Modification of Electronic Structure of Mesoscopic Perchlorate-Doped Polypyrrole Films by Ion Irradiation

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ABSTRACT: The effects of low-energy (1−3 keV) argon ion irradiation on a 100 nm thick polypyrrole film deposited potentiostatically in an aqueous perchlorate solution have been studied by X-ray photoelectron spectroscopy (XPS). Dramatic spectral changes in the valence band structure and Cl 2p region with increasing ion impact energy and total ion dose have been observed for the perchlorate-doped conductive polymer surface. Higher impact energy (3 keV) is found to be more effective in modifying the polymer backbone, particularly in the breakage and formation of terminal bonding units, while higher ion flux (for impact energy above 1 keV) appears to produce complete dissociation of the perchlorate counterions, leaving behind only Cl atoms. These observations are also consistent with the spectral changes in the C 1s, N 1s, and O 1s regions observed under different ion irradiation conditions.

1. Introduction

Electronically conductive polymers, such as polypyrrole (PPy), have been extensively studied in the past two decades because of their unique properties of high conductivity and chemical stability and their ease of preparation. These materials promise new applications in many technological areas, including anticorrosion,[1] batteries,[2] sensors,[3] and functional electronic devices.[4−6] Despite the availability of many synthesis methods, electropolymerization remains as the most popular technique for preparing PPy (and other conductive polymer) films. Because of the insolubility and noncrystalline nature of PPy,[7] the mechanism for the electropolymerization process remains unclear. Earlier studies show that the morphology, conductivity, and stability of the conducting polymer are directly affected by different deposition conditions, including the types of solvents, dopants, and electrolytes, the applied potential and current density, the temperature and pH, and the methods of electropolymerization (potentiostatically, galvanostatically, or cyclic voltammetrically).[7] Because pyrrole is light-sensitive, different types of radiation, including UV light,[8] electron beam,[9] high-energy ion beam,[10] and γ-ray,[11] have also been used in the preparation and characterization studies of PPy. Furthermore, investigations of the structural and other physical properties as well as the stability and reactivity of the polymers under different treatments are particularly important for developing new and improving existing technological applications of these novel materials. In the present work, we investigate the effects of ion irradiation at impact energies of 3 and 1 keV on a ca. 100 nm thick electropolymerized PPy film as a function of ion flux and total ion dose.

XPS is one of the most useful techniques for studying the bonding structures and local chemical environments of polymer materials by means of the measured core−shell chemical shifts. Despite the large number of XPS studies for the core shells,[12] there are only a limited number of studies for the valence band of PPy, mostly by using ultraviolet photoelectron spectroscopy,[13] due in part to the difficulties in resolving the complex valence band features. Considering the conjugation of PPy, the valence band information could be quite important in elucidating its physical bonding (or structural) and electronic properties. In the present work, we demonstrate that the valence band features of PPy can be used, together with the core−shell spectra, as a fingerprint to delineate the effects of low-energy argon ion irradiation on submicron-thick electropolymerized PPy films.

2. Experimental Details

Three polypyrrole films were deposited potentiostatically at +0.8 V (vs Ag/AgCl) on polished gold electrodes (6 mm diameter) at room temperature in deoxygenated aqueous solutions containing 0.05 M pyrrole and 0.1 M sodium perchlorate.[14] $NaClO_4$ was used as an electrolyte for electrodeposition because the ClO_4^- ions could serve as an effective dopant for improving the conductivity of the polymer. Given that the charge-transfer efficiency of electropolymerization of pyrrole was reported to be 55% for PPy films prepared in $NaClO_4$,[15] the film thickness could be controlled (and estimated) by the amount of charge transferred between the solution and the electrode.[14] Furthermore, the surface morphology of the PPy film has been found to be independent of the dopant for film thickness below 1000 nm.[16] In the present work, the film thickness of PPy prepared in the $NaClO_4$ electrolyte solution was therefore chosen to be approximately 100 nm. After electrodeposition, the resulting PPy films were rinsed thoroughly with distilled water (Millipore) and flushed with dry nitrogen for 24 h. XPS analysis was then performed using a multitechnique ultrahigh-vacuum Imaging XPS system (Thermo VG Scientific ESCALab 250) equipped with a hemispherical analyzer (of 150 mm mean radius) and a monochromatic Al Kα (1486.60 eV) X-ray source. The high sensitivity of this instrument obtained at a routine instrumental energy resolution of 0.5 eV fwhm at 20 eV pass energy allowed us to characterize spectral features in the core−shell regions and to resolve valence band structure of PPy (with ClO_4^- as the counterions) in finer details[14] than earlier valence band spectra.[17]

In addition to sputtering, ion irradiation offers a powerful technique to activate the surface by modification of the surface morphology, composition, and electronic structure. To produce a sufficiently high ion flux on the sample, the impact energies of the argon ion beam generated in a differentially pumped microfocused ion gun (Thermo VG Scientific EX05) were set

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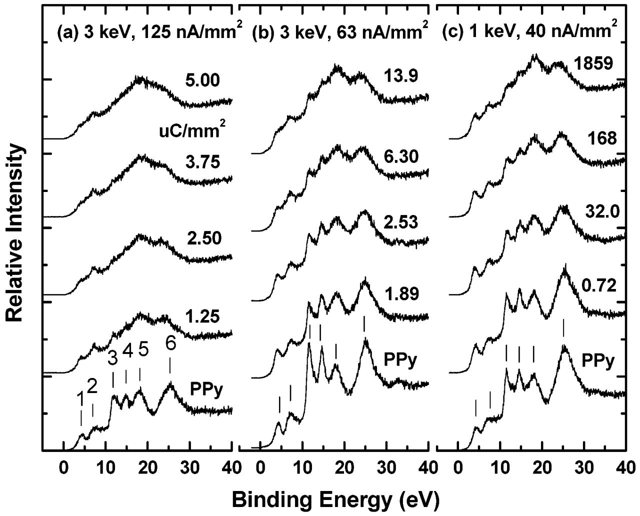

Figure 1. XPS spectra of the valence band region of polypyrrole (PPy) as a function of total ion dose (in μC mm^{-2}) under different ion irradiation conditions: (a) 3 keV−125 nA mm^{-2}, (b) 3 keV−63 nA mm^{-2}, and (c) 1 keV−40 nA mm^{-2}.

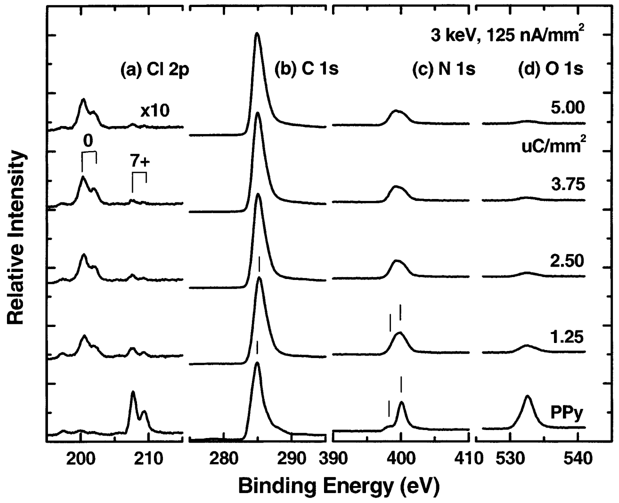

Figure 2. XPS spectra of (a) the Cl 2p, (b) C 1s, (c) N 1s, and (d) O 1s regions of polypyrrole (PPy) as a function of total ion dose (in μC mm^{-2}) under the ion irradiation conditions of 3 keV−125 nA mm^{-2}.

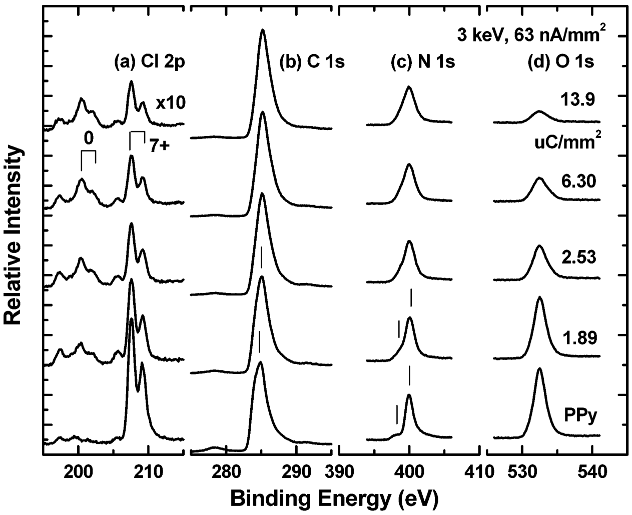

Figure 3. XPS spectra of (a) the Cl 2p, (b) C 1s, (c) N 1s, and (d) O 1s regions of polypyrrole (PPy) as a function of total ion dose (in μC mm^{-2}) under the ion irradiation conditions of 3 keV−63 nA mm^{-2}.

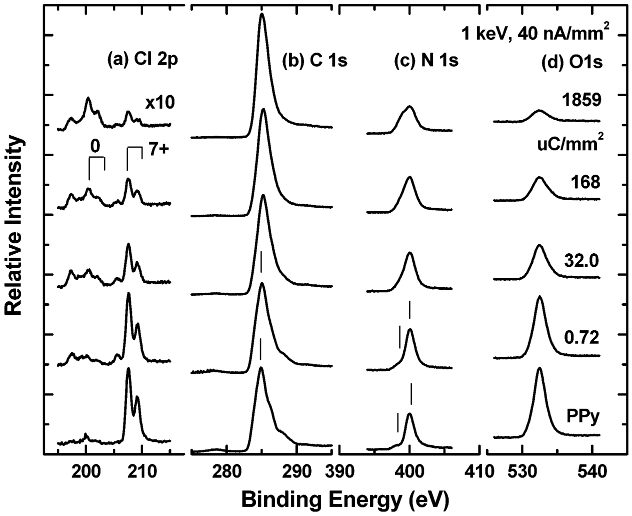

Figure 4. XPS spectra of (a) the Cl 2p, (b) C 1s, (c) N 1s, and (d) O 1s regions of polypyrrole (PPy) as a function of total ion dose (in μC mm^{-2}) under the ion irradiation conditions of 1 keV−40 nA mm^{-2}.

to 3 and 1 keV in the present work. For an illumination sample area of 3 × 3 mm^2, two ion fluxes used for the 3 keV irradiation were 125 and 63 nA mm^{-2} while the ion flux for the 1 keV irradiation was 40 nA mm^{-2}. A number of cycles of ion irradiation at 3 and 1 keV impact energy (corresponding to different total amounts of accumulated ion dose) were performed on the PPy sample in a working pressure of (2−3) × 10^{-8} mbar. The resulting ion irradiated samples were subsequently analyzed in situ by XPS.

3. Results and Discussion

Figure 1 compares the valence-band XPS spectra of the PPy film as a function of ion irradiation time (or effectively total ion dose) under three different ion irradiation conditions of impact energy and ion flux: (a) 3 keV−125 nA mm^{-2}, (b) 3 keV−63 nA mm^{-2}, and (c) 1 keV−40 nA mm^{-2}. The corresponding Cl 2p, C 1s, N 1s, and O 1s core−shell XPS spectra as a function of the total ion dose for the three irradiation conditions are shown in Figures 2−4, respectively. A survey XPS spectrum (from 0 to 1200 eV binding energy) for the PPy sample before the ion irradiation experiments indicates that no contaminant was introduced during the electrode preparation and film electrodeposition procedures. For the three PPy films used for the ion irradiation experiments, there is apparently no shift in the energy positions of the Cl 2p, C 1s, N 1s, and O 1s features (Figures 2−4 bottom traces). However, the ratios of C 1s to N 1s peak intensities [using relative sensitivity factors (RSF's) of 1.0 for C 1s and 1.6 for N 1s[18]] were found to be 7.2, 4.8, and 5.6 for sample treatments a, b, and c, respectively, which are also different from that of PPy prepared using tosylate as the dopant.[17] For sample treatments a, b, and c, the corresponding ratios of Cl 2p to N 1s (using a RSF of 2.6 for Cl 2p[18]) were 0.066, 0.129, and 0.098, corresponding to ClO_4^- dopant levels of 6.6%, 12.9%, and 9.8%, respectively. Despite the large variation in the dopant levels, the difference in the ClO_4^- dopant levels does not appear to affect the morphology of the PPy film[14] or the energy positions of the XPS features obtained in the present work, which suggests that there is no direct bonding between the perchlorate ions and the pyrrole rings in the PPy film.

It should be noted that the large variation of the C-to-N moiety is generally consistent with the polymer preparation method based on electrochemistry.[17]

Figure 1 (bottom traces) shows the sharp valence band spectra for PPy with different ClO_4^- dopant levels before various ion irradiation treatments. The origin of the binding energy scale is referenced to the Fermi level.[18] The lowest-lying feature at 3.7 eV (feature 1) can be assigned to the highest-lying π_1* and π_1 bands,[13,17] which are found to be at 1.79 and 5.4 eV, respectively, in the band structure calculation by Brédas et al.[19,20] This peak is attributed to the delocalized C 2p electrons in the conjugated C−C backbone of the polymer. The broad feature centered at 7.6 eV (feature 2) is attributed to a mixture of localized π_2 and σ_1 bands, which are estimated at 6.1 and 9.1 eV, respectively, according to the band structure calculation.[20] Unlike the π_1 band, both C 2p and N 2p contribute to the π_2 band, which is localized within the aromatic ring. The three strong peaks at 12.0 eV (feature 3), 15.0 eV (feature 4), and 18.0 eV (feature 5) are derived from the remaining σ bands of the polymer and partially from the valence contributions of the perchlorate counterions. The contribution to the peaks at 12.0 eV (feature 3) and 15.0 eV (feature 4) from ClO_4^- is particularly evident from the different relative intensities found for the three samples with different dopant levels (Figure 1), and this assignment is also supported by the lack of sharp features at these energies for a reduced PPy sample (with a Cl-to-N moiety < 1%). In the calculation by Brédas et al., the unit cell contained one pyrrole molecule and the PPy was modeled by binding monomers via the α−α′ linkage with alternating adjacent rings.[20] Our XPS spectra are in good accord with this model, indicating that the polymer consists of well-defined chains, and at a low dopant level it has chemical and physical properties resembling those of pristine (undoped) polymer. The strong peak at 25 eV (feature 6) has been attributed mainly to O from the perchlorate ion and overoxidation during electropolymerization.[21] It is of interest to note that the different (low) dopant levels of the electrodeposited PPy films evidently have little effect on the valence band structures, as reflected by their similarities to the calculated properties of pristine polymer.[20] Even in the case of highly doped PPy (with a dopant level greater than 33%), all other band levels remain at nearly identical binding energies with respect to the undoped case, except for the narrowing of the band gaps.[19]

Figure 1 (upper traces) shows the effects of ion irradiation with different impact energies and ion fluxes on the valence band structure. In particular, the intensities of the valence band features are found to be reduced at a considerably faster rate at a high ion flux (Figure 1a) than a low ion flux (Figure 1b), both at 3 keV ion impact energy. This is most evident for the sharp lowest-lying π_1 feature (feature 1) and the features at 12 eV (feature 3) and 15 eV (feature 4), which are significantly reduced upon a small ion dose of 1.25 μC mm^{-2} at 3 keV−125 nA mm^{-2} (Figure 1a), in contrast to an ion dose of over 6.30 μC mm^{-2} required at 3 keV−63 nA mm^{-2} (Figure 1b). Because π_1 represents delocalized bonding in PPy, the reduction of the π_1 feature suggests that ion irradiation at 3 keV can effectively destroy the conjugation in PPy. The concomitant reductions in the intensities of the ClO_4^--related features at 12 eV (feature 3) and 15 eV (feature 4) as well as 25 eV (feature 6) are consistent with the weak electrostatic interactions between the ClO_4^- counterions and the polymer. On the other hand, there is nearly no apparent reduction in the intensities for the π_2 feature at 7.6 eV (feature 2) and the primary σ bands at 18 eV (feature 5), in good accord with the strong aromatic bonding character of the pyrrole ring itself. At 1 keV ion impact energy, the changes in the valence band features with increasing total ion dose (Figure 1c) are found to be qualitatively similar to that of 3 keV ion impact energy for a similar ion flux (Figure 1b), except for the low-lying π_1 feature at 3.7 eV (feature 1). For the 1 keV case, a considerably higher total ion dose is required in order to produce the equivalent amount of intensity change as for the 3 keV case. Furthermore, ion irradiation at 1 keV is evidently insufficient to destroy the delocalized π_1 bonding in PPy (at 3.7 eV) but adequate for reducing the amount of attached ClO_4^- counterions (as indicated by the changes in the features at 12, 15, and 25 eV).

Figure 2 shows the corresponding XPS spectra of the Cl 2p, C 1s, N 1s, and O 1s regions of PPy upon ion irradiation at 3 keV−125 nA mm^{-2}. In particular, the strong Cl 2p$_{3/2}$ (2p$_{1/2}$) peak at 207.6 eV (209.6 eV) corresponding to the ClO_4^- counterions with a Cl oxidation state of +7 is found to be greatly reduced, with a concomitant increase in the respective Cl 2p$_{3/2}$ (2p$_{1/2}$) feature at 200.1 eV (202.1 eV) corresponding to the Cl atoms covalently bonded to the PPy (with a zero oxidation state)[22] (Figure 2a). Other weak Cl 2p$_{3/2}$ features at 205.8 and 197.5 eV corresponding to the Cl oxidation states of +5 and −1, respectively, are also observed.[12] The dramatic intensity change in the Cl 2p features of ClO_4^- with respect to the covalently bonded Cl features suggests that ion irradiation at 3 keV with a high ion flux predominantly causes complete atomization of the perchlorate counterions, leaving behind Cl atoms to bond with the pyrrole ring. On the other hand, only a small shift of 0.3 eV toward a higher binding energy is discernible for the strong C 1s peak at 284.8 eV (with minimal change in the peak shape) upon irradiation (Figure 2b). This small binding energy shift is consistent with plausible interaction between the dissociated Cl atoms and the pyrrole ring, most likely at the β position.[21] Furthermore, the weak N 1s peak at 398.5 eV corresponding to the imine-like group (=N−)[12] is found to shift toward the strong N 1s peak at 400.0 eV in the pyrrole unit, resulting in a broaden feature with a maximum at ca. 399 eV (Figure 2c). The intensity increase and the apparent dispersion of the lower-lying N 1s feature(s) to higher binding energy upon ion irradiation could be due to increased defects formation in the conjugated polymer chain, which is consistent with the intensity change of the π_1 band observed in the valence band region (Figure 1). Bonding of the N with dissociated Cl atoms can also be ruled out by the lack of intensity increase at the higher binding energy side of the N 1s peak at 400.0 eV (because Cl is more electronegative than N). The total intensity ratio between the C 1s and the N 1s features remains essentially constant throughout the ion irradiation process, suggesting that the elemental composition of the PPy film obtained by electropolymerization is uniform and/or that ion irradiation predominantly produces atomic mixing instead of sputtering effects in the case of polymer materials. This latter hypothesis is also consistent with the lack of discernible morphologi-

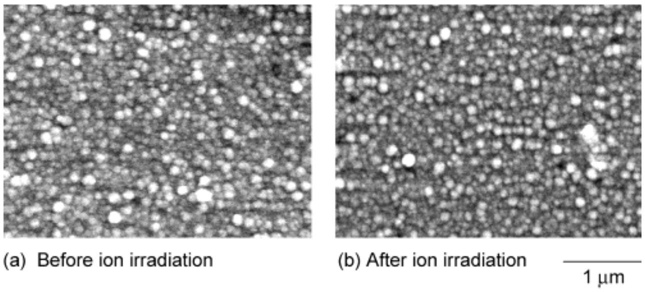
(a) Before ion irradiation (b) After ion irradiation

Figure 5. Scanning electron micrographs of polypyrrole (a) before and (b) after ion irradiation at 3 keV−195 nA mm^{-2} for a total ion dose of 6.8 μC mm^{-2}.

cal changes on the PPy surface even after an extended period of ion irradiation at 3 keV with a high ion flux of 195 nA·mm^{-2} as revealed by scanning electron microscopy (Figure 5). Finally, there is no observable change in the binding energy position of the O 1s peak at 532.5 eV (Figure 2d). In contrast to the relatively constant total Cl 2p intensity with increasing total ion dose (Figure 2a), the large intensity reduction of the O 1s peak upon ion irradiation (Figure 2d) supports our hypothesis that the $\mathrm{ClO_4}^-$ ions completely dissociate upon ion impact and only the O atoms predominantly undergo recombinative desorption leaving behind the Cl atoms (with a zero oxidation state) on the polymer surface.

Qualitatively similar changes in the Cl 2p, C 1s, N 1s, and O 1s spectral regions with increasing total ion dose can be obtained for PPy films treated with the other two ion irradiation conditions, i.e., 3 keV−63 nA mm^{-2} (Figure 3) and 1 keV−40 nA mm^{-2} (Figure 4), as with the 3 keV−125 nA mm^{-2} case (Figure 2). The intensity of the Cl 2p feature at 200.1 eV apparently increases with the total ion dose in all three spectra (Figures 2a, 3a, and 4a). This similarity among all three treatments (with different ion impact energies and ion fluxes) suggests that the formation of C−Cl (with a zero oxidation state for Cl) represents the final evolution of the $\mathrm{ClO_4}^-$ counterion upon ion irradiation. On the other hand, the intensity changes with increasing total ion dose most notably for the Cl 2p features are more gradual for the lower ion flux case at 1 keV (Figure 4a) than at 3 keV (Figure 3a), both of which are considerably more gradual when compared with that for the higher ion flux at 3 keV (Figure 2a), which suggests that the dissociation of the $\mathrm{ClO_4}^-$ counterions is more sensitive to the ion flux than the ion impact energy (above 1 keV). Furthermore, the intensity of the lowest-lying Cl $2p_{3/2}$ feature at 197.5 eV corresponding to Cl^- (with an oxidation state of −1) appears to increase to a saturation level for both lower ion flux cases at 3 keV (Figure 3a) and 1 keV (Figure 4a), in contrast to the higher ion flux case at 3 keV (Figure 2a). The presence of the Cl^- ions can be attributed to reduction of the $\mathrm{ClO_4}^-$ ion, with Cl^- replacing $\mathrm{ClO_4}^-$ as the counterion, which is consistent with the relative stabilities of the two ions. The existence of the Cl^- ions also suggests that a certain amount of positive charges (corresponding to different dopant levels) remains in the polymer after irradiation treatments with a lower ion flux.

In summary, the ion impact energy and ion flux both play crucial roles in modifying the nature of the PPy film obtained by electropolymerization in an aqueous perchlorate electrolyte solution. Higher impact energy (3 keV) is found to be more effective in affecting the polymer backbone, particularly in the breakage and formation of terminal bonding units, while higher ion flux (for impact energy above 1 keV) tends to produce complete dissociation of the $\mathrm{ClO_4}^-$ counterions, leaving behind only Cl atoms. Interesting C−Cl bonding at the β-C position could produce a very active polymer surface for further reactions that could be used in sensor applications. Furthermore, these ion-induced changes are found to be nonlinear with respect to the ion impact energy and total ion dose, within the ion irradiation conditions used in the present study. Finally, the correlation between the XPS spectral features for the valence band with those of the core shell shows that XPS is an effective tool for elucidating the effects of ion irradiation on conducting polymer materials.

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