XPS characterization of nanosized overoxidized polypyrrole films on graphite electrodes

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X-Ray photoelectron spectroscopy (XPS) analysis was used to verify the structure of nanosized overoxidized polypyrrole (OPPy) films that were grown on glassy carbon. The films were electrochemically grown to ca. 1.2–1.6 nm thickness from acetonitrile with tetrabutylammonium perchlorate (TBAP) and from water with adenosine triphosphate (ATP) as dopant. The films have been previously characterized by electrochemical methods, but this represents the first study of the ultrathin films by XPS. XPS analysis verifies that the key structural features of nanosized OPPy films are the same as those of much thicker films previously studied by XPS on metal substrates, where differential charging effects are much less severe. Some differences between the microstructures of OPPy and OPPy/ATP films are highlighted by the results. In addition, XPS results confirm a two-domain model of the polymer films that has been proposed from previous studies of PPy and OPPy. The results show that XPS can be used to characterize nanosized films on graphite, after correction for differential charging. Graphite represents a substrate of choice for the fabrication of permselective ultrathin membranes for biosensors from materials such as OPPy.

Introduction

X-Ray photoelectron spectroscopy (XPS) is a selective and sensitive surface characterization technique. It is widely applied to the analysis of polymers, and has been used to investigate conducting and non-conducting polymer films. For such films, the long-range order does not impinge very heavily on the main photoemission spectral features, while short-range effects are crucial.

XPS has proven particularly useful in the characterization of conducting polypyrroles (PPy) and non-conducting overoxidized polypyrroles (OPPy). Both polymers are porous to solvent and electrolyte and PPy can undergo charge transfer reactions with species in solution, while OPPy is an ion conductor with permselective properties.

The structure of oxidized conducting PPy is depicted below:

![PPy Structure](image)

Conducting PPy films, of 1–5 μm thickness, grown on Pt substrates, have been studied by Pflug and Street using XPS. The presence of counterions was detected in the polymer and, for PPy/ClO4− polymer, the anion to ring ratio was 1:3 confirming that every third repeat unit had a positive charge.

Neoh et al. galvanostatically deposited thick films of PPy at 2 mA cm−2 on a stainless steel electrode from various acid electrolytes for 10 to 15 min. Their films were characterized by XPS. All binding energies were referred to the C 1s carbon peak at 284.6 eV to take into account surface charge effects due to the different electronic environments of the carbon atoms.

In this work, we investigated the feasibility of structural characterization of ultrathin (ca. 1.2–1.6 nm thick) films of OPPy by XPS, directly on the substrate on which the films were grown, which was glassy carbon. To our knowledge, XPS characterization of ultrathin polymer films on graphite has not been reported. The main difficulties are due to differential charging effects and high background which hinder the interpretation of the results. These problems were overcome in this work. The chemical structure of ultrathin OPPy films has been proposed previously based on electrochemical results and is of considerable importance because of important applications in sensors. Electrochemical results have indicated a similar structure for ultrathin and thick OPPy films. This is verified here by XPS. Additional information about a two-phase

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The information that was obtained by XPS cannot be easily obtained by other methods, especially for ultrathin polymer films grown on graphite.

PPy was electrodeposited on glassy carbon surfaces using short (ms) potential step pulses. The resulting thickness of the films was ca. 1.2–1.6 nm. To limit pinholes in the ultrathin films, pyrrole was first polymerized and then overoxidized, and this procedure was repeated until the response of 0.010 M Fe(CN)₆³⁻ in buffer was suppressed. After coating with OPPy, the electrode was rinsed with doubly distilled water, and stored in vacuum until XPS analysis was performed. The film thickness was about 1.2 mm, as calculated from Faraday’s law, from the deposition charge for the three applied coatings, 35 μC cm⁻² per coating, using 1.5 × 10⁻¹⁰ mol cm⁻² as the monolayer coverage, 2.25 as the number of electrons involved in the oxidation of PPy, and 0.4 nm as the diameter of pyrrole in a monolayer. The charge in excess of 2 electrons (12%) is associated with the oxidation of the PPy film.

To investigate OPPy polymer films with ATP as the counterion dopant, GC was coated using a modification of the procedure described previously. The polymerization was from a 0.003 M Py/0.010 M ATP aqueous solution, by a potential step from +0.40 to +0.85 V vs. SCE, for 40 ms. PPy was overoxidized as described above, at +0.95 V vs. SCE in 0.5 M pH 7.0 potassium phosphate buffer, by bulk electrolysis until the current reached a low steady state value. Four coatings were needed to suppress the cyclic voltammetric response of 0.010 M Fe(CN)₆³⁻ in 0.5 M pH 7.0 potassium phosphate buffer. The OPPy/ATP film was ca. 1.6 nm thick as determined from the deposition charge of 35 μC cm⁻² per coating, as above. The modified electrode was rinsed with doubly distilled water and dried before XPS analysis.

**Experimental**

**Reagents and solutions**

All chemicals were used as received, HPLC grade acetonitrile (MeCN), tertbutylammonium perchlorate (TBAP) and potassium phosphate monobasic were obtained from Fisher. Pyrrole (Py) and adenosine-5’-triphosphate disodium salt (ATP) were obtained from Sigma (St. Louis, MO, USA). Potassium ferricyanide, K₃Fe(CN)₆, and potassium phosphate dibasic were obtained from Mallinckrodt (St. Louis, MO, USA), and sodium perchlorate from Aldrich (St. Louis, MO, USA). Ruthenium hexamine chloride, Ru(NH₃)₆Cl₂, was obtained from Johnson Matthey (Ward Hill, MA, USA). All solutions were made with doubly distilled water. Py, when of brown color, was purified to obtain pure monomer by passing it over activated silica gel. All determinations were conducted at room temperature.

**Electrodes**

A saturated calomel electrode (SCE) and a Pt foil of ca. 0.2 cm² were used as reference and counter electrodes, respectively. Working glassy carbon (GC) electrodes were made from 3 mm diameter GC rods obtained from Electro synthesis (Lancaster, NY, USA). For XPS experiments, a 0.5 mm thick GC disk of 3 mm diameter was glued to the XPS sample holder with silver epoxy. To modify electrochemically GC attached to the XPS sample holder, electrical contact to the GC was made via a copper wire coated with silver epoxy, and a water-tight Teflon casing was designed to fit around the sample holder. Before modification, the GC electrode was polished with alumina suspension of 0.1 μm particle size (Gammal, Fisher), on a microcloth (Mark V Laboratory, East Granby, CT, USA), and sonicated in doubly distilled water for 1 min.

**Overoxidized polypyrrole films on glassy carbon electrodes**

Ultrathin OPPy film electrodes were prepared for characterization by XPS in three polymerization/overoxidation steps. PPy was first electrodeposited on the GC by chronocoulometry using a 30 ms potential step from +0.40 to +0.85 V vs. Ag wire pseudo-reference electrode. The polymerizing solution was 0.020 M Py in acetonitrile with 0.10 M TBAP as a supporting electrolyte. PPy was then overoxidized by bulk electrolysis in 0.50 M potassium phosphate buffer solution of pH 7.0 at +0.95 V vs. SCE, for ca. 5 min, until the current reached a constant value. To limit pinholes in the ultrathin OPPy film, this procedure was repeated until the response of 0.010 M Fe(CN)₆³⁻ in 0.50 M pH 7.0 potassium phosphate buffer was suppressed. Although the Fe(CN)₆³⁻ response was not suppressed to the background level after the third coating, the fourth coating did not diminish the response any further and thus the process was not repeated.
Silica tends to segregate to the surface of these materials as a result of normal aging. Even with freshly synthesized materials, heating or ion bombardment will cause silica to segregate to the surface, if present in the bulk. The silver is present on the surface because of the rapid diffusion of silver from the silver epoxy used to glue the electrode to the sample holder to the sample surface. Rapid diffusion of silver is well known.

One method of removing a contamination overlayer several monolayers thick from a surface is by means of Ar⁺ etching. Before etching, the C/O atom ratio of the bare GC was 1.5. After a 2 h Ar⁺ etch, the C/O ratio was 1.7. A peak fit of the O 1s level of the etched GC gave two Gaussian peaks at 530.9 and 532.8 eV, with the binding energies referenced to the Fermi level of the etched GC. The peak at 532.8 eV accounts for about 45% of the observed oxygen, and is due to silica at the GC surface. The remaining oxygen could be due to oxygenated carbon, which Ar⁺ etching reduced only slightly.

The deconvolution of the C 1s level peak produced three peaks at binding energies of 284.9, 286.8, and 288.4 eV which correspond to different forms of oxidized carbon, including C–OH and more oxidized functional groups at higher binding energies. Since the C/O ratio remains fairly constant with etching, the GC background can be expected to be essentially the same from electrode to electrode.

The amount of silver on the surface is very small, but its presence on all of the surfaces that were studied is extremely useful. In effect, we have inadvertently created silver-decorated surfaces so that the Ag 3d5/2 peak can be used to reference all the spectra, of all samples, to the Fermi level of etched GC. The Fermi referenced binding energy of the Ag 3d5/2 peak on etched GC is 369.2 eV. This method of referencing permits compensation for any surface charging which may occur on the polymer-coated surfaces. This method of referencing is analogous to the well-known gold decoration technique.24

**XPS analysis of ultrathin overoxidized polypyrrole films on glassy carbon electrodes**

A wide survey scan, low resolution XPS spectrum (0 to 1100 eV) of an ultrathin (ca. 1.2 nm thick) OPPy film on a GC substrate is shown in Fig. 1. It shows the presence of C, O, and N 1s atoms. Various core energy levels of other atoms (binding energy window, 50 eV) are shown in Fig. 2(A) and (B). A spectrum of valence levels (binding energy window, 0–50 eV) for GC and OPPy-modified GC is given in Fig. 3.

As displayed in Fig. 3, the XPS valence band spectra for bare and OPPy-modified GC are significantly different, verifying a change in the chemistry at the GC surface after electrodeposition of an ultrathin OPPy film. By comparing the C/Si area ratios for bare GC and for the OPPy-coated GC, it was concluded that about 13% of the GC electrode area remained uncovered by the film. This is not surprising since the basal planes of graphite cannot be perfectly tiled with OPPy and the more hydrophilic regions on the GC surface may not support the growth of PPy. Finally, only three polymerization and over-oxidation steps were carried out in constructing the OPPy polymer which did not lead to a complete suppression of the
cyclic voltammetric response of Fe(CN)$_6^{3-}$. In general, the OPPy film-coated regions charged more than the bare carbon, as expected for a non-conducting OPPy polymer film.

In order to examine the chemical speciation at the film-coated electrode, the high resolution XPS spectra were peak fitted. When the surface charges uniformly, all peaks shift by the same charge correction factor and the determination of binding energies, and the interpretation, becomes straightforward. However, if differential charging occurs, the interpretation depends on the ability to model the results in a consistent way. In the present case, charging uniformity, or lack thereof, may be examined by the analysis of the Ag 3d spectrum. This spectrum was fitted with one doublet ($\chi^2 = 10.7$), two doublets ($\chi^2 = 4.8$), and three doublets ($\chi^2 = 4.2$). A value of $\chi^2 = 0.0$ means a perfect fit, so the three-doublet fit is best. This indicates three regions of different charge at the surface. The difference between the binding energy (BE) of a fitted Ag 3d$_{5/2}$ peak and 369.2 eV, the Fermi referenced BE, is a measure of the extent of charging, and the corresponding charge shift correction is the negative of this difference. The peak areas of the Ag 3d$_{5/2}$ peaks may be used to estimate the relative amounts of the three regions. The results are as follows: region I, $\Delta = 4.6$ eV, shift $= -4.6$ eV, relative amount = 13.9%; region II, $\Delta = 6.6$ eV, shift $= -6.6$ eV, relative amount = 27.6%; and region III, $\Delta = 8.1$ eV, shift $= -8.1$ eV, relative amount = 58.5%.

The peak fits of the spectra of C 1s, N 1s, and others are easily obtained using this approach. However, in this case, each peak may be due to different species from one charge region, to overlapping peaks from two charge regions, or to overlapping peaks from all three charge regions. It is not possible to unravel uniquely the overlapping spectra. We have corrected the BE of each peak by the charge shift correction factor corresponding to uniquely the overlapping spectra. We have corrected the BE of peaks from all three charge regions. It is not possible to unravel its exact distribution in the regions with the chemical composition predicted from the literature.

The high resolution spectrum for region I is at most a doublet with peaks at 284.9 and 286.6 eV (Table 1). The lower BE corresponds to less oxidized carbon and the peak at 284.9 eV can be assigned as due to the C–OH group. Nitrogen peaks and minor peaks due to phosphorus, chlorine, and potassium are associated with this region. The C 1s spectrum for charge region II is at most a triplet (Table 1). Nitrogen peaks are also associated with this region but none of the other peaks. The peak at 288.0 eV could be at the high end of the –C–N region or be due to COOH. Based on the structure of the OPPy polymer and the XPS data which show less charging in region II, it appears unlikely that the less oxidized polymer in region II has the more highly oxidized functional groups, unless the peaks originate from the carbon substrate. If the polymer is being detected, the C 1s spectrum for region II is assigned only as a doublet with peaks at 284.8 and 286.4 eV. Therefore, regions II and III correspond to regions on the electrode surface coated with the polymer which charge to different extents.

The high resolution spectrum for N 1s yielded four Gaussian peaks displayed in Table 1. The first two peaks are barely above the detection level and can be assigned to nitrogen at an uncharged surface. The nitrogen most likely comes from the polymer film on the stainless steel sample holder which is somewhat illuminated by X-rays since the GC electrode does not completely fill the illumination window. The other two peaks dominate the spectrum. Notice that, in region II, there is very likely a peak at 399.3 eV which corresponds to main poly(PPy). In general, the O/Si atom ratio at the polymer-covered surface is much smaller, as expected for the polymer. The O/Si atom ratio at the polymer-covered surface is much larger than the corresponding ratio for the bare GC, indicating an absolute increase in the amount of oxygen at the polymer-covered GC surface. Since chlorine and phosphorus are also observed [Fig. 2(A) and 2(B)], the additional oxygen content may be attributed to H$_2$PO$_4^-$, HPO$_4^{2-}$, and ClO$_4^-$, as discussed below. Because of the numerous sources of oxygen, it is impossible to unravel its exact distribution in the regions with the three charge environments.

**Table 1** XPS data for OPPy film-modified GC electrode

<table>
<thead>
<tr>
<th>Element and level</th>
<th>Observed BE/eV</th>
<th>Region I (shift = −4.6 eV)</th>
<th>Region II (shift = −6.6 eV)</th>
<th>Region III (shift = −8.1 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>289.5</td>
<td>284.9</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>291.4</td>
<td>286.8</td>
<td>284.8</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>284.9</td>
<td>288.4</td>
<td>286.4</td>
<td>284.9</td>
</tr>
<tr>
<td>N 1s</td>
<td>397.7</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>502.2</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>O 1s</td>
<td>509.5</td>
<td>399.3</td>
<td>397.8</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>509.5</td>
<td>402.2</td>
<td>400.7</td>
<td>—</td>
</tr>
<tr>
<td>P 2s</td>
<td>207.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>207.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ag 3d$_{5/2}$</td>
<td>273.8</td>
<td>369.2</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>375.8</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>377.3</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

*Film thickness of ca. 1.2 nm.*

The structure of OPPy films is revealed in part by the types of nitrogen on the surface. According to Ge et al. and Pfuger et al. who studied OPPy films, the charge corrected N 1s peak at 397.7 eV is due to =N– of OPPy. Although no polymer

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**Proposed structure of oxidized polypyrrole film**

The structure of OPPy films is revealed in part by the types of nitrogen on the surface. According to Ge et al. and Pfuger et al. who studied OPPy films, the charge corrected N 1s peak at 397.7 eV is due to =N– of OPPy. Although no polymer
structure was proposed by either group, the presence of this nitrogen is consistent with the structure of OPPy proposed by Beck et al.,12 which is schematically shown below. The peak at 400.7 eV could be a NH\textsuperscript{+} nitrogen with a partial positive charge, as suggested by Pfluger et al.\textsuperscript{5,25} and Ge et al.\textsuperscript{11} In the work of Ge et al.,\textsuperscript{11} the intensity of the high BE nitrogen NH\textsuperscript{+} at 402.2 eV was reduced as the low BE component at 400.7 eV increased.

Palmisano et al.\textsuperscript{13} showed that the carbon to nitrogen ratio remained nearly constant as a result of overoxidation of PPY to OPPy, and the oxygen content as measured by the oxygen to nitrogen ratio increased. Their films were grown in chlorine, and were overoxidized in phosphate, and a diminished Cl 2p signal persisted after overoxidation. Ge et al.\textsuperscript{11} found that, after overoxidation, their films prepared and oxidized in sodium perchlorate lost the Cl 2p signal at 207 eV due to perchlorate.

The XPS spectra of Palmisano et al.\textsuperscript{13} also displayed a small P 2p signal, possibly belonging to the phosphate buffer, and the presence of a positive charge in the OPPy structure. However, the residual –NH\textsuperscript{+} group charge was not fully balanced by phosphate ions, so that the partial formation and ionization of COOH groups was postulated, based on the chemical derivatization experiments. They argued that both α and β carbons of pyrrole sub-units were involved in the formation of COOH groups, implying that the loss of PPY conductivity during overoxidation was due to breakage of polymer chains with a loss of conjugation.

### Structure of ultrathin overoxidized polypyrrole films from XPS data

The XPS data in Table 1, obtained for ultrathin OPPy films on GC, are consistent with previous results and the structure shown above for OPPy, proposed by Beck et al.\textsuperscript{12} The presence of two charge regions in the polymer (regions II and III) indicates a non-homogeneous structure of the polymer, and this is consistent with the model of PPY proposed by Ren and Pickup.\textsuperscript{26,27} This is further discussed below.

The XPS results confirm the presence of nitrogen films on the GC surface, and the C/O ratio of 4.5, compared to 1.5 at the bare GC (Table 2), is consistent with the presence of an overoxidized OPPy film.\textsuperscript{13} The ultrathin film contains a high fraction of overoxidized sites, as deduced from the intensity of the oxidized carbon peaks (not shown).

As in previous work, the structure of an ultrathin OPPy film is revealed by the types of nitrogen on the surface (Table 1). These results are in total accord with those obtained previously for thick films. Thus the structure above illustrates well the structure of an ultrathin OPPy film prepared and analyzed by XPS on GC.

Ren and Pickup\textsuperscript{26,27} proposed that PPY films behave like a porous electrode, in which ion flow within the film matrix is due to migration. To explain PPY permelectivity and ionic conductivity, they proposed a two-phase model, where ion transport is due to counterions in the polymer phase and the excess electrolyte present in the pore solution-like phase of the polymer. This model of PPY is consistent with the XPS results obtained here for OPPy and the previous model of OPPy from electrochemical results.\textsuperscript{14} The results show the presence of two regions in the polymer, charge regions II and III. Less oxidized region II may be the bulk polymer phase, while region III, which is more oxidized, is likely the solution-like polymer.

Furthermore, from the C/P area ratios of the 2s (area ratio, 2.8) and 2p (area ratio, 2.3) peaks of phosphorus and from the K\textsubscript{α} value of H\textsubscript{2}PO\textsubscript{4}\textsuperscript{−}, 6.32 × 10\textsuperscript{−6}, the pH in the film was calculated to be 6.84 compared to pH 7.0 of the solution used for the overoxidation. This indicates that the buffer is inserted into the ultrathin film. The apparent porosity of the film is consistent with ca. 13% of the uncovered GC surface, and the high porosity of region III of the polymer, which can act like a solution-like phase. The XPS results are also in agreement with the electrochemical results which show high apparent permeability and rapid response time of pinhole-free OPPy films on GC.\textsuperscript{16,17} The presence of phosphate ions may be for charge balancing purposes.\textsuperscript{13} According to the XPS results, –NH\textsuperscript{+} groups are present in the film after overoxidation of PPY to OPPy. During overoxidation, counterions move in and out of the film.\textsuperscript{12,27}

It is clear that a complete understanding of the film structure requires that anions and cations in the film be identified and quantified. In addition to phosphorus, weak peaks due to chlorine, silicon, aluminum [Fig. 2(A) and 2(B)], and potassium were observed in the XPS spectra of OPPy films on GC. Both silica and alumina are due to the GC background, as discussed above. The presence of potassium is likely from the potassium phosphate buffer. Some cation\textsuperscript{27} transport into PPY has been observed in aqueous electrolytes and has been attributed to pores/channels in the film. The presence of HPO\textsubscript{4}\textsuperscript{2−} leads to the low BE phosphorus component (187.1 eV P 2s, 132.4 eV P 2p after charge correction), and the presence of H\textsubscript{2}PO\textsubscript{4}\textsuperscript{−}, in larger quantity, was assumed to be the high BE phosphorus component (191.5 eV P 2s, 134.3 eV P 2p after charge correction).

The most likely source of Cl is from Cl\textsuperscript{−} from the reference electrode (SCE). The C/K area ratio of 83, and the C/Cl area ratio of 34 (Table 2), indicate that more chlorine than potassium is present in the film. Cl\textsuperscript{−} may balance the charge in the film from the presence of residual –NH\textsuperscript{+} groups. The BE of 207.0 eV could belong to ClO\textsubscript{4}\textsuperscript{−} in the uncharged region or, if present in region III, it must be Cl\textsuperscript{−}.

### XPS analysis of ultrathin overoxidized polypyrrole films polymerized with ATP as dopant

Ultrathin film electrodes that were prepared from water with ATP as dopant\textsuperscript{17} (OPPy/ATP) showed three charging regions similar to those of films prepared from acetonitrile with TBAP (OPPy). The area ratio for C/Si [Si spectrum shown in Fig. 4(A)] indicates that about 10% of the electrode is not covered by the film (the C/Si area ratios for the film-covered and the bare

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**Table 2** Atomic area ratios\textsuperscript{a} from XPS spectra for bare GC, OPPy-modified and ATP-templated OPPy-modified OPPy/ATP GC electrodes\textsuperscript{b}

<table>
<thead>
<tr>
<th>Atomic ratio</th>
<th>Observed binding energy/eV</th>
<th>Bare GC electrode</th>
<th>OPPy/GC electrode</th>
<th>OPPy/ATP/GC electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>C/N</td>
<td>405.9 + 408.8</td>
<td>33</td>
<td>190</td>
<td></td>
</tr>
<tr>
<td>C/P (HPO\textsubscript{4}\textsuperscript{2−})</td>
<td>195.0</td>
<td>101</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td>C/P (H\textsubscript{2}PO\textsubscript{4}\textsuperscript{−})</td>
<td>200.0</td>
<td>36</td>
<td>101</td>
<td></td>
</tr>
<tr>
<td>C/K</td>
<td>301.0</td>
<td>83</td>
<td>−</td>
<td></td>
</tr>
<tr>
<td>C/Ca</td>
<td>356.9</td>
<td>&lt;</td>
<td>147</td>
<td></td>
</tr>
<tr>
<td>C/Cl</td>
<td>207.4</td>
<td>34</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>C/Al</td>
<td>76.0</td>
<td>41</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>C/Si</td>
<td>111.2</td>
<td>9.4</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>C/O</td>
<td>353 + 541</td>
<td>1.5</td>
<td>4.5</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} XPS peak area normalized for time of scan and size of window, C/X = (area C\textsubscript{s}/area X\textsubscript{s}), where \(d\) is the Scofield cross-section.\textsuperscript{21} \textsuperscript{b} Electrode area, 0.07 cm\textsuperscript{2}; film thickness, ca. 1.2 nm (OPPy) and ca. 1.6 nm (OPPy/ATP). \textsuperscript{−} Undetected.

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*Analyst, 1999, 124, 1215–1221*
GC were 1.2 and 9.4, respectively). Thus, polymerization from two different solvents, with two different dopants, produces similar coverage by the ultrathin films. It has been shown that PPy films formed in water are structurally similar to the films formed in acetonitrile.

The XPS valence band spectrum of an ultrathin OPPy/ATP film is illustrated in Fig. 5. The spectrum shows differences and similarities with the equivalent spectrum of the OPPy film, shown in Fig. 3. The area ratios in Table 2 confirm some differences in the surface compositions of the two films. The C/N area ratio for OPPy/ATP is 190 compared to 33 for OPPy. Hence, polymerization of PPy with ATP as dopant, which is followed by overoxidation to OPPy, which removes ATP from the film, results in less nitrogen in the film than polymerization with TBAP. The high C/N and C/P ratios of the OPPy/ATP films verify that the contribution of ATP nitrogen to the XPS signal is small.

Less phosphorus is present in the ultrathin OPPy/ATP film than in OPPy, as shown in Fig. 4(B) [compare with Fig. 2(A)], and the distribution of phosphate ions is different. If phosphate is present in the film to balance the charge of positive nitrogen, less observed nitrogen means less phosphorus, as is found. K+ was not detected in the OPPy/ATP film, but small amounts of Ca2+ (area C/Ca = 147), in Table 2, were present. Ca2+ is an impurity in ATP, and thus is not observed in OPPy films. The presence of Ca2+ is indirect evidence for the initial presence of ATP in the film. It is very likely that Ca2+ replaced K+ in balancing the charge in the OPPy/ATP film. The ATP-doped OPPy film also contained chlorine, probably due to Cl− from the SCE, but the film had somewhat less Cl− than OPPy.

Since OPPy and OPPy/ATP films show similar charging, with three charging regions, the two-phase model appears to apply to both films. For the ATP-doped films, the signal-to-noise ratio was poorer and the amount of charging was greater. Since fewer ions were found at the surface of OPPy/ATP than at the surface of OPPy, the films must have a different morphology. This is consistent with the model of ATP as a template in the polymerization of OPPy which can alter the film morphology. Electrochemical studies have indicated that water as a polymerization solvent, in the presence of dopants other than ATP, has a different effect on film selectivity than water/ATP.

**Conclusions**

XPS characterization of nanosized OPPy films, directly on the electrode surface, was expected to provide a new insight into film structure and morphology. Film morphology is of importance when considering properties such as ionic conductivity, permselectivity, electrocatalysis, and sensor design. Knowledge of the morphology of the ultrathin films is of interest because of the considerable analytical importance of permselective ultrathin membrane electrodes, such as OPPy electrochemical measurements, that are sensitive and stable. The important finding here is that new information about ultrathin films on graphite can be obtained by XPS. It should be possible to investigate, in a controlled manner, the effect of the electrode surface structure on the properties of the films.

The investigation of nanosized films was conducted in this study by XPS to verify film structure and morphology, which were deduced previously from indirect electrochemical measurements. XPS confirms the electrochemical results which indicated a similar structure of ultrathin and thick films. XPS results also verify that the ultrathin films grown on GC are porous, as shown in electroanalytical applications. Additionally, new evidence for a two-phase structure of the films was obtained by XPS. Finally, morphological differences between OPPy and OPPy/ATP films were confirmed.

XPS confirmed that the properties of OPPy films are influenced by ATP. However, the change of solvent and dopant did not significantly affect surface coverage, and the two-phase film morphology was observed for OPPy and OPPy/ATP. It is possible that coverage is determined by the morphology of the substrate. A film formed from water has a different chemical microenvironment from a film formed from acetonitrile. In an aqueous solution, there is extensive interfacial polymer growth, unlike in an organic solvent, and water is trapped within the polymer chains. This may affect membrane morphology, although this has not been reported for PPy. The electrochemical studies have shown that a simple change of
solvent in the presence of other dopants does not have the same effect on film selectivity as the presence of ATP. 17

Previous XPS studies of PPy have been conducted on metal electrodes (Au, Pt), on glass, 34 on stainless steel supported films, or on films stripped from such electrodes. The films had a thickness that ranged from 50 nm to 15 μm and more recently of several nm. 34 In the spectra of the supported films, metal background peaks did not appear. The thickness of the stripped films, or on films stripped from such electrodes. The films had a thickness that ranged from 50 nm to 15 μm and more recently of several nm. 34 In the spectra of the supported films, metal background peaks did not appear. The thickness of the stripped films was ≳1 μm. When such films are attached to the XPS sample holder with double sticky adhesive tape, 11 C and O peaks from the tape do not appear in the XPS spectra because the films are much thicker than 3λ, where λ is the inelastic electron mean free path. In this study, we have characterized nanosized PPy films (thicknesses ≲3λ) by XPS directly on the GC electrodes A priori, such a study would be expected not to be unique to the polymer film and be obscured by background peaks. However, we have found that differential charging (normally an undesirable process) accompanied by cold metal decoration allowed structural information to be obtained about the films. Unlike vapor deposition, cold metal decoration, which we accomplished serendipitously, did not damage the polymer films.

References


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