Synth. Met. 101, 479-480 (1999)

Photoemission study of polypyrrole and polyaniline

H. Sakamoto[a], K. Mizoguchi[a], H. Ishii[a], T. Miyahara[a], S. Masubuchi[b], S. Kazama[b],
T. Matsushita[c], A. Sekiyama[c], S. Suga[c]
[a]*Dept. of Phys., Tokyo Metropolitan Univ., Hachioji, Tokyo, 192-0397 Japan*
[b]*Dept. of Phys., Chuo Univ., Bunkyo-ku, Tokyo, 112 Japan*
[c]*Dept. of Material Phys., Osaka Univ., Toyonaka, Osaka, 560-8531 Japan*

Abstract

Photoemission spectra were observed for polypyrrole doped with PF_6^- and polyaniline protonated by camphorsulfonic acid. These samples were taken from the same films well studied by ESR, electrical resistance, and X-ray measurements. The valence band structures for both samples were similar to each other. The comparison between the spectral intensities at the Fermi level of both samples suggests that the electronic states of polypyrrole is more metallic, which is consistent with the results acquired through the other experiments. Not so sharp Fermi edge in polypyrrole shows that its electronic states are not completely free from disorder giving rise to localization.

Keywords: Photoelectron spectroscopy, Polypyrrole and derivatives, Polyaniline and derivatives

Electronic states of conducting polymers have been intensively investigated with many kinds of measurements. So far we have obtained much information about them through mainly magnetic resonance, electrical resistance, and X-ray experiments. Photoelectron spectroscopy is also useful to observe the electronic and chemical structure simultaneously and the surface state etc. in conducting polymers. [1] In this report, we performed the ultraviolet photoemission spectroscopy (UPS) on two polymers; PF_6^- doped polypyrrole (PPY-PF) and polyaniline protonated with camphorsulfonic acid (PANI-CSA). Although PPY and PANI have been studied using the photoelectron spectroscopy by many researchers, [2] we were interested in comparing the UPS results with our other data taken in the same batch of films.

Ultraviolet photoemission spectra were measured using synchrotron radiation with a SCIENTA SES200 analyzer at the beam line BL-3B of the Photon Factory at High Energy Accelerator Research Organization. The overall instrumental resolution was set to 50 meV at the photon energy of 50 eV. The pressure and the temperature were about 5×10^{-10} Torr and 50 K, respectively. The used samples were taken from the same self-standing films studied by ESR etc. The clean surfaces were obtained by scraping the films *in situ* with a diamond file.

In Table 1 we summarize the experimental results of PPY-PF and PANI-CSA obtained by X-ray, electrical resistance, and magnetic resonance experiments. The electrical resistance was measured by a voltage shorted compaction method (VSC) [3] for PPY-PF. The quasi-1-dimensional (Q1D) motion of spins can be studied by observing frequency dependence of ESR linewidth. [4] Magnetic susceptibility was determined by Shumacher-Slichter method. [5] These results suggest that the crystallinity was higher in PPY-PF than in PANI-CSA and the electronic states of PPY-PF were metallic while those of PANI-CSA were localized.

Valence band photoemission spectra of PPY-PF and PANI-CSA at the photon energy of 50 eV are shown in Fig.1. The whole structures for both samples are not so different except for relative intensity. Comparing the observed spectra with the band calculation, [8] we ascribed the structure around 3.5 eV to the π band, around 8 eV to π and σ band, and around 13.5 eV to σ band for both polymers. In the photon energy dependence of the valence band spectra for PPY-PF between 35 eV and 60 eV, two structures were observed around 10 eV that gradually grow with increasing the photon energy compared with other structures. Since they are attributed to 3s and 3p subshells of phosphorus atoms in the dopant, these structures are considered to come from the dopant. This means that the dopant PF_6^- is not thoroughly extracted even in the ultra high vacuum chamber and hence the observed spectra are regarded as those of the doped conducting polymers.

As indicated in Fig.1 the finite spectral intensity at the Fermi level (E_F) was observed in PPY-PF while the intensity in PANI-CSA is considerably smaller. A similar structure with finite intensity at E_F was also reported for the tosylate doped polypyrrole and the proof of metallicity of its electronic states. [9] Although we did not measure undoped samples, Ref.9 demonstrates that the valence band spectrum of the undoped PPY has no intensity at E_F. Therefore it is concluded that the doping

Table1 Summary of the experimental results of PF_6^- doped polypyrrole (PPY-PF) and camphorsulfonic acid protonated polyaniline (PANI-CSA).

	PPY-PF	PANI-CSA
X-ray pattern	sharp [6]	broad
electrical resistance	metallic	*
Q1D motion of spins	not observed	observed
ESR linewidth	Elliott mechanism [7]	not Elliott mechanism
Curie spins	1 per 2000 rings	1 per 300 rings

produced the observed finite intensity at E_F . The origin of the density of states near E_F is the polaron band, because no finite intensity is expected near E_F in the case of bipolaron. [9,10] Our results also imply that the electronic states of PPY-PF is metallic with polaron band due to the interaction among the polarons whereas the electronic state of PANI-CSA is not so metallic. These are consistent with the magnetic resonance and the other results described above.

Although the spectrum of PPY-PF at E_F is finite, the Fermi edge is not sharp but the intensity tails off across E_F. This feature is similar to those reported for $Bi_2Sr_2(Ca_zY_{1-z})Cu_2O_{8+y}$. [11] In this material, the electrons were localized due to the random distribution of Ca^{2+} and Y^{3+}, but the degree of disorder decreased and the electronic state became more extended as z approached unity. Then the shape of photoemission spectrum near E_F changed from the slope to the obvious edge. On the basis of this observation, the gradual decrease of the spectrum intensity of PPY-PF across E_F suggests that the electronic states are metallic, but is not so completely because of remaining localization caused by inevitable disorder. The extremely small intensity of PANI-CSA spectrum at E_F corresponds to the much localized electronic state with high degree of disorder. It turns out that the observation of the photoemission spectrum at E_F gives the information about electronic localization in conducting polymers.

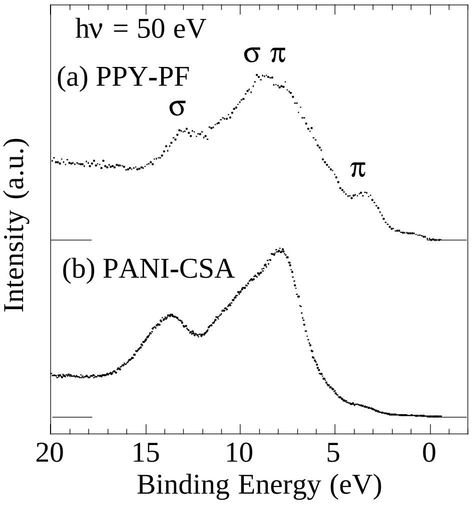

Fig.1 Photoemission spectra of the valence bands of (a) PF_6^- doped polypyrrole (PPY-PF) and (b) polyaniline protonated with camphorsulfonic acid (PANI-CSA) at the excitation photon energy of 50 eV. π and σ indicate that the structures are attributed to the π band and σ band.

[1] see, for example, E. T. Kang, K. G. Neoh, and K. L. Tan, in H. S. Nalwa (eds.), Conductive Polymers: Spectroscopy and Physical Properties, (John Wiley & Sons, Sussex, 1997), Vol.3, p.121.

[2] W. K. Ford, C. B. Duke, and W. R. Salaneck, J. Chem. Phys. **77** (1982) 5030, W. R. Salaneck, R. Erlandsson, J. Prejza, I. Lundström, and O. Inganas, Synth. Met. **5** (1983) 125, P. Pfluger, U. M. Gubler, and G. B. Street, Solid St. Commun. **49** (1984) 911, G. Tourillon and Y. Jugnet, J. Chem. Phys. **89** (1988) 1905, W. R. Salaneck, I. Lundström, T. Hjertberg, C. B. Duke, E. Conwell, A. Paton, A. G. MacDiamid, N. L. D. Somasiri, W. S. Huang, and A. F. Richter, Synth. Met. **18** (1987) 291, C. B. Duke, A. Paton, E. M. Conwell, W. R. Salaneck, and I. Lundström, J. Chem. Phys. **86** (1987) 3414, C. B. Duke, A. Paton, E. M. Conwell, W. R. Salaneck, and I. Lundström, Synth. Met. **21** (1987) 163, E. M. Conwell, C. B. Duke, A. Paton, and S. Jeyadev, J. Chem. Phys. **88** (1988) 3331, Ph. Snauwaert, R. Lazzaroni, J. Riga, and J. J. Verbist, Synth. Met. **21** (1987) 181.

[3] S. Masubuchi, K. Mizoguchi, K. Mizuno, and K. Kume, Synth. Met. **22** (1987) 41.

[4] K. Mizoguchi, Jpn. J. Appl. Phys. **34** (1995) 1.

[5] R. T. Shumacher and C. P. Slichter, Phys. Rev. **101** (1956) 58.

[6] Y. Nogami, J.-P. Pouget, and T. Ishiguro, Synth. Met. **62** (1992) 257.

[7] R. J. Elliott, Phys. Rev. **96** (1954) 266.

[8] M. André, J. Chem. Phys. **78** (1983) 6137, J. L. Brédas, B. Thémans, J. G. Fripiat, and J. M. André, Phys. Rev. **B29** (1984) 6761, S. Stafström, J. L. Brédas, A. J. Epstein, H. S. Woo, D. B. Tanner, W. S. Huang, and A. G. MacDiarmid, Phys. Rev. Lett. **59** (1987) 1464.

[9] P. Bätz, D. Schmeisser, and W. Göpel, Phys. Rev. **B43** (1991) 9178.J. L. Brédas, B. Thémans, and J.

[10] R. Lazzaroni, M. Logdlund, S. Stafström, W. R. Salaneck, and J. L. Brédas, J.Chem. Phys. **93** (1990) 4433.

[11] C. Quitmann, D. Andrich, C. Jarchow, M Fleuter, B. Beschoten, G. Güntherodt, V. V. Moshehalkov, G. Mante, and R. Manzke, Phys. Rev. **B46** (1992) 11813.