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X-ray photoelectron spectroscopy investigation on the interaction of polyvinylcarbazole and fullerene

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Summary

Using X-ray Photoelectron Spectroscopy (XPS) technique, the interaction mechanism between polyvinylcarbazole (PVK) and fullerene (C_{60}) in photoconductive PVK film doped with C_{60} was studied. PVK and fullerene can form electron transfer complex according to the molar ratio of PVK unit and C_{60} being about 2:1 in room temperature, and the formation and dissociation of the complex are reversible with the change of temperature. The formation of complex is the key to improve the photoconductivity of PVK.

Introduction

Polyvinylcarbazole (PVK) is of great interest recently because of its photoconductivity and has already been applied in xerox technique. A lot of experiments have been done to improve its photoconductivity, among which PVK doped with strong electron-withdrawing materials, such as TNF (trinitrofluorone), TCNQ (tetracyanoquinodimethane) or ultrafine semiconducting powder, is relatively successful[1-4]. Lately, people have synthesized highly stable C_{60} cluster with macroscopic amounts, and owing to its special structure and wonderful perspective, it has led to great interest for scientists to study its structure and application, concerning various fields in physics, chemistry and materials science. Furthermore, due to the simplification of preparation of C_{60}, its commercial price has dropped sharply, which makes the investigations relative to it more active. There has been some reports[5,6] on C_{60} for being the sensitizer of photoconductive polymers. These experimental results suggest its invaluable potential in this area. The study on the PVK doped with C_{60}, however, stays at its initial step, so there are many questions remained insoluble, such as the way C_{60} interacts with PVK and how C_{60} improves the photocondutivity of polymers.

In this paper, X-ray photoelectron spectroscopy (XPS) technique is used to study the interaction between PVK and C_{60}, through the change of oxidation state of nitrogen atom in PVK at different temperatures. A probable mechanism has been demonstrated.

Experimental

The X-ray photoelectron spectrometer, model SKL-12, was produced in Shenyang Scientific Instrument Factory, China with a MgKα X-ray source (Ex=1253.6 eV). The measurements were made on this spectrometer with vacuum tightness of 2.0×10^{-7} Pa, applied voltage of 10 KV, working current of 10 mA and N_{1s} (of Nitrogen atom) peak position was calibrated with Fermi energy level. Surface contamination was removed by argon ion etching, in which pressure was 2.0×10^{-4} Pa, current was 10 mA and ion beam energy was 2.5 KV. The photoconductive film was prepared at the aluminum matrix through spin casting. In detail, PVK and C_{60} were resolved in benzene in some concentration respectively, mixed in a special molar ratio of PVK unit to C_{60} (this ratio is 3:1 in this experiment) and then the solution mixture was casted on a spin casting machine and after annealing for two hours in vacuum, the film was prepared.
Using XPS technique, we obtained XPS spectra of N_{1s} of the sample above (film) in 40°C and 195°C respectively. Based on the change of the XPS signals of N_{1s}, an interaction mechanism of PVK and C_{60} was discussed.

Results and Discussion

The XPS spectra at 40°C and 195°C are given in fig.1(a) and the repeated experimental results (after temperature is decreased to 40°C) in fig.1(b). As shown, the changes of XPS spectrum following the temperature are reversible. It is definitely clear that change of temperature does lead to the change of XPS spectrum of PVK/C_{60}. At higher temperature, the portion of N_{1s} peak with higher binding energy decreases while the portion with lower binding energy increases, which can be concluded that during the change of temperature, the oxidation state of nitrogen atom has changed. In other words, there is electron transfer existing in the system. Based on the difference of binding energy, the raw peak could be resolved into several peaks corresponding to different binding energies, following the method of peak resolution narrated in references [7,8]. The resolution results are given in fig.2 and data in table 1. In fig.2, the peaks in both cases (a) and (b) may be resolved into there peaks, with binding energies of 400.6 eV (peak-1), 399.4 eV (peak-2) and 398.0 eV (peak-3). Peaks 1, 2 and 3 belong to oxidation state, normal state and reduction state of nitrogen of PVK in turn. The binding energy of normal state (399.4 eV) is consistent with the result reported by K. Napo et al.[9], in which this energy was 399.5 eV. During heating process, only peak-1 and peak-2 have changed and there is no change for peak-3, probably because it originates from the interaction between nitrogen atom of PVK and Al atom of matrix[10]. This interaction will be discussed in another paper. Now we will discuss the two peaks located at 400.6 eV and 399.4 eV more detailed.
We can see that, from fig.1 and fig.2, with temperature raising, peak area at 400.6 eV decreases gradually while the area at 399.4 eV increases. So, there is a trend for some nitrogen atoms to be reduced into the state that they possessed in pure PVK, which agrees with the typical theory of electron transfer. This phenomenon is also consistent with our previous result[11], that is, at lower temperature the isolated electron pairs in nitrogen atoms of PVK tend to transfer to fullerene and some nitrogen atoms are then oxidized to form charge transfer complex, $[(PVK^{\delta+})_n—C_{60}{}^{n\delta-}]$. When temperature is higher, electron

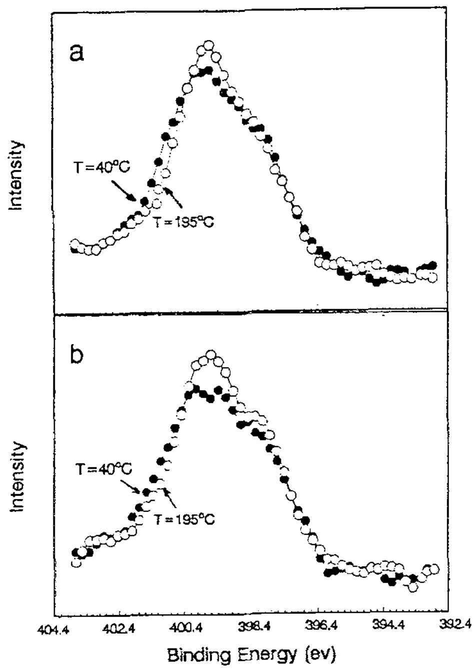

Fig.1. XPS spectra of PVK/C_{60}(=3:1) film
(a) Spectra at 40°C and 195°C;
(b) Repeated spectra of this film after its temperature is decreased to 40°C.

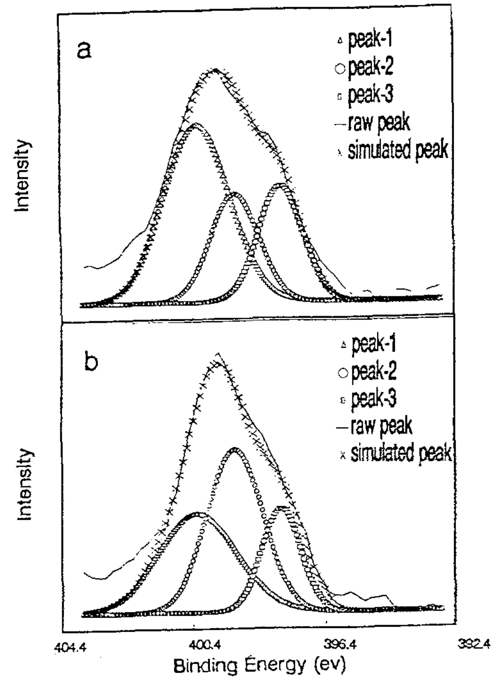

Fig.2. Resolution results of XPS spectra of N_{1S} in PVK/C_{60} film
(a) T = 40°C;
(b) T = 195°C.

Table 1. Resolution results of XPS spectra of N_{1S} in PVK/C_{60} film

	Peak No.	Peak / Shift (eV)	Peak Area (%)
a	1	400.6/-1.2	58
	2	399.4/0	21
	3	398.0/1.4	21
b	1	400.6/-1.2	36
	2	399.4/0	43
	3	398.0/1.4	21

transfer effect will weaken and the complexation equilibrium will shift to the direction of dissociation, which leads to the results depicted in fig.2(b). From the data in table 1, at 40° C the proportion of nitrogen atom with binding energy of 400.6 eV is 58%, exceeding 33%, which suggests that not one carbazole group only transports electrons to one C_{60} molecule to form electron transfer complex with the molar ratio of 1:1 (PVK unit : C_{60}) (If the ratio is 1:1, the proportion of peak-1 should be 33%), but it is more probable that two or more carbazole groups interact with one C60 molecule to form the complex with ratio of approximately 2:1(PVK unit : C_{60}). After heating to 195°C, the proportion of nitrogen atom with binding energy of 400.6 eV decreases to 36%, so the quantity of nitrogen atoms in oxidation state is almost equal to the quantity of fullerene, which may be attributed to that heating makes the complexation ratio between PVK unit and fullerene change from 2:1 to 1:1. If heated any more, the complexation ratio will decrease more, and at last maybe lead to full decomposition of the complex. The probable mechanism is illustrated in fig.3.

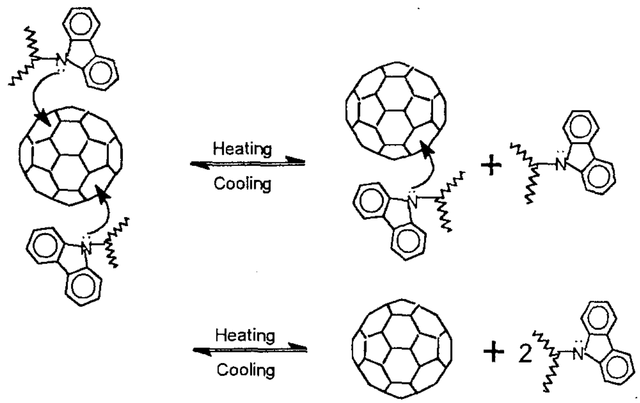

Fig.3. Scheme of change of interaction between PVK and C60 with different temperature

Because fullerene has higher electron affinity potential and a delocalized bond of 60 π electrons, its electron-withdrawing ability is very strong. There are some reports[12] in which C_{60} is said to be able to accept 4 electrons, so PVK and fullerene may form electron transfer complex with ratio (PVK unit : C_{60}) of 3:1, 4:1 under appropriate conditions.

In conclusion, the probable mechanism of the improvement of photoconductivity of PVK doped with C_{60} is as following: C_{60} and PVK form electron transfer complex in room temperature, and upon irradiation of light with photon energy exceeding the band gap energy, complete transfer of electron takes place, which will increase the concentration of charge carrier and improve significantly the photoconductivity of polymer. In order to get the greater improvement of photoconductivity, however, further study should be done to determine the optimum ratio between PVK unit and C_{60} in this system.

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