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SHORT COMMUNICATION

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Intrinsic redox states of polyaniline studied by high-resolution X-ray photoelectron spectroscopy

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Abstract High-resolution X-ray photoelectron spectroscopic (XPS) measurements of the various intrinsic redox states of polyaniline (PANI), using a monochromatized Al—Kα source, were carried out. The presence of the imine, amine and positively charged nitrogen species corresponding to a particular intrinsic redox state and protonation level of the polymer was resolved quantitatively and unambiguously. The result confirmed the peak assignments of former XPS core-level studies using the lower resolution non-monochromatized Mg—Kα X-ray source. Thus, the high-resolution XPS using a monochromatized Al—Kα X-ray source is a truly unique tool for the convenient and quantitative analysis of the various intrinsic redox states of PANI.

Key words Polyaniline · XPS · High-resolution · Oxidation states · Protonation

Introduction

In the study of electroactive polymers, the century-old aniline polymers [1] have been of particular interest because of their environmental stability, controllable electrical conductivity, and interesting redox properties associated with the chain nitrogen atoms [2–4]. The aniline polymers have the general formula $[(\text{—B—NH—B—NH})_y(\text{B—N=Q=N})_{1-y}]_x$, where B represents the benzenoid ring while Q represents the quinonoid ring. The intrinsic oxidation state of the polymer can be varied from the fully reduced leucoemeraldine state (LM, $y = 1$) through the 50% intrinsically oxidized emeraldine state (EM, $y = 0.5$) to the fully oxidized pernigraniline state (PNA, $y = 0$). The 75% intrinsically oxidized polymer has been termed nigraniline (NA, $y = 0.75$) [2–3]. The above intrinsic structures of polyaniline (PANI) have been studied by optical absorption spectroscopy [5], electron spin resonance (ESR) [6], nuclear magnetic resonance (NMR) [7], magnetic susceptibility [8], electrochemical measurements [9], Fourier transform infrared (FTIR) spectroscopy [10], and Raman spectroscopy [11]. X-ray photoelectron spectroscopy (XPS) has been shown to provide a truly unique tool in the quantitative analysis [12–14] of the various intrinsic redox states ([imine]/[amine] or [=N—]/[—NH—] ratios) of polyaniline (PANI) and its derivatives. In XPS studies, peak synthesis or deconvolution of the core-level spectra remains largely a personal judgment. However, with proper reference to model compounds, it is possible in many cases to resolve unambiguously the various species and components contained in a core-level spectrum. In addition, a large amount of core-level energy information has been accumulated over the years [15]. Furthermore, with the availability of the high-resolution photoelectron spectrometers, identification of the intrinsic redox states of PANI can be made more precisely. In this study, we use a high energy-resolution XPS to investigate chemical shifts in the N 1s core-level spectra of the various intrinsic structures of PANI. The results confirm the binding energy assignments in the former peak synthesis of the lower resolution XPS core-level spectra. The distinct N 1s core-level lineshape from the high-resolution photoelectron spectrometer reveals, unambiguously, the presence of the various intrinsic redox states and protonation levels in PANI.

Materials and methods

Polymer synthesis

Polyaniline (PANI) in its emeraldine (EM) salt form was prepared via oxidative polymerization of aniline by ammonium persulfate in 0.5 M H_2SO_4 according to the method reported in the literature [3]. It was then converted to the emeraldine base (EM) by treatment with excess 0.5 M NaOH for 1 h, thoroughly washed with deionized water until neutral and then dried by pumping under reduced pressure. The free-standing EM film was prepared by exhaustive pumping of the concentrated *N*-methylpyrrolidinone (NMP) solution (containing 8% EM base by weight) under reduced pressure at room temperature. In order to further remove the residue NMP in the EM films, the above EM films were immersed in distilled water for 3 h, followed by pumping under reduced pressure. The 75% intrinsically oxidized nigraniline (NA) film was obtained by successive treatment of EM film with 1 M H_2SO_4 for 1 h and 0.5 M NaOH for 1 h [12]. The fully reduced leucoemeraldine (LM) was prepared by treatment of EM film with hydrazine (NH_2NH_2) for 1 h, followed by washing with distilled water. In all cases, the samples were dried by pumping under reduced pressure. The chemical structures corresponding to the various intrinsic oxidation states of PANI and the inter-conversions among the various intrinsic redox states of the polymer are illustrated in Fig. 1 [12].

XPS measurements

XPS measurements were made on a Kratos Analytical AXIS HSi 165 spectrometer with a monochromatized Al—Kα X-ray source (1486.6 eV photons). The X-ray source was run at a reduced power of 150 W (15 kV and 10 mA) and a pass energy of 40 eV. The line width resolution is about 0.7 eV. The polymer film was mounted on the standard sample stud by means of double-side adhesive tape. The core-level spectra were obtained at the photoelectron take-off angle (with respect to sample surface) of 90°. The pressure in the analysis chamber was maintained at 10^{-8} Torr or lower during each measurement. To compensate for surface charging effects, all binding energies were referenced to the C 1s hydrocarbon peak at 284.6 eV. In peak synthesis, the line width (full width at half maximum or FWHM) of Gaussian peaks was maintained constant for all components in a particular spectrum. In our earlier XPS work, a VG ESCALAB MkII spectrometer with a non-monochromatized Mg-Kα X-ray source (1253.6 eV photons) was used. The X-ray source was run at a reduced power of 120 W (12 kV and 10 mA) and the core-level spectra were obtained at the photoelectron take-off angle of 75°. The line width resolution was of 1.1 eV or more. In all cases, surface elemental stoichiometries were determined from peak area ratios, corrected with the experimentally determined sensitivity factors, and were accurate to within ± 5%. The elemental sensitivity factors were calibrated using binary compounds of well-defined stoichiometries.

Results and discussion

XPS has been shown to be a unique tool in the quantitative evaluation of the various intrinsic redox states of PANI [12–14]. In our earlier studies [15, 16], a VG ESCALAB MkII spectrometer with a non-monochromatized Mg—Kα X-ray source (1253.6 eV photon) was employed to differentiate the three nitrogen species in the aniline polymers. Thus, the proportions of the quinonoid imine (=N—), benzenoid amine (—NH—), and the positively charged nitrogen (N^+) corresponding to any particular intrinsic oxidation state and protonation level of the polymer can be quantitatively resolved in the properly curve-fitted N 1s core-level spectrum. The three nitrogen species correspond, respectively, to peak components with binding energies (BEs) at about 398.2, 399.4 and >400 eV in the properly curve-fitted N 1s core-level spectrum. The different ratios of the imine and amine species were used to distinguish the different intrinsic redox states of the aniline polymer. The various intrinsic redox states of PANI can be interconverted, as illustrated in Fig. 1 [12]. The ambiguities in peak assignments and component resolution, which arise from the limited line width resolution when using a non-monochromatized XPS source, are minimized in the present work by the high-resolution XPS apparatus.

Figure 2 shows the N 1s core-level spectra of the LM base [(*a*) and (*b*)], EM base [(*c*) and (*d*)], and NA base

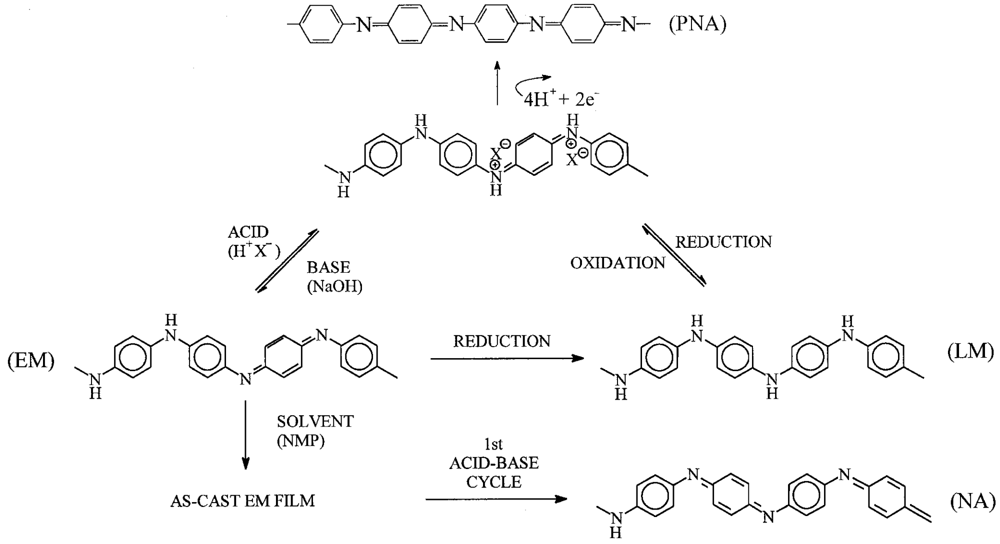

Fig. 1 Chemical structures of the aniline polymers and the interconversions among the various intrinsic redox states of the polymers

[(*e*) and (*f*)] obtained from the non-monochromatized Mg Kα and monochromatized Al Kα X-ray sources, respectively. Figs. 2(*a*) and (*b*) show that the N 1s core-level spectra of LM are dominated by the amine nitrogen species. The spectral line shape is consistent with the fully reduced LM state of PANI. Except for a minor difference in line width, the spectra in Fig. 2(*a*) and Fig. 2(*b*) are similar with a peak component BE at about 399.4 eV. The residual imine species may be attributed to the incomplete reduction of imine to amine by NH_2NH_2. The residual high BE component above 400 eV in the N 1s core-level spectra of Figs. 2(*a*) and (*b*) may have resulted, at least in part, from surface oxidation products or weakly charge-transfer complexed oxygen [12, 15]. The assignment is supported by the presence of a fairly strong O 1s signal in the LM base films. This conclusion is also consistent with the more reactive nature of the conjugated polymer surface [17], in comparison to the surfaces of the polymers with saturated backbones.

Based on comparison with model compounds and accumulated core-level energy information, the less well-resolved N 1s core-level spectrum of EM base obtained from the non-monochromatized Mg—Kα X-ray source had been curve-fitted [15] [Fig. 2(*c*)]. The accuracy in peak synthesis is confirmed by the present high-resolution XPS spectrum shown in Fig. 2(*d*). Fig. 2(*d*) shows, unambiguously, the presence of two peak components in the N 1s core-level spectrum of the EM base. These two peaks correspond to the imine and amine nitrogen, and are located at the BEs of 398.2 and 399.4 eV, respectively. Furthermore, the fact that these two peak components have about the same intensity is consistent with the intrinsic redox state of the EM base. Generally, the N 1s core-level spectrum obtained from the VG ESCALAB MkII spectrometer with the non-monochromatized Mg—Kα X-ray source, as shown in Fig. 2(*c*), lacks the line width resolution to allow a visual distinction of the imine and amine components. On the contrary, the obvious concavity in the line shape of Fig. 2(*d*) reveals unambiguously the presence of the imine and amine species. Thus, the curve-fitted high-resolution N 1s core-level spectrum of Fig. 2(*d*) confirms our former peak synthesis for the EM base of PANI. The N 1s core-level spectra of the NA base in Figs. 2(*e*) and (*f*) show that the imine nitrogen makes up about two-thirds to three-fourths of the area of the N 1s spectra. The spectral lineshape of Fig. 2(*f*) in particular is consistent with the structure of the 75% intrinsically oxidized nigraniline (NA). Moreover, the presence of the imine and amine species in Fig. 2(*f*) is also unambiguous. Thus, the presence of a stable NA-like state of PANI is ascertained.

Figure 3 shows the respective C 1s core-level spectra of the EM base obtained with the non-monochromatized and monochromatized X-ray sources. Figure 3(*a*) shows that the C—N component at the BE of 285.5 eV [18] cannot be resolved unambiguously in the low-resolution C 1s core-level spectrum. However, the C—N component can be identified unambiguously in the C 1s core-level spectrum of the high-resolution spectrum and must be included to obtain the best fit in peak synthesis. The area ratio of the C—H component at the BE of 284.6 eV to the

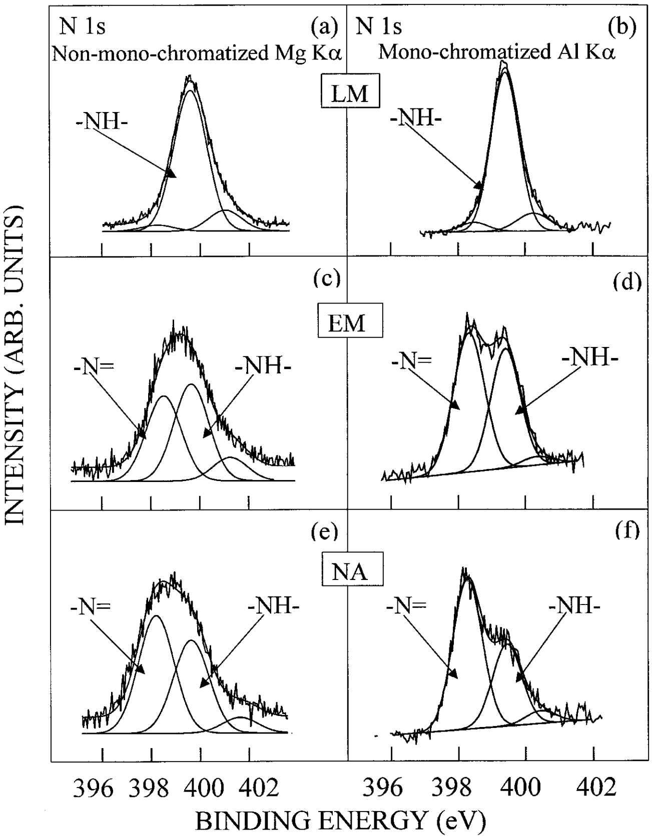

Fig. 2 N 1s core-level spectra of LM base [(*a*) and (*b*)], EM base [(*c*) and (*d*)], and NA base [(*e*) and (*f*)] obtained by using the non-monochromatized and monochromatized X-ray sources

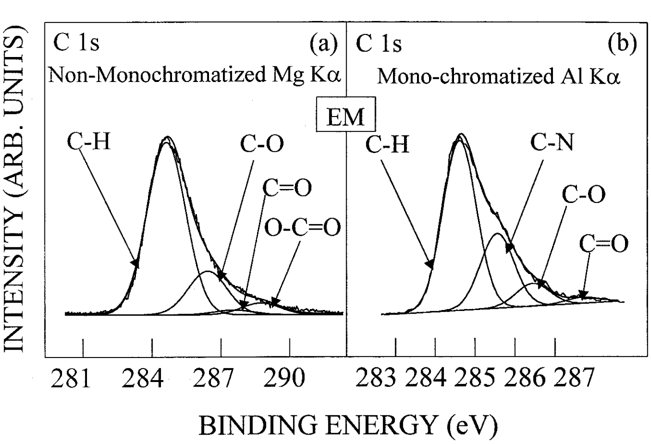

Fig. 3 C 1s core-level spectra of EM base obtained with (*a*) the non-monochromatized and (*b*) the monochromatized X-ray sources

C—N component is about 4:2, in good agreement with the chemical structure of aniline. The presence of residual amounts of C—O and C=O species in the C 1s core-level spectra suggests that the EM film surface has been oxidized to some extent. This phenomenon has been widely observed [12] and is consistent with the reactive nature of most conjugated polymer surfaces [17].

PANI becomes conductive when protonated. Fig. 4 shows the N 1s core-level spectra of the EM base films protonated by 1 M H_2SO_4 [(*a*) and (*b*)] and 1 M $HClO_4$ [(*c*) and (*d*)]. The line shape of the spectra in Fig. 4 suggests the absence of imine structure in the protonated EM. On the other hand, there is a high intensity of the positively charged nitrogen in each N 1s core-level spectrum. Comparison of the N 1s spectra in Figs. 4(*a*)–(*d*) to those in Figs. 2(*c*) and (*d*) shows that all the imine units have been converted to the positively charged nitrogen atoms as a result of protonation. This phenomenon is consistent with the fact that protonation occurs preferentially at the imine sites [2, 3]. In Fig. 4, the resolution of the amine and positively charged nitrogen peak components is unambiguous in both the low and high resolution spectra. The protonated nitrogen exists as a distinct peak component at BEs above 400 eV. Nevertheless, the visual distinction of the two nitrogen species in the high-resolution spectra of Figs. 4(*b*) and (*d*) is more obvious than that of the low-resolution spectra in Figs. 4(*a*) and (*c*). The slight difference in the intensity ratios of the -NH- and N^+ components arising from protonation by H_2SO_4 and by $HClO_4$ probably has resulted from the difference in the extents of surface oxidation and hydrolysis induced by the two protonic acids [19].

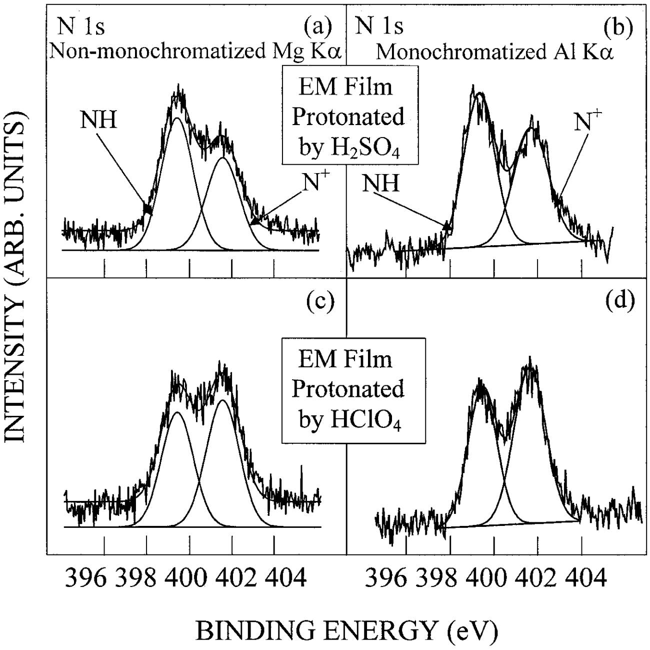

Fig. 4 N 1s core-level spectra of EM base potonated by 1 M H_2SO_4 [(*a*) and (*b*)] and 1 M $HCLO_4$ [(*c*) and (*d*)], obtained with the non-monochromatized and monochromatized X-ray source

Conclusions

The various intrinsic redox states of polyaniline (PANI) were examined by high-resolution X-ray photoelectron spectroscopy (XPS), using the monochromatized Al-Kα X-ray source. The imine, amine and positively charged nitrogen species in the N 1s core-level spectra, corresponding to any particular intrinsic oxidation state and protonation level of the aniline polymers, were resolved unambiguously. The results confirmed the earlier peak assignments based on the lower resolution core-level spectra.

References

1. Green AG, Woodhead AE (1910) J Chem Soc 1117
2. MacDiarmid AG, Chiang JC, Richter AF, Epstein AJ (1987) Synth Met 18:285
3. Ray A, Asturias GE, Kershner DL, Richter AF, MacDiarmid AG, Epstein AJ (1989) Synth Met 29:E141
4. Kang ET, Neoh KG, Tan KL (1992) Surf Interf Anal 19:33
5. McManus PM, Cushman RJ, Yang SC (1987) J Phys Chem 91:744
6. Kaya M, Kitani A, Sasaki K (1986) Chem Lett 147
7. Stafstrom S, Sjogren B, Wennerstrom O, Hjertberg T (1986) Synth Met 16:31
8. Ginder JM, Richter AF, MacDiarmid AG, Epstein AJ (1987) Solid State Commun 63:97
9. Genies EM, Tsintavis C (1986) J Electroanal Chem 200:127
10. Shacklette LW, Wolf JF, Gould S, Baughman RH (1986) J Phys Chem 88:3955
11. Cao Y, Li S, Xue Z, Guo D (1986) Synth Met 16:305
12. Kang ET, Neoh KG, Tan KL (1998) Prog Polym Sci 23:277
13. Snauwaert P, Lazzaroni J, Riga J, Verbist JJ, Gonbeau DJ (1990) J Chem Phys 92:2187
14. Kumar SN, Gaillard F, Bouyssoux G, Sartre A (1990) Synth Met 36:11
15. Kang ET, Neoh KG, Khor SH, Tan KL, Tan BTG (1989) J Chem Soc Chem Commun 696
16. Kang ET, Neoh KG, Tan TC, Khor SH, Tan KL (1990) Macromolecules 23:2918
17. Diaz AF, Castillo JL, Logan JA, Lee WY (1981) J Electroanal Chem 129:115
18. Muilenberg GE (ed) (1977) Handbook of X-ray Photoelectron Spectroscopy. Perkin Elmer, New York, p 38
19. Kang ET, Neoh KG, Tan KL (1995) Synth Met 68:141