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CARRIER PHOTOGENERATION IN POLY(*N*-VINYL-CARBAZOLE)-BASED PHOTOCONDUCTIVE THIN-FILM DEVICES*

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Abstract In this paper, photoexcitation processes in the bilayer devices based on inorganic materials and poly(*N*-vinyl-carbazole) (PVK) were investigated. In order to clarify the roles of inorganic materials in photoconductive properties of bilayer devices, TiO_2 and ZnS were chosen to combine with PVK. A model for generation of photocurrent (I_{ph}) in single layer device of PVK was obtained. It is deduced that the recombination rate constant (P_{comb}) and the ionization rate constant (γ) of excitons should be considered as the most important factors for I_{ph}. For inorganic materials (TiO_2 or ZnS)/PVK bilayer devices, in reverse bias of –4 V, the photocurrent of 115 mA/cm^2 in the TiO_2/PVK device was observed, but the photocurrent in the ZnS/PVK device was only 10 mA/cm^2 under the illumination light of 340 nm and the light intensity of 14.2 mW/cm^2. The weaker photocurrent is attributed to the absorption of ZnS within UV region and the energy offset at the interface between PVK and ZnS, which impedes the transport of charge carriers.

Keywords: Polymer; Inorganic semiconductor; Photoconductive; Photogeneration.

INTRODUCTION

Since 1987 when Tang brought the breakthrough of organic electronic materials (OEM) for application in organic electroluminescence devices (OELD), OEM have largely been developed[1]. With this background, great interests have been stimulated in organic photovoltaic devices and optoelectronic detectors. Considering that performance of organic optoelectronic devices is limited by poor charge transport and short charge diffusion length, many approaches, including the synthesis of new materials, the self-assembly and the combination of inorganic materials or nanoparticles, are developed to tackle these problems[2–5]. Among these approaches, organic/inorganic thin-film devices have been proposed, since an inorganic component may improve the transport of electrons. In fact, most of the recent developments in improving performances of organic photovoltaic devices were based on the model of donor-acceptor heterojunction[6, 7]. Two main applications of this model were developed in polymer/nanoparticles composite structures and polymer/inorganic semiconductor bilayer structures, respectively. Although composite devices can produce a larger output of photocurrent than undoped polymer devices, the dark current also increases. Besides, the composite devices may limit the occurrence of charge transfer[8]. In this paper, the photoconductive properties of inorganic materials (ZnS or TiO_2)/polymer bilayer devices were investigated.

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EXPERIMENTAL

In our work, we prepared single layer devices made from poly(*N*-vinyl-carbazole) (PVK) and bilayer devices based on inorganic semiconductors (TiO_2 or ZnS) and PVK. The molecular structure of PVK is shown in the upper inset of Fig. 1. The pure PVK device's structure is ITO/PVK/Al. Inorganic materials (TiO_2 or ZnS) of 40 nm were deposited onto ITO glass by means of electron beam evaporation. In order to deposit high-quality films, the substrate was heated to 200°C during deposition. PVK in chloroform solution was spin-coated on the top of the layer of inorganic materials. The thickness of the PVK film depends on various conditions, such as the spinning speed or the concentration of PVK solution. In our experiments, the thickness was around 80 nm. Aluminum electrode was eventually evaporated on PVK films with the active area of *ca.* 10 mm^2. The structures of inorganic/polymer bilayer devices are ITO/TiO_2 (40 nm)/PVK (80 nm)/Al and ITO/ZnS (40 nm)/PVK (80 nm)/Al, respectively.

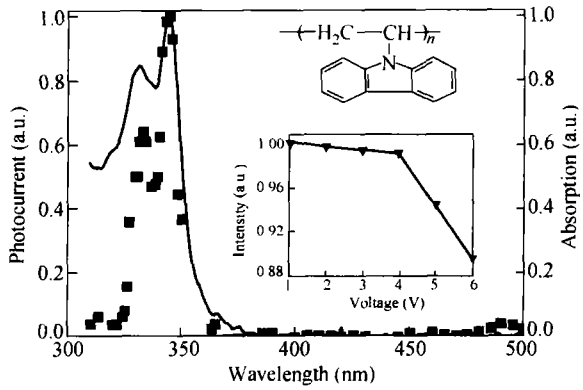

Fig. 1 Absorption spectrum of PVK (solid line), and photocurrent spectrum of PVK in reverse bias (square dot)
The upper inset shows the molecular structure of PVK and lower inset shows the PL quenching of PVK at different voltages.

Current-voltage curves were recorded by a Keithely 2410 Source Measure Unit both in the dark and under illumination. The incident light from a Xe lamp was passed through a monochromator to select a wavelength at 340 nm with an intensity of 14.2 mW/cm^2. The spectral responses of photocurrent in reverse bias of 4 V were measured. The reverse bias was applied by the positive pole of the power supply connecting with the Al electrode. All samples were illuminated through the ITO electrode.

RESULTS AND DISCUSSION

Generation of Photocurrent in Single Layer Devices of PVK

Figure 1 shows the absorption spectrum of PVK and the photocurrent spectrum of the device made from PVK. In Fig. 1, the maximum of photocurrent is close to the absorption peak at approximately 3.6 eV, and the onset of the photocurrent spectrum is near to the absorption edge. Traditionally, photoexcitation of carriers in polymer was assumed to be a two-step process: the first is photogeneration of excitons; the second is dissociation of excitons[9]. Our previous work on the electric field-induced quenching of PVK photoluminescence (PL) at various bias[10], to some extent, provided an evidence for two-step photoexcitation of exciton (shown at the lower inset of Fig. 1). And on the other hand, direct photogeneration of charge carriers has been proposed by Moses *et al.* in recent years[11]. Therefore, for devices based on single layer of PVK the photoexcitation can be derived from two parts: one part comes from the direct photogeneration of charge carriers, and the other is from dissociation of photogenerated excitons. Then, the photocurrent (I_{ph}) can be given as follows:

$$I_{ph} = n_{ch} e \mu F \quad (1)$$

where n_{ch} is the density of charge carriers, e is the elementary charge, F is the electric field, and μ is the mobility of charge carriers in PVK. Reasonably, n_{ch} and F are believed to be the two key factors whose changes will lead to significant differences in the photocurrent of single layer devices.

As was mentioned above, n_{ch} is determined by both the density of excitons (n_{ex}) and the density of directly photogenerated charge carriers (n_{dir}). According to Moses *et al.*[12, 13], n_{ex} and n_{ch} can be expressed by the following rate equations:

$$\frac{dn_{ex}}{dt} = \alpha_{ex} - n_{ex}P_{comb} - n_{ex}\gamma = 0$$

$$\frac{dn_{ch}}{dt} = \alpha_{dir} + n_{ex}\gamma - \frac{n_{ch}}{\tau_{ch}} = 0 \tag{2}$$

where α_{ex} is the rate of exciton generation and α_{dir} the rate of direct photogeneration of charge carriers, P_{comb} the recombination rate constant of exciton, γ the ionization rate constant of excitons, and τ_{ch} the life time of charge carriers. Then, under steady states, n_{ch} is given by:

$$n_{ch} = \left(\alpha_{dir} + \frac{\alpha_{ex}\gamma}{P_{comb} + \gamma}\right)\tau_{ch} \tag{3}$$

It is well known that α_{ex} and α_{dir} are not only related to the properties of polymers, but also proportional to the intensity of the incident light. In our experiments, materials and the light intensity are kept unchanged, and therefore, the recombination rate constant (P_{comb}) and the ionization rate constant of excitons (γ) become most important for n_{ch}. Under steady-state conditions, Eq. (2) can be similarly reformed as $\alpha_{ex} = (P_{comb} + \gamma)n_{ex}$. Because in a given system (unchanged incident light intensity and unchanged materials), α_{ex} changes a little, and the processes corresponding to P_{comb} compete with those to γ, that is, if γ increases P_{comb} will decrease, the promising breakthrough for enhancing the photoconductive properties of polymer thin-film photodetective devices can rely on the improvement of γ or the inhibition of P_{comb}.

As is shown in Eq. (1), another key factor which influences the photocurrent of single layer devices is the electric field (F). In single layer device made from organic or polymeric materials, the difference in work function of conducting contacts provides a build-in electric field (F_{in}). The main role of F_{in} here is to drive separated charge carriers toward the respective contacts. Therefore, when an electric-field is applied on the devices, the internal and external fields will influence the photocurrent together. Therefore, in Eq. (1), the photocurrent flow can be influenced by a combined electric field of internal field (F_{in}) and external one (F_{ex}). Then, F can be expressed by the equation:

$$F = F_{in} + F_{ex} \tag{4}$$

Combining Eqs. (1), (3) and (4), the photocurrent (I_{ph}) of single layer PVK devices can be given as follows:

$$I_{ph} = n_{ch}e\mu F = \left(\alpha_{dir} + \frac{\alpha_{ex}\gamma}{P_{comb} + \gamma}\right)\tau_{ch}e\mu(F_{in} + F_{ext}) \tag{5}$$

The above analysis regarding the photoexcitation processes and the photocurrent generation in single layer devices based on PVK provides, to some extent, a base for the research in PVK/inorganic materials bilayer devices.

Photocurrent in Inorganic Materials/PVK Bilayer Devices

In our experiments, bilayer devices produce better photoconductive effects than single layer devices made from PVK. As reported by others, dissociation of excitons (γ in the Eq. (5)) is not so effective in most single layer photocells based on organic semiconductors[14]. However, the usage of two materials with different affinities and ionization potentials will facilitate dissociation of excitons: the electron will be accepted by materials with the

larger electron affinity and the hole by the materials with the lower ionization potential, that is, there is an increase of the item of $\alpha_{ex}\gamma/(P_{comb} + \gamma)$ in Eq. (5). The valance and conduction bands of both ZnS and TiO_2 satisfy the above-mentioned requirements of energy levels (as is shown in Fig. 2). Therefore, both ZnS and TiO_2 are qualified to be an electron-accepting component in inorganic material/polymer bilayer systems. However, the improved photocurrent in the TiO_2/PVK bilayer device is much higher than that in the ZnS/PVK one. In reverse bias of −4 V, the maximal photocurrent of single layer device with PVK is 3.5 mA/cm^2 under the illumination wavelength of 340 nm and the intensity of 14.2 mW/cm^2. And under the same conditions, the maximal photocurrent of the TiO_2/PVK device is 115 mA/cm^2 and of the ZnS/PVK device is only 10 mA/cm^2. Which factor induces the worse output of photocurrent in ZnS/PVK devices than that in PVK/TiO_2 devices?

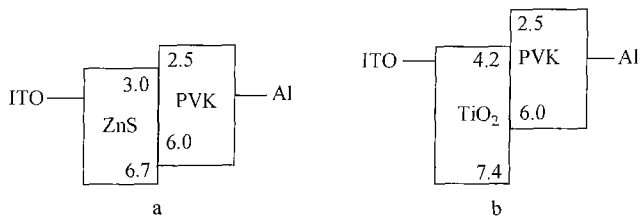

Fig. 2 The energy level diagram of the ZnS/PVK (a) and the TiO_2/PVK (b) bilayer devices

Figure 3 shows the normalized photocurrent spectra of investigated devices, ITO/PVK/Al, ITO/ZnS/PVK/Al, and ITO/TiO_2/PVK/Al in reverse bias of −4 V. The main difference in the three photocurrent spectra mainly lie in the short wave region between 300 and 350 nm. The photocurrent spectrum of ZnS/PVK bilayer device is slightly wider than that of PVK or TiO_2/PVK devices from 300 to 350 nm. According to the absorption spectra of ZnS and TiO_2 in Fig. 4, both inorganic materials may absorb the incident light and cause photogeneration of charge carriers. Traditionally, ZnS is chosen as a kind of photoconductive semiconductors. The photocurrent spectrum of the single layer device of ZnS is shown in Fig. 4, which indicates that upon illumination of UV light, free carriers can be generated in ZnS. The broader photocurrent spectrum of ZnS/PVK devices within short wave region suggests that ZnS layer absorbs the incident light and produces photoexcited carriers. Figure 5(a) proves this suggestion and that the photocurrent spectrum of ZnS/PVK in forward bias of

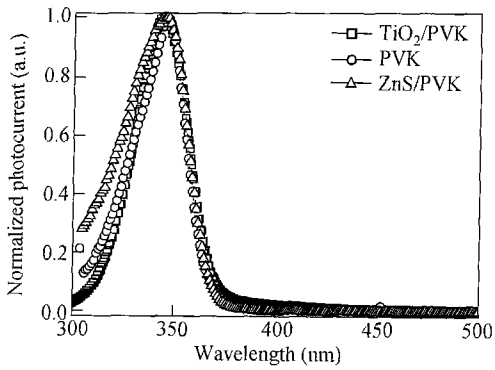

Fig. 3 Photocurrent spectra of ITO/PVK (80 nm)/Al (circle), ITO/ZnS (40 nm)/PVK/Al (triangle), and ITO/TiO_2 (40 nm)/PVK/Al (square) under reverse bias

3 V is much wider than that in reverse bias of −3 V between 300 and 350 nm. Since the illumination light passes through the ITO electrode, for the device of ITO/ZnS/PVK/Al, being absorbed by the layer of ZnS, the incident light is seriously weakened before arriving at PVK layer, and thus the number of photoexcited excitons in PVK greatly decreases. In reverse bias, the energy offset between the conduction band of ZnS and the LUMO energy level of PVK becomes a potential barrier for the transportation of photoexcited electrons in ZnS to Al electrode

via PVK. And there is also a barrier for the traverse of photoexcited holes remaining in PVK to ITO electrode. Accordingly, although the layer of ZnS absorbs the main part of the incident light, the photogenerated carriers in ZnS only contribute a little to the photocurrent due to potential barriers. In forward bias, electrons and holes transport in a reverse direction, electrons traversing to ITO electrode and holes to Al electrode, photoexcited carriers in ZnS can join in the flow of photocurrent, which leads to a wider photocurrent spectrum. Therefore, it is the absorption of ZnS and the barrier at the interface between ZnS/PVK in reverse bias that induce much low photocurrent.

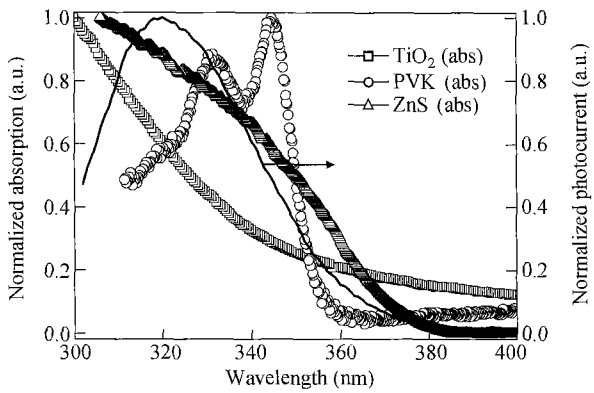

Fig. 4 Absorption spectra of TiO_2 (square), ZnS (triangle), and PVK (circle)
The photocurrent spectrum of single layer device of ZnS (solid line) is also shown.

In our experiments, however, it was found that TiO_2 mainly acts as a transporting material. Figure 5(b) presents the normalized photocurrent spectra of ITO/TiO_2/PVK/Al in forward and reverse bias of ±4 V. Unlike those of ZnS/PVK devices, photocurrent spectra of TiO_2/PVK devices with reverse polarity are similar. This similarity indicates that TiO_2 is almost transparent for incident light and produces few photoexcited carriers. According to Fig. 4, the absorption of TiO_2 is weaker than that of ZnS within UV region. Thus, PVK film is the main region where photogenerated excitons are generated and TiO_2 hardly influences the photocurrent of TiO_2/PVK bilayer devices. At TiO_2/PVK interfaces, although there is also a barrier for carriers to traverse to respective electrodes in reverse bias, the photocurrent does not decline as much as that of ZnS/PVK devices. One of the reasons is that PVK absorbs most of the incident light, and photogenerated excitons are effectively dissociated at the interface between TiO_2 and PVK, resulting in a great increase of γ in Eq. (5). Another possible reason is that the defects in TiO_2 facilitate tunneling of charge carriers to electrodes and reduce barrier at interfaces of TiO_2/PVK. But it needs further detailed research work to prove.

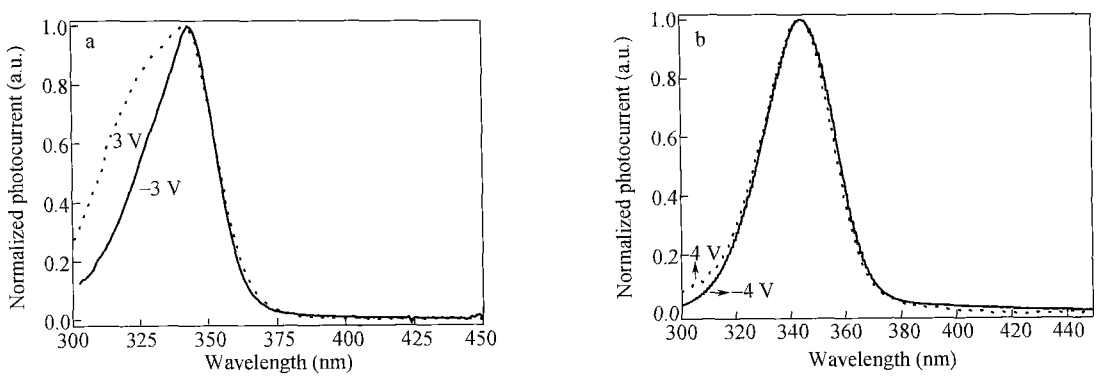

Fig. 5 The normalized photocurrent spectral responses of ITO/ZnS/PVK/Al in bias of ±3 V (a) and ITO/TiO_2/PVK/Al in bias of ±4 V (b)

CONCLUSIONS

In summary, the photoexcitation process and the photocurrent generation of devices based on polymer PVK were investigated. The recombination rate constant (P_{comb}) and the ionization rate constant (γ) of excitons play a very important role in determining the photoconductive properties of polymer-based devices. When the incident light intensity remains unchanged, the recombination process of exciton will compete with the ionization one. In inorganic materials/PVK thin-film bilayer devices, although inorganic materials provide sufficient energy offset required for the effective dissociation of exciton at the donor-acceptor interface, the absorption of inorganic material for incident light may cause a big difference in photoconductive properties. The layer of TiO_2 mainly accepts and transports photogenerated electrons transferred from PVK, and thus the photocurrent of the TiO_2/PVK device is greatly improved. However, the ZnS layer absorbs the incident light and causes the direct photogeneration of carriers. Due to the absorption of ZnS and the energy offset at the interface between PVK and ZnS, photogenerated carriers in ZnS cannot join the flow of photocurrent. Therefore, the photoconductive properties of the ZnS/PVK bilayer device are seriously limited.

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