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XPS Study of Highly Sulfonated Polyaniline

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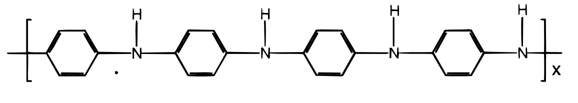
ABSTRACT: Highly sulfonated polyaniline prepared via a synthetic scheme using leucoemeralding base (LEB−SPAN) has been studied using X-ray photoelectron spectroscopy (XPS). A sulfonation level ($^{S}/_{N}$ ratio) as high as 0.80 ± 0.10 has been revealed in XPS analysis, agreeing well with the element chemical analysis results (~0.78). This contrasts to an $^{S}/_{N}$ ratio of 0.50 for SPAN made via the earlier reported synthetic method. The detailed S 2p and N 1s peak analyses both show that the oxidation level is ~50%, implying a better thermal stability of emeraldine oxidation state over those of leucoemeraldine and pernigraniline oxidation states. These XPS analysis results are supported by UV−vis and FT-IR analysis results. The method of resolving $2p_{3/2}$ and $2p_{1/2}$ peaks in the S 2p spectrum is discussed.

Introduction

XPS has been utilized extensively as an analytical tool to determine the chemical structures of polyaniline (PANI; **1a**−**c**)[1−5] because of its capability of obtaining both the chemical composition and oxidation state information. It has been especially useful in studies of both the sulfonation and the doping level of sulfonated polyaniline (SPAN; **1d**).[1,5] Recently an alternate synthetic route for preparation of highly sulfonated polyaniline (LEB−SPAN[6]) has been developed by this group.[7] $^{S}/_{N}$ ratios as high as ~0.75 have been obtained, as compared with 0.50 as the typical $^{S}/_{N}$ ratio from other synthetic methods.[8] Novel physical properties have been measured and reported for LEB−SPAN, and a mechanism has been proposed to account for the higher sulfonation level.[6]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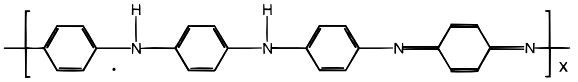
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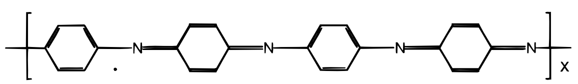
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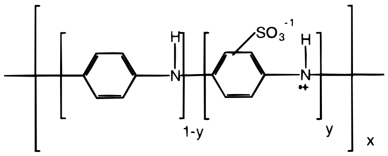

(1d)

The higher sulfonation level leads to questions concerning the oxidation state of the resulting SPAN when leucoemeraldine base (LEB) is the starting material for sulfonation instead of the emeraldine base (EB) and pernigraniline base (PNB) forms of polyaniline[8] and whether all of these ring-attached sulfonic acids self-dope nearby imine or amine nitrogen atoms. Though FT-IR and UV−vis data showed that the oxidation state is similar to that of the emeraldine salt,[6] these questions remained to be answered more thoroughly.

In this paper, we address the questions by presenting relevant XPS analysis results for LEB−SPAN, providing direct evidence of a higher $^{S}/_{N}$ ratio (>0.5), emeraldine oxidation state, and protonation level.

Experimental Section

Sample Preparation. The synthetic route of preparing LEB−SPAN[7] is briefly summarized: EB (~0.5 g) prepared via a reported procedure[9] was placed in a glass mortar. Phenyl hydrazine (2.5 mL) was then added and pressed with a glass pestle for ~5 min. This mixture was stirred for 1 h to allow EB to be reduced to LEB.[10] At the same time, 10 mL of fuming sulfuric acid was cooled to ~5 °C for later use. The reduced EB (LEB) was washed repeatedly with ethyl ether and then suction-dried. The dried LEB was sulfonated in the 10 mL of precooled fuming sulfuric acid for 1 h, maintaining the reaction flask in an ice−water bath environment. The reaction mixture was subsequently introduced into 0.75 L of 75:25 ice−water mixture to ensure that the SPAN product was precipitated out. The SPAN product was washed with three portions of 250 mL of cold water, and the remaining powder was dried utilizing the common procedure.[7,9] The LEB−SPAN powder was pressed into pellets with a clean FTIR pellet press before being introduced into the XPS instrument chamber.

Data Collection and Analysis. The XPS spectra were collected on a VG SIMS-ESCA-ME system (model no. SIM-ESCA-ME 1448) with Mg Kα X-ray source (1253.6 eV photons). The X-ray source was operated at 14 kV and 20 mA. The polymer powder samples were mounted onto standard VG sample studs with double-sided adhesive tapes and pumped into the preparation chamber to 10^{-8} mbar before being introduced into the XPS chamber. The pressure in the XPS analysis cham-

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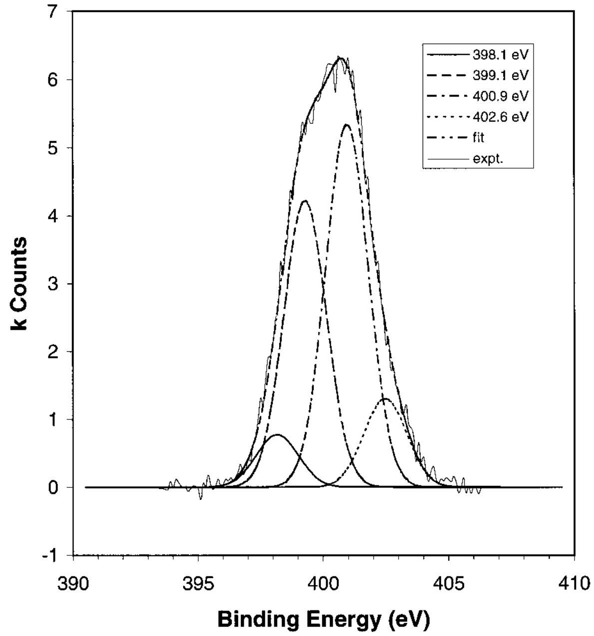

Figure 1. XPS N 1s core level spectrum. The fit component peaks are labeled in the legend box with their peak positions in electronvolts.

ber was maintained at 10^{-9} mbar or lower during collection. The sample position and tilt angle (20° for small-area XPS) were fine-tuned for optimal data acquisition.

In the data analysis, the binding energy (BE) of the core level C 1s peak was set at 284.5 eV to compensate for surface-charging effects.[11] The Shirley background[12] was subtracted and satellite peaks were removed for all element peaks before curve fitting. The iteration curve fit program (Levenberg–Marquardt method)[13] was customized in order to meet the specific needs of resolving $2p_{3/2}$ and $2p_{1/2}$ peaks in the S 2p spectrum. The experimental spectra were fit into components of Gaussian line shape.[14] The surface elemental compositions were determined by the ratios of peak areas corrected with empirical sensitivity factors.[11] All of the individual spectra were smoothed with a three-point averaging routine.

Results and Discussion

Determination of Elemental Chemical Composition. The chemical composition analyses of LEB–SPAN was determined utilizing both elemental chemical analysis[7] and XPS analysis. A typical XPS data analysis yields an $^{S}/_{N}$ ratio of 0.80 ± 0.10. The experimental atomic concentration is $C_{6.12}N_{1.00}S_{0.80}O_{2.53}$, corresponding to an assumed formal formula of $(C_6N)_{1.00}H_{3.50}(SO_3H)_{0.80}(CH_2O)_{0.12}$. The small excess carbon and oxygen is assumed to be carbohydrate deposited on the sample surface during the XPS sample preparation process.[11] This result is consistent with the elemental chemical analysis result, that is, an $^{S}/_{N}$ ratio of 0.78. Anal. found: C, 46.9; N, 9.03; H, 3.01; S, 16.1; O, 25.0; total, 100%. Calcd: $(C_6)_{1.00}N_{0.99}H_{3.73}(SO_3H)_{0.77}$; total, 99.1% (note that the "measured" oxygen content is determined by weight difference).

Determination of Oxidation State and Doping Level. The XPS spectra and the model fits are shown in Figures 1–4 for N 1s, S 2p, C 1s, and O 1s peaks, respectively. The optimized parameters such as the fit component peak positions, peak widths, and area percentages are summarized in Table 1. These spectra will be discussed sequentially below.

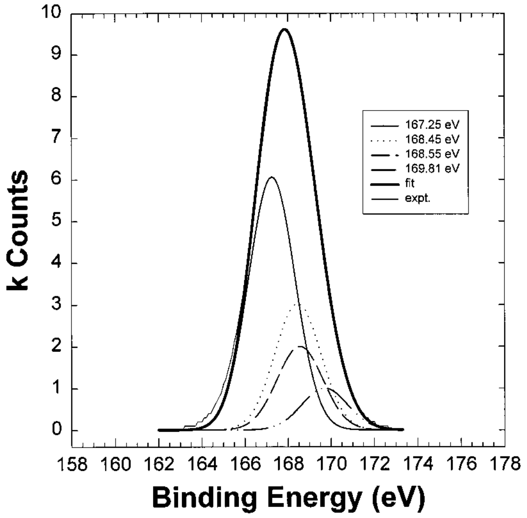

Figure 2. XPS S 2p core level spectrum. The fitted component peaks are labeled in the legend box with their peak positions in electronvolts.

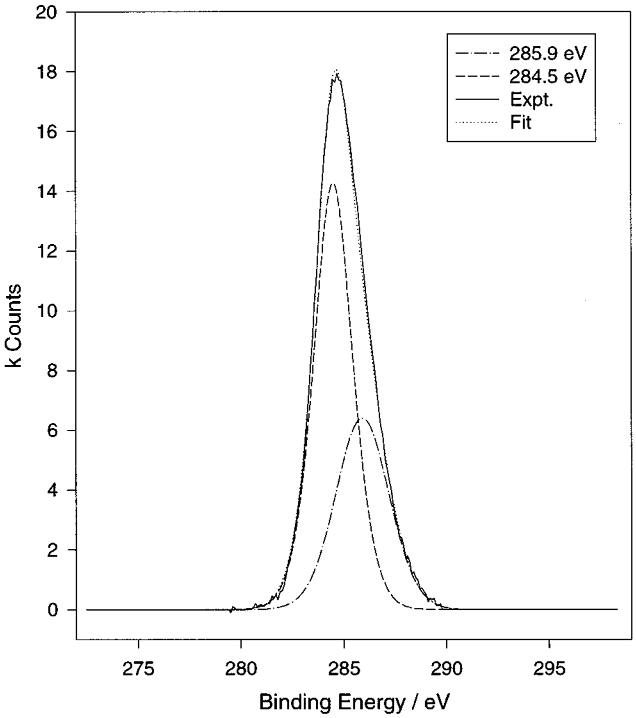

Figure 3. XPS C 1s core level spectrum. The fitted component peaks are labeled in legend box with their peak positions in electronvolts.

First, the N 1s spectrum was fitted smoothly into four component peaks. The 398.1 eV peak is associated[1,4,5,15] with undoped imine units. The peak at 399.1 eV is at the same energy as that earlier reported[1] for the N 1s in undoped amine units. In contrast, the 400.9 eV peak is associated with cationic nitrogen atoms (polarons and bipolarons).[1,5,15] The 402.6 eV peak is proposed to correlate with protonated amine units which are at a higher binding energy because of the stronger electron localization associated with poorer conjugation at sp^3-bonded sites. Their percentages of the total N 1s intensity are 398.1 (5%), 399.1 (38%), 400.9 (46%), and 402.6 eV (11%) peaks. The sum of the fraction of cationic nitrogen and undoped imine site for LEB–SPAN is the

Table 1. Binding Energies (eV) with Their Corresponding Atomic Concentrations and Peak Full Widths at Half Maximum (in parentheses; area % and eV, respectively) of Various Charge-Corrected XPS Components of C 1s, N 1s, O 1s, and S 2p Peaks[a]

peak	component 1	component 2	component 3	component 4
N 1s	398.1 (5, 2.0)	399.1 (38, 2.0)	400.9 (46, 2.0)	402.6 (11, 2.0)
S 2p	167.25 (75, 1.1)	168.55 (25, 1.1)		
C 1s	284.5 (61, 2.4)	285.9 (39, 3.3)		
O 1s	530.7 (30, 2.2)	531.5 (70, 3.5)		

[a] For brevity, only the binding energy and the percentage of S $2p_{3/2}$ component of each doublet are listed in parentheses.

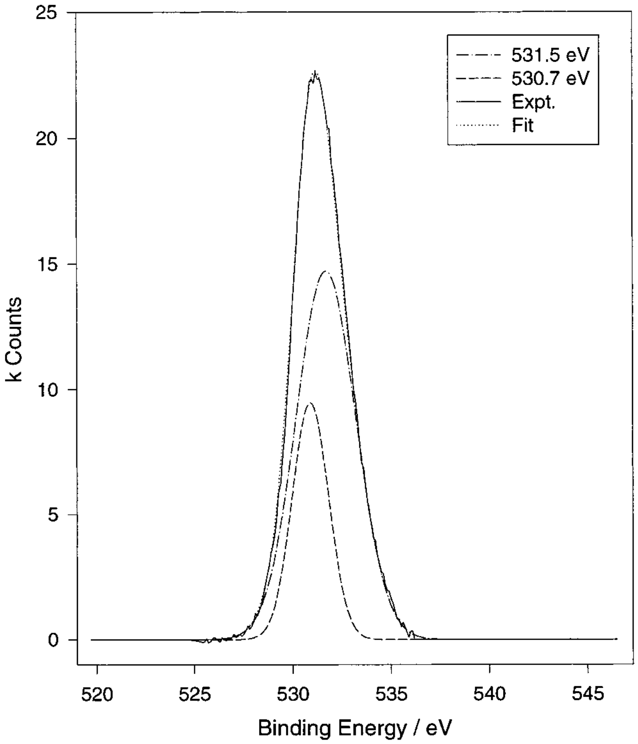

Figure 4. XPS O 1s core level spectrum. The fitted component peaks are labeled in legend box with their peak positions in electronvolts.

same as those for EB−SPAN and PNB−SPANs, supporting the claim that LEB−SPAN is still in the emeraldine oxidation state and implying that the emeraldine oxidation state is more stable than the other oxidation states. However, a small portion of imine is not protonated, which might imply that at the higher sulfonation level the protonation may be more difficult compared to the parent polyaniline in the ES form, consistent with sulfonation lowering the electron density at imine nitrogen sites. The higher $^{S}/_{N}$ (larger than 0.50) might be associated with partially sulfonated amine, which supports the above assignments. It was noted[1] that sulfonation at the ring will tend to localize polarons due to the proximity of the SO_3^- group to the chain.

The S 2p spectra are fit using two doublets that reflect the S 2p spin−orbit interaction ($\Delta E \approx 1.2$ and the relative intensity of spin-up state, $j = {}^{3}/_{2}$, and spin-down state, $j = {}^{1}/_{2}$, are equal to 2).[11] The peak widths, the peak energy separation, and the peak intensity ratio of the two components in each doublet are kept the same during simulation while the height and the energy of one component peak in each doublet are allowed to vary freely. We propose the origin of the two doublets are as follows: the doublet with lower BE is from the sulfur in the anion of the ring-attached sulfonic acid that protonates the amine ring units or the imine ring unit, leading to cationic nitrogen sites. The doublet with higher BE is from the sulfur in neutral sulfonic acid substituents. The rationale for these assignments are from following consideration: the sulfur in the sulfonic acid groups protonating the amine or imine nitrogens mentioned above have a higher electron density than the neutral sulfonic acid groups, "$-SO_3H$". The local electron density on the sulfur atom reflects its charge and environment and, therefore, its binding energy.

Table 2. Oxidation State and Doping Level in LEB−SPAN Sample Obtained from both the N 1s and the S 2p XPS Peak Analyses[a]

peak analyzed	undoped (amine and imine)	doped imine	doped amine	total doping
N 1s	43	46	11	57
S 2p	40			60

[a] The S/N ratio used in S 2p peak analysis is 0.8; the undoped amine and imine percentages are calculated by percentage difference.

On the basis of the above assignments, it is found that ~75% of "$-SO_3H$" protonate the aromatic imine and amine and ~25% are in neutral substituent form. Combining with the sulfonation level (80%), these doping percentages of sulfonic acid convert to doped aromatic amine and imine percentages, which are listed and compared with the percentages obtained from N 1s peak analysis in Table 2, where the undoped amine and imine are calculated by difference. It is seen that the two sets of the percentages are self-consistent, as well as consistent with the UV−vis and FT-IR spectra analysis of LEB−SPAN.[6]

The C 1s and O 1s spectra have unique features. Both peaks are smoothly fit as two component peaks, indicating that carbon as well as oxygen have differing chemical environments among themselves, which is expected to be true because as ring carbon atoms are attached with several different types of substituents whereas oxygen atoms connect to different sulfur atoms as discussed above. At the present time, the further assignment of these two spectra are not pursued because the unavoidable surface contamination of carbon hydrates, $(CH_2O)_n$, though small, complicates the interpretation.

Conclusion

The XPS analyses of LEB−SPAN given above show that the LEB−SPAN is in the emeraldine salt oxidation state and the sulfonation level is ~80%, consistent with the UV−vis, FT-IR, and element chemical analysis results, implying a better thermal stability of the emeraldine oxidation state than those of PNB and LEB. The analyses also suggest that the aromatic amine are partially doped. On the other hand, a small portion of aromatic imine is not protonated because of the high sulfonation level caused by electron density deficiency. The novel analysis of S 2p spectrum is self-consistent with the more traditional N 1s analysis, providing supporting evidence for the above conclusions.

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