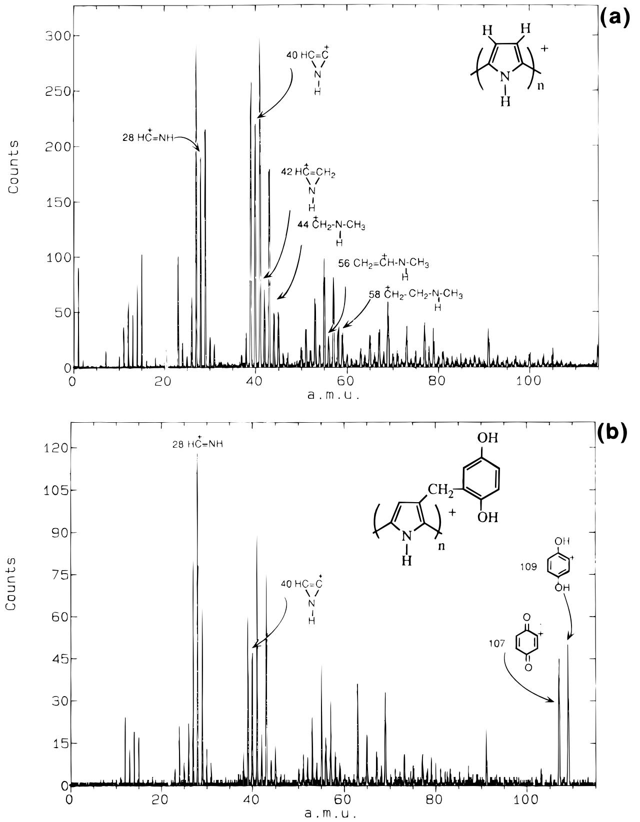

Figure 6. Positive ion mass spectra of conductive polymer-coated platinum wire (TOFSIMS) (a) parent polypyrrole and (b) 3-(2,5-dihydroxybenzyl)polypyrrole (**4**).

X-ray Photoelectron Spectroscopic Analysis. The structure of polypyrrole, a poly(five-membered heterocycle), corresponds to the coupling of monomeric pyrrole units in 2,5-positions (α and α′ carbons) with preservation of the aromatic nucleus.[26] Coupling could also occur at 2,4-positions (α and *β*′ carbons) and substitution at carbons in 3- or 4-positions (*β* and *β*′ carbons). The contribution of α and *β* carbons are distinguished because of their characteristic binding energies.

Figure 7 shows the C 1s photoelectron spectrum for PPy grown on Pt wire. Four-component peaks were fitted to the spectrum using Gaussian−Lorentzian line shapes, as shown in Figure 7a.[27] The component peak centred at a binding energy of 285.0 eV with a full width at half-maximum (fwhm) of 1.8 eV corresponds to the pyrrole α carbons. The component peak at the lowest binding energy (284.1 eV) is due to the pyrrole *β* carbons and also has a fwhm of 1.8 eV.[28] The pyrrole α and *β* carbon peaks are therefore split by 0.9 eV.[29] Asymmetry on the high binding energy side of the C 1s spectrum was assigned to "disorder" carbon species associated in part with non-α,α′ carbon linkages.[28] This broad shoulder structure is due to contributions from alcohol/hydroperoxide bonds (C−O) and carbonyl bonds (C=O), separated by about 1.5 eV. The concentration of C−O species concentration is greater than that of the carbonyl species, indicating full oxidation to carbonyl species has not occurred.

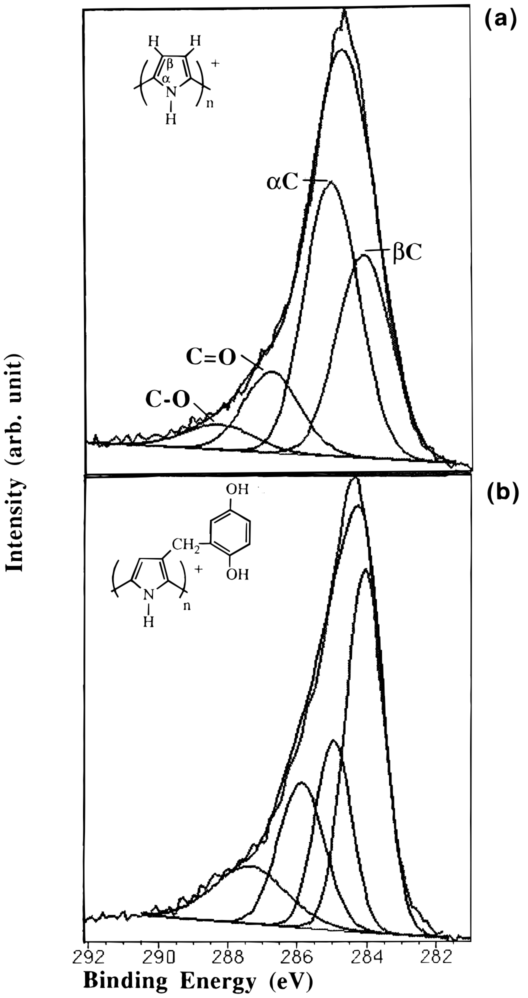

Figure 7. C 1s XPS core level spectrum of the (a) polypyrrole perchlorate and (b) 3-(2,5-dihydroxybenzyl)polypyrrole (**4**) perchlorate with the contributions from *β*,α, C−O and C=O carbon atoms.

Chemical functionalization of the pyrrole results in the *β* hydrogen at 3-position of the pyrrole ring being substituted by dihydroxybenzyl group, (**4**, Scheme 2). This modification to the monomer ensures that the pyrrole rings are bonded via the α,α′ carbons. The overall width of the carbon 1s photoelectron peak for the 3-(2,5-dihydroxybenzyl)polypyrrole is reduced to 2.08 eV (Figure 7b) in comparison with a width of 2.13 eV for the parent PPy (as shown in Figure 7a).[29] It should be noted that the carbon 1s photoelectron peak for the dihydroxybenzylPPy in this case includes additional contributions from methylene ($-CH_2-$) group of the functionality at ∼285.0 eV, aromatic carbons at ∼284.7 eV and C−O carbons at 287.4 eV. In addition, the asymmetry at the high binding energy side of the C 1s spectrum is reduced in comparison with the parent PPy. The reduction in peak width is due to the absence of the non-α,α′ carbon linkages which are eliminated by the presence of blocking dihydroxybenzyl group. Shake up transitions due to aromaticity are observed in the carbon 1s photoelectron spectra for both polymers as small peaks centered around 292 eV.[27]

The asymmetry at the high binding energy side of the nitrogen 1s photoelectron peak is observed for both the parent PPy (Figure 8a) and the 3-(2,5-dihydroxybenzyl)-PPy (Figure 8b) due to electrostatic screening of the counterions. The three nitrogen features are assigned

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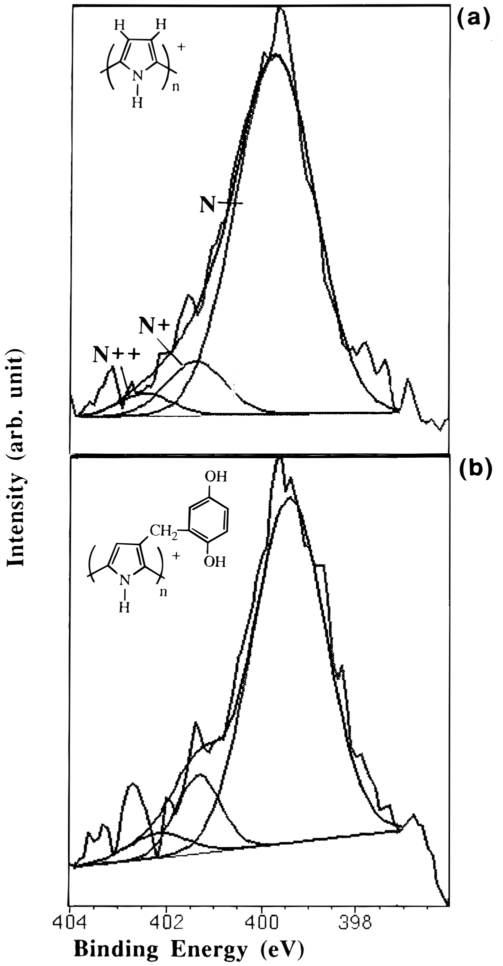

Figure 8. N 1s XPS core level spectra showing the contributions from three inequivalent nitrogen sites of (a) parent PPy perchlorate and (b) 3-(2,5-dihydroxybenzyl)polypyrrole (**4**) perchlorate.

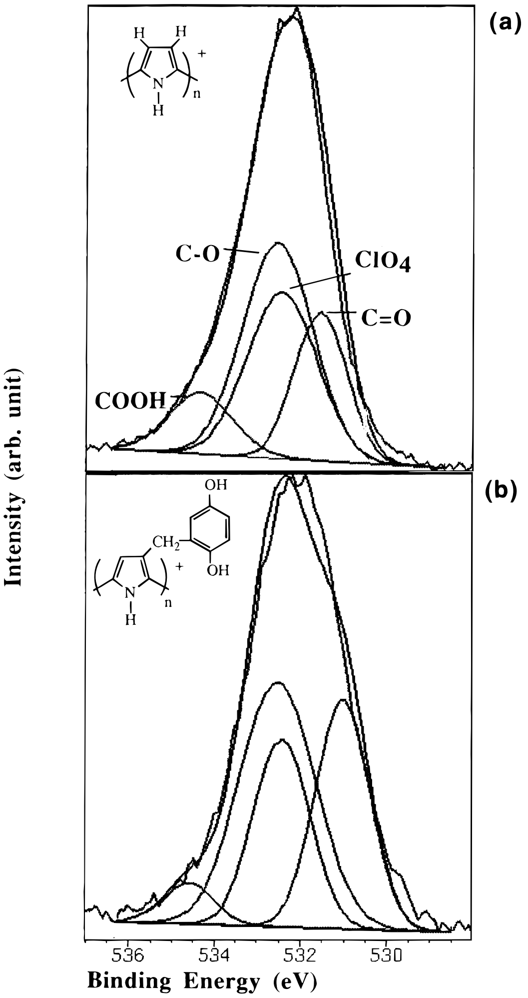

Figure 9. O 1s XPS core level spectra curve fit with contributing oxygen species for (a) parent PPy perchlorate and (b) 3-(2,5-dihydroxybenzyl)polypyrrole (**4**) perchlorate.

to three electrostatically inequivalent nitrogen environments. For every perchlorate anion there are three- to four-pyrrole units,[20] and these anions located between the polypyrrole chains will produce electric fields at the nitrogen sites making atoms in the proximity appear more positive. Figure 8a shows nitrogen 1s photoelectron spectrum for the parent PPy in which the main peak centred at 399.7 eV corresponds to neutral pyrrole nitrogen and the two higher energy peaks, separated from the main peak by 1.3 and 2.3 eV, correspond to pyrrole nitrogen with a partial charge of $\sim +^1/_6$ and $\sim +^1/_2$, respectively. This method of peak deconvolution was developed by Eaves et al.[30] and Pfluger et al.[29] to explain the nonideality of the peak. Figure 8b shows the nitrogen 1s photoelectron spectrum for 3-(2,5-dihydroxybenzyl)PPy in which the higher binding energy N^+ and N^{2+} component peaks are enhanced due to the electron-withdrawing inductive effect. The presence of a dihydroxybenzyl substituent, a strong electron-withdrawing group at the 3-position, acts to make the pyrrole nitrogen appear more positive.

Figure 9a,b shows the oxygen photoelectron spectra for the parent PPy and the 3-(2,5-dihydroxybenzyl)PPy, respectively. The oxygen peak width for the 3-(2,5-dihydroxybenzyl)PPy is 2.5 eV in comparison with the reduced value of 2.2 eV for the parent PPy. The oxygen concentration is increased for the functionalized PPy, as expected, by oxidation sequences during polymerization and by a contribution of oxygen-containing species in the hydroquinone functionality centered at ~532.6 eV. These contributions together with a peak due to the perchlorate dopant (ClO_4^-) centered at ~532.5 eV result in peak asymmetry at high binding energy.

The anionic sites also appear to be better defined, as shown in Figure 10, by the reduction in the line width of the Cl $2p_{3/2}$ from typically ~1.5 eV in the unsubstituted polypyrrole (Figure 10a) to <1.4 eV in the hydroquinone functionalized polymer (Figure 10b). This result is consistent with electron diffraction studies which show that the chains are crystallographically more aligned for the substituted polymer.[6] The perchlorate anion shows the characteristic Cl 2p doublet corresponding to Cl $2p_{3/2}$ and Cl $2p_{1/2}$ orbitals at about 207 and 209 eV. These occur at higher binding energy compared to ground-state Cl 2p at ~200 eV[15] as the four oxygens attached to chlorine in perchlorate anion make the chlorine highly positive (+7 electronic state for ClO_4^-).

Scanning Electron Microscopic Analysis. SEM studies of surface morphology (Figure 11) show that the parent PPy has nonuniform rough surface in contrast with the smooth surface of the hydroquinone-function-

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(30) Eaves, J. G.; Munro, H. S.; Parker, D. *Polym. Commun.* **1987**, *28*, 38.

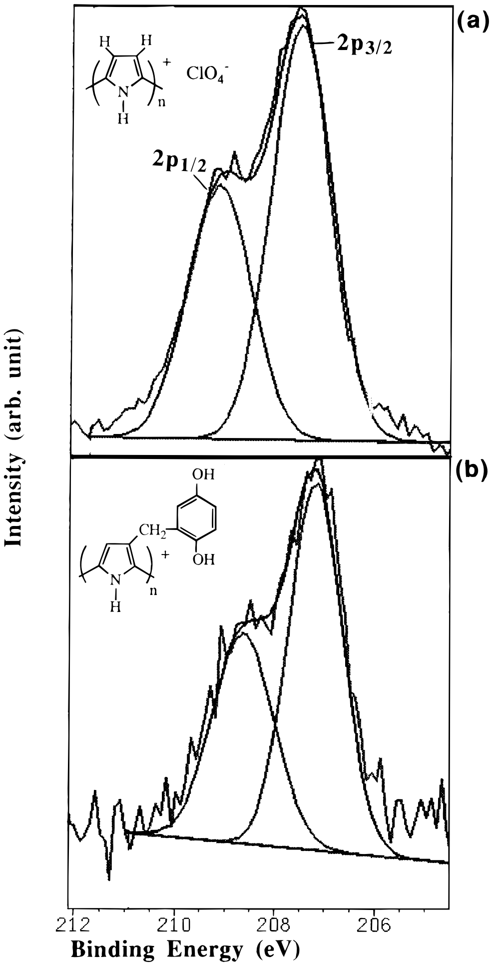

Figure 10. Cl 2p XPS core level spectra curve fit to $2p_{3/2}$ and $2p_{1/2}$ orbitals for (a) parent PPy perchlorate and (b) 3-(2,5-dihydroxybenzyl)polypyrrole (**4**) perchlorate.

alized PPy. A series of SEM micrographs of the parent PPy, 3-(2,5-dimethoxybenzyl)PPy, and 3-(2,5-dihydroxybenzyl)PPy shows that the structure changes with the type of functionality attached to the PPy backbone for the same polymerization conditions. The parent PPy (Figure 11a) has a cauliflower type surface, while 3-(2,5-dimethoxybenzyl)PPy (Figure 11b) and 3-(2,5-dihydroxybenzyl)PPy (Figure 11c) are smooth layered films. The smoothness of the surface of the polymer film may affect the response time and sensitivity of the polymer film sensor. At the electrode surface, there are two competing electrode properties: sensitivity and response time. A rough electrode surface may give higher sensitivity than smooth surface due to increased surface area and therefore an increased concentration of the electroactive species. Roughness, however, slows the diffusion of H^+ through the surface due to the presence of valleys on the electrode surface. A uniform and smooth surface is relatively less sensitive but makes the diffusion of the H^+ in and out the surface faster. This surface roughness may affect the response time of the electrode, but both parent Ppy and functionalized PPy gave almost identical response times of about 6 min.

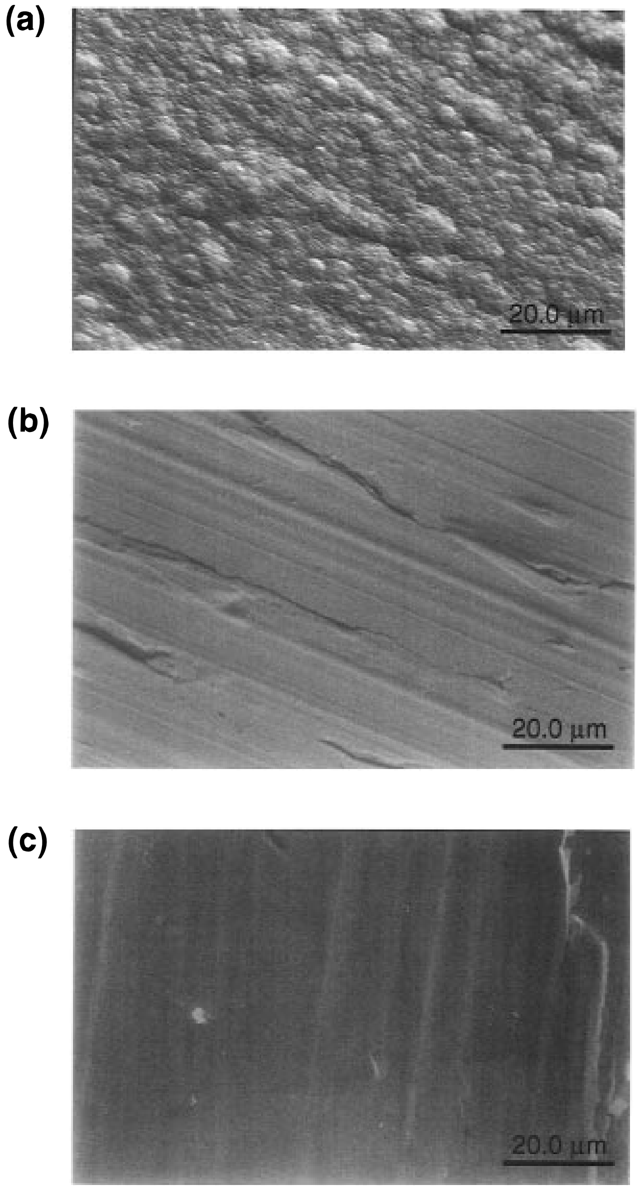

Figure 11. Micrograph images of (a) parent polypyrrole, (b) 3(-2,5-dimethoxybenzyl)polypyrrole (**3**) and (c) 3-(2,5-dihydroxybenzyl)polypyrrole (**4**).

Conclusions

Polypyrrole with a hydroquinone functionality was synthesized with superior yield, and the pathway is highly regioselective in comparison with previous work. Surface-sensitive analytical techniques, cyclic voltammetry, and potentiometric measurements have shown that the hydroquinone-functionalized polypyrrole films can be successfully polymerized and have hydroquinone species at the outermost surface of the film and that these species are electronically active. A reduction in photoelectron peak widths for carbon and chlorine species from functionalized films demonstrates substituent-enhanced order.

The functionalized polypyrrole films show good pH response, a sub-Nernstian slope, low detection limit, and minimum electrode hysteresis. The advantage of this approach in terms of processability is that the sensor has an integrated structure with the polymer and attached functional groups acting as electroactive species, conductive support, and mechanical support.

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