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X-Ray Photoelectron Spectroscopy of Sodium-doped Polyacetylene

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Synopsis. The change of the C ls peak shape in an X-ray photoelectron spectrum was studied for sodium-doped polyacetylene. The C ls peak due to negatively-charged carbon atoms was found to appear on the low-binding-energy side of a peak due to neutral carbon atoms. An electron, which is transferred to a polyacetylene chain from the sodium atom, has been determined to reside over several carbon atoms.

Previously, we studied bromine-doped polyacetylene by X-ray photoelectron spectroscopy[1] and found that the shape of the C ls peak varied markedly with the bromine content. The observed change of the peak shape suggested that the peak was composed of two components, mutually separated by 1.7—2.0 eV, and that the intensity of the higher-binding-energy component increased while that of the lower-binding-energy component decreased on increasing the bromine content. We attributed the former characteristic to the carbon atoms in the metallic domain where carbon atoms are positively charged as the result of a charge transfer to bromine to form a Br_3^- ion, and the other component to the carbon atoms in the low conductive (or undoped) domain. However, the intensity of the higher-binding-energy component continues to increase even when the bromine content exceeds the value where the conductivity shows a steep decrease because of the progress of the addition and/or substitution reaction of bromine with the polyacetylene chain.[1,2] Thus, in a heavily-doped case the higher-binding-energy component might contain a large contribution from carbon atoms which form a bond with bromine. Furthermore, a recent EXAFS study of the bromine-doped polyacetylene revealed that the C–Br bond is formed even in a lightly-doped polyacetylene.[2] Thus, there remains the question whether the higher-binding-energy component of the C ls peak is actually due to the positively-charged carbon atoms in the metallic domain.

Salaneck *et al.* studied AsF_5- and I_2-doped polyacetylene by XPS.[3,4] They also observed two components in their C ls peaks. However, they attributed a shoulder which appeared on the higher-binding-energy side of the peak upon doping with AsF_5 (or I_2), to the conduction-electron-plasmon shake-up. The main, rather sharp component on the lower-binding energy side moves to the higher-binding energies, relative to undoped polyacetylene. They concluded that all the carbon atoms in polyacetylene were uniformly charged and that the average charge per carbon atom depends on the amount of the dopant.

In the case of the sodium-doped polyacetylene where carriers are different from those in the bromine-doped polyacetylene, doped sodium atoms will change to sodium ions giving an electron to the polyacetylene chain, and none of the addition or substitution reaction can occur between sodium and polyacetylene. According to the interpretation proposed by Salaneck *et al.*, the main, rather sharp C ls peak would shift to the lower binding energy and a shoulder due to the conduction-electron-plasmon shake-up would appear on the higher-binding-energy side of the main peak. The chemical shift of the main peak may depend on the amount of the dopant. On the other hand, if we consider the presence of the doped and undoped domains in the sodium-doped polyacetylene, the component due to the negatively-charged carbon atoms in the doped domain would appear on the lower-binding-energy side of the component due to the carbon atoms of the undoped domain. The intensity of the former component would increase and the latter would decrease with the increase of sodium content.

Since the sodium-doped polyacetylene is extremely sensitive to air, we have to prepare specimens under an ultra-high vaccum condition and immediately carry out all XPS measurements without exposing the doped polyacetylene film to air. The present experiment was done by use of a VG ESCA LAB 5. A polyacetylene film, prepared by a previously described method,[5] was introduced into the sample chamber of the apparatus by keeping the film in a nitrogen atmosphere. The polyacetylene film, thus introduced into the apparatus, did not show any detectable O ls peak. Then, the film was exposed to a sodium vapor in a sample-preparation chamber, a sodium-metal dispenser by S.A.E.S. Getters S.p.A. being used as the sodium source. The C ls and Na ls peaks were measured immediately after the deposition of sodium onto the film. The same procedure was repeated in order to study the effect of an increase of the amount of the doped sodium, which means that we measured the sodium-doped polyacetylene with various dopant contents. The Na ls/C ls intensity ratio and the approximate Na/C atomic ratio derived from the intensity ratio, and the C ls peak width (f.w.h.m.) with the repetition of sodium deposition are summarized in Table 1. The Na/C atomic ratio derived from the intensity ratio might be smaller since sodium is only on the surface of the polyacetylene film. The shape of the C ls peak of the undoped polyacetylene and those of two sodium-doped polyacetylenes (after 4th and 7th depositions which correspond to $(CHNa_{0.045})_x$ and $(CHNa_{0.075})_x$, respectively) are shown in Fig. 1(a). The shape of the C ls peak varied markedly upon increasing the sodium content. The f.w.h.m. of the C ls peak increased to 2.8 eV by doping sodium from 1.5 eV of the undoped polyacetylene. However, the total intensity of the C ls

Table 1. XPS Results of sodium-doped polyacetylene

Number of Depositions	Na 1s/C 1s intensity ratio	Na/C atomic ratio	f.w.h.m. of C 1s peaks/eV
0	0.00	0.000	1.5
1	0.04	0.005	1.6
2	0.10	0.015	1.6
3	0.28	0.035	1.9
4	0.34	0.045	2.0
5	0.45	0.055	2.5
6	0.50	0.065	2.7
7	0.60	0.075	2.8

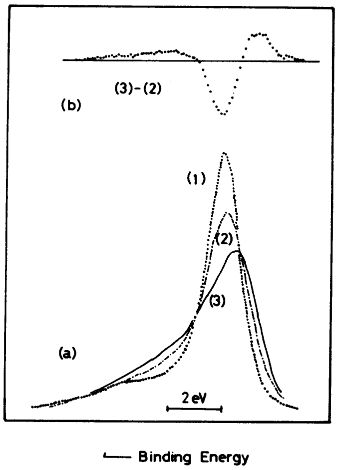

Fig. 1. (a): The C 1s peaks of (1) polyacetylene, (2) Na-doped polyacetylene (4th deposition) and (3) Na-doped polyacetylene (7th deposition).
(b): Difference spectrum of the C 1s peaks of (2) and (3).

peak was found to remain constant. We took the difference between the spectra of the doped samples which have different amounts of sodium in order to see the effect of the increase of the amount of the doped sodium. One of the difference spectrums (Fig. 1(b)) indicates that there are at least two main components in the C 1s peak of the sodium-doped polyacetylene. Upon doping sodium, a lower-binding-energy peak (or shoulder) begins to appear and its intensity increases with the sodium content keeping the binding energy constant. The higher-binding-energy peak which corresponds to neutral carbon atoms decreases in intensity. That is, a part of the neutral carbon atoms changes their state upon the sodium doping. Therefore, we attribute the former to the negatively-charged carbon atoms and the latter to the neutral carbon atoms. The chemical shift between the two main components is about 1.2 eV, from which we can estimate the average negative charge per carbon atom to be about −0.2 e. This means that an electron transferred from a sodium atom spreads over at least five carbon atoms. The difference spectrum also shows that the lower-binding-energy peak has a tail on the higher-binding-energy side. This might be attributable to the conduction-electron-plasmon shake-up as suggested by Salaneck *et al.*[3,4] Including this component, there are three components in the C 1s peak of the sodium-doped polyacetylene, which cannot be explained by the interpretation proposed by Salaneck *et al.* The difference between the binding energies of the higher-binding-energy component in the C1s level and the Na 1s level stays almost constant while increasing of the sodium content. This means that the sodium is in the same state, that is, in the form of Na^+ irrespective of the sodium content.

In conclusion, the XPS data of the sodium-doped polyacetylene suggest that the charge transfer from sodium to polyacetylene results in the formation of negatively-charged carbon atoms and an electron transferred from a sodium atom spreads over several (possibly more than five) carbon atoms of the polyacetylene chain. Based on these facts, we conclude that in the bromine-doped polyacetylene, the higher-binding-energy component is mainly due to the positively-charged carbon atoms, at least in the lightly-doped regions. However, the small contribution of the conduction-electron-plasmon shake-up to this component cannot be excluded.

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