XPS Investigations on Conducting Polymers

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X-ray photoelectron spectroscopy, XPS, was used for the characterization of electrically conducting polymeric materials. In the spectrum of polypyrrole, PPy, the Nls region exhibits two peaks, at 402.0 and 399.8 eV, corresponding to -N$^+$- and -N- moieties, respectively. The intensity of the N$^+$ peak decreases as the material loses its conductivity, hence the ratio of the experimentally derived N$^+$/C atomic ratio correlates exponentially with the measured conductivity. A similar observation also exists between the F$^-$/C atomic ratio both in polypyrrole and polythiophene. In the XPS spectrum of the composite material prepared using polyaniline, PAN and polyvinylchloride, PVC, two different kinds of Cl2p spin-orbit doublets are present after irradiation by ^{60}Co γ-rays. One of the Cl2p doublets can be assigned to the C-Cl in PVC and the other one is assigned to Cl$^-$ ions appearing after radiation. Since no Cl$^-$ peak is observed in PVC even after radiation, the presence in the composite must be related to dehydrochlorination of PVC and subsequent capture of the H-Cl by the neighboring PAN moieties. The measured Auger parameter of the Nals level of NaBr deposited on an oxidized form of the conducting polymer is between the values of NaBr deposited on Au (metal) and on Si (semiconductor). However, when NaBr is deposited on a reduced form of conducting polymer, the corresponding value approaches to that deposited on quartz (insulator).

Introduction

Analysis of conducting or electroactive polymers by conventional chemical spectroscopic methods such as IR or NMR is difficult. In the case of IR, the difficulty arises due to the strong coupling of the electronic and nuclear components within the polymeric network, hence the breakdown of the Born-Oppenheimer approximation. For NMR, the problem arises because of the difficulties of finding suitable solvents. Electron spectroscopic techniques, X-Ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES), mainly developed for their surface specifities[1-2], have been somewhat successful because of their ability to differentiate between various chemical forms of certain atoms or their oxidation states[3-5].

In the XPS technique, the kinetic energy of electrons created by the impinging monochromatic x-radiation (Mg Kα at 1253.6 or Al Kα at 1486.6 eV) are measured. The information sought, binding energy, is derived from the energy conservation principle: [B.E. = hv(x-ray energy)-K.E.]. The variations in the binding energy are used to differentiate between different chemical forms and the intensity of the peaks. The

intensity (area under each peak) is proportional to the abundance of that species after correction for the instrumental function and elemental photoemission cross-section[6].

When both photo and Auger electrons are observed together within the spectrum, more detailed information about the chemical environment of the species under examination can be obtained using the so-called Auger Parameter, defined as

$$\alpha_{AP} = \text{B.E. (photoelectron)} + \text{K.E. (Auger electron)}$$

Wagner[8] was the first to introduce the concept of the Auger parameter, and others further developed experimental and theoretical methods of obtaining information about the structure of the particles created or the matrix in which they are imbedded[7,9].

In our previous studies[10−11], we have investigated polymers and glasses by XPS, and in this study we further our applications to conducting polymers.

Experimental

Polypyrrole and polythiophene were prepared electrochemically in acetonitrile using tetrabutylammonium tetrafluoroborate as the dopand[10]. The polyaniline/polyvinylchloride composite films were prepared chemically. Aniline and PVC were dissolved in THF and cast into films. These films were later subjected to ^{60}Co γ-rays, doses of which varied between 1-10 kGy. For the Auger parameter measurements 2 drops of 0.1 M NaBr solution was deposited on electrochemically prepared 3 × 10 mm polypyrrole films. After the water was evaporated, the films were inserted into the XPS chamber. The XPS spectrometer used was a Kratos ES 300 equipped with a double Mg/Al anode. The vacuum was kept below 5×10^{-9} torr during measurements.

Results and Discussions

i- XPS of Polypyrrole and Polythiophene

XPS spectra of Polypyrrole in its oxidized and reduced forms and shown in Figure 1. The low resolution (survey) spectrum of PPy consists of 4 peaks: Cls around 285 eV, Nls around 400, Ols around 530 and Fls around 680 eV. The high resolution spectrum, however, reveals at least two chemically different nitrogens. The stronger peak at 399.8 eV can be assigned to neutral -N- whereas the higher binding energy peak at 402.0 eV is assigned to the oxidized -N$^+$- moieties. The observed ratio of N$^+$/N = 0.30 in the conducting PPy correlates well with the value obtained electrochemically[5], which decreases drastically in the reduced sample. The presence of fluorine is due to the dopant with used BF$_4^-$. The intensity of the Fls correlates well with the -N$^+$- peak, and when it is corrected by the instrumental transmission function and the cross-section, a stoichiometric ratio of N$^+$/F$^-$ = 0.25 is obtained. The spectra of polythiophene in oxidized and reduced forms are shown in Figure 2.
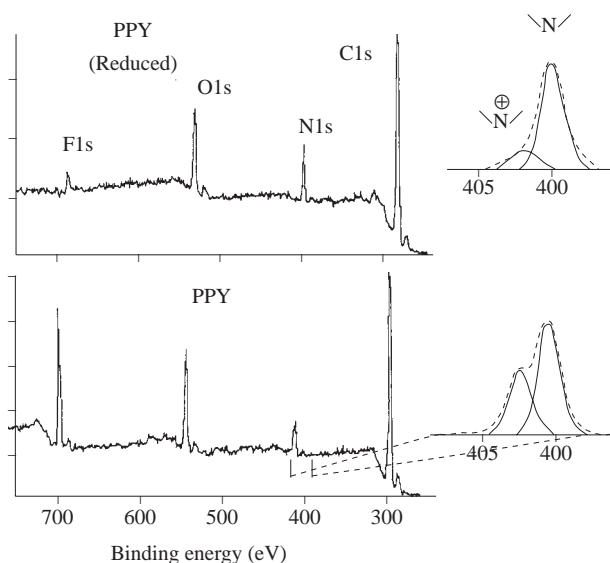
Figure 1. XPS spectra of oxidized and reduced forms of PPy (polypyrrole)
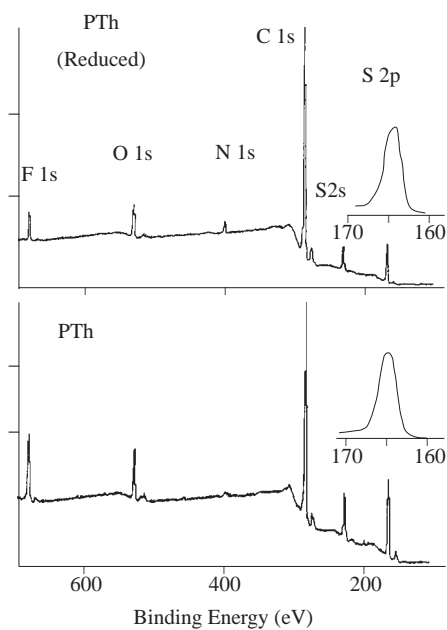

Figure 2. XPS spectra of oxidized and reduced forms of PTh (polythiophene).

In this case, S2p peaks are analyzed rather than N1s peaks. Unfortunately, the chemical shift between the neutral and the oxidized S2p peaks is too small to differentiate within XPS. However, the intensity of the F1s peak can be used to extract information about the electrical conductivity of the samples under investigation. Figure 3 shows the variation of the N^+/C or F^-/C atomic ratios determined by XPS with the measured electrical conductivity of these films. Since the amount of both N^+ and F^- is related to the number of charge centers and the films are semiconductors, the expected semilogarithmic variation is confirmed[3−5].
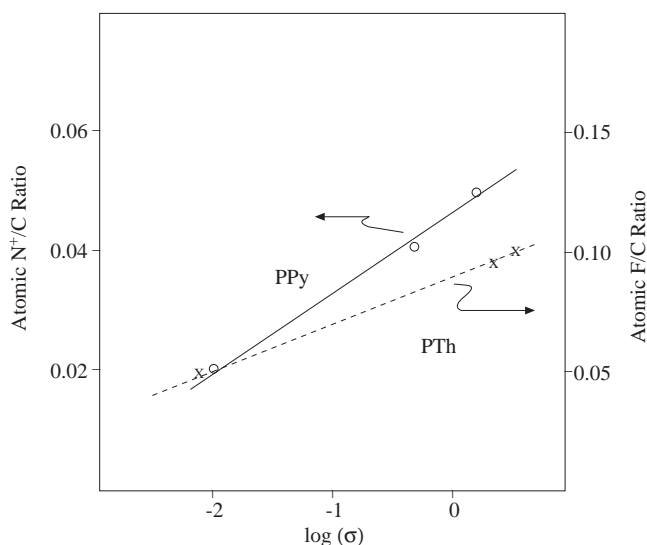
Figure 3. XPS-derived atomic N^+/C and F^-/C atomic ratios of three PPy and PTh films respectively against the logarithm of their measured electrical conductivities.

ii- XPS of Polyaniline-PVC Composites

PVC undergoes a high degree of dehydrochlorination when exposed to energetic particles like γ-rays, electrons, etc. This property limits its use to radiation processing. The electrical conductivity of polyaniline (PAN), on the other hand, increases under exposure to acids (e.g. HCl). A synergism is expected to take place in a suitable prepared composite of PAN-PVC such that the decomposition product of PVC (i.e. HCl) would be expected to be captured by the neighboring PAN moieties when exposed to radiation, which in turn is expected to increase the electrical conductivity of the films. Figure 4 shows the spectra of PVC and PAN-PVC composite films before and after exposure to Co-γ radiation in vacuo. In addition to the Ols, Nls and Cls peaks, the spectra contain two C12p spin-orbit doublets with varying intensity patterns around 200 eV. One of the doublets with $C12p_{3/2}$ at 201.0 eV is assigned to C-Cl moieties which are still intact, and the other with $C12p_{3/2}$ at 199.0 eV to the ionic Cl^- moieties. The latter Cl^- 2p-doublet, naturally, is not present in PVC.

ii- The Nals Auger Parameter

Wagner et.al. showed that the Auger parameter of the NaX (X = F, Cl, Br, I, NO_3 and SO_4) varies as much as 3 eV and becomes more or less equal when analyzed in frozen aqueous solutions[8]. Hence, the shift in the Nals Auger parameter is related to differences in the final state extra-atomic relaxation energy, which is affected by its chemical/physical environment. Moretti et.al., making use of electrostatic interaction between the core hole and nearest-neighbor ligands, derived a theoretical expression for the shift in the Auger parameter as follows:

$$\Delta\alpha(eV) = (14.4)n\delta/R^4(1 + D\delta/R^3)$$

where δ is the electronic polarizability in Å^3, R is the distance of the ligands from the core-ionized atom in Å, D is a parameter related to the local geometry and n is the number of the nearest-neighbor ligands[9]. In metals, the electronic polarizability is large and hence the shift to a larger Auger parameter is justified. In NaX the shift to larger values with larger, more polarizable ligands is also easily understood.

When dilute solutions of a sodium salt is deposited on different matrices, the electronic polarizability of the matrix, which is related to the electronic density near the Fermi level, is expected to contribute to the shift on the Auger parameter as well. In order to test this trend, we measured the Nals Auger parameter by

depositing a 0.1M solution of NaBr on Au (metal), Si (semiconductor) and Quartz (insulator), as given in Table 1. In Figure 5, the Auger parameter measured is shown with along with those previously published. A good correlation exists between the available electron density of the host matrix and the measured Nals Auger parameter of NaBr. In the same figure, we also show the same parameter for oxidized and reduced forms of the conducting polymer (PPy), which exhibits a good correlation between the shift and the electronic conductivity of the matrix.
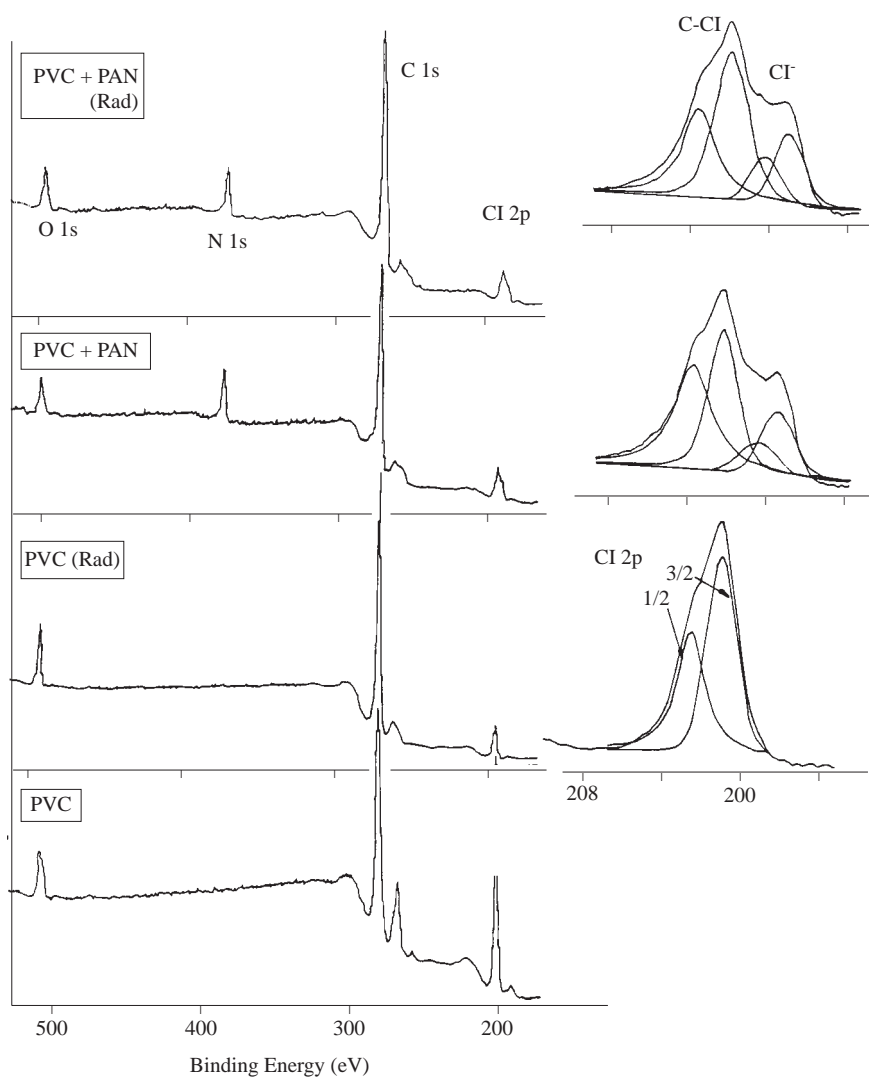

Figure 4. XPS spectra of PVC (polyvinylchloride) and the composite of PAN (polyaniline) and PVC before and after ^{60}Co γ-radiation

Table 1. The measured Na1s Auger parameter of NaBr deposited on various matrices together with the previously reported Auger parameters of Na (Reference 1 and 8).

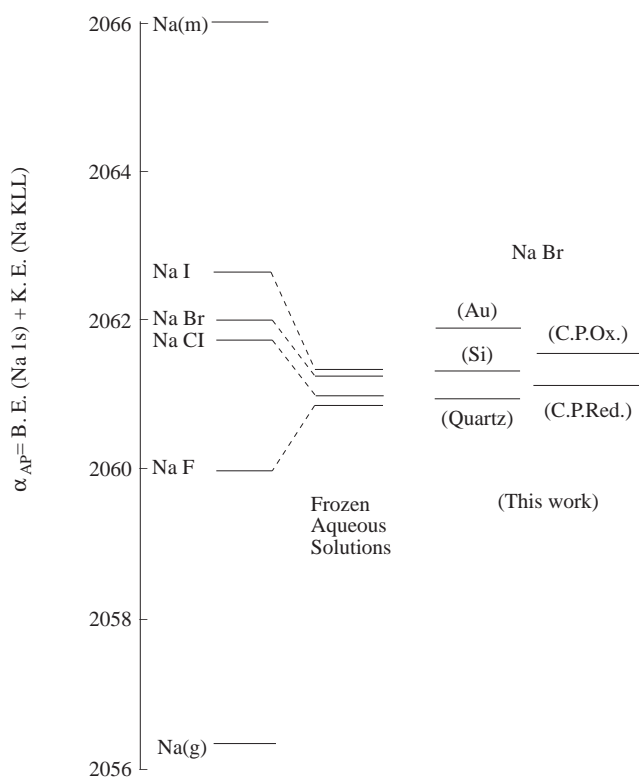|	Medium	Auger Parameter (ev)
	Au	2062.0
NaBr	Si	2061.4
	Quartz	2061.0
	PPy (ox.)	2061.7
	PPy (red.)	2061.2
Na	Metal	2066.0
NaI	Salt	2062.7
	Frozen Aq. Soln.	2061.0
NaBr	Salt	2062.0
	Frozen Aq. Soln.	2061.0
NaCl	Salt	2061.8
	Frozen Aq. Soln.	2061.0
NaF	Salt	2059.4
	Frozen Aq. Soln.	2060.6
Na	Gas Phase	2056.3

Figure 5. The previously reported Auger parameters of various Na salts, Na metal and Na atom in the gas phase as well as those of the salts in frozen aqueous solutions. The measured Auger parameters of NaBr on Au (metal), Si (semiconductor), Quartz (insulator) as well as on oxidized and reduced forms of a conducting polymer (PPy) are shown as well.

Acknowledgement:

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