PERGAMON

Current Opinion in Solid State and Materials Science 4 (1999) 373–378

Current Opinion in
**Solid State &
Materials Science**

Polymeric photovoltaic materials

N. Serdar Sariciftci*

Physical Chemistry, Johannes Kepler University of Linz, Altenbergerstr. 69, A-4040 Linz, Austria

Abstract

Recent developments in conjugated polymer-based photovoltaic elements have been reviewed. The photophysics of such photoactive devices is based on the photoinduced electron transfer from donor-type semiconducting conjugated polymers onto acceptor-type conjugated polymers or acceptor molecules such as Buckminsterfullerene, C_{60}. Photoinduced electron transfer in solid composite films of fullerenes embedded into conjugated polymers is reversible, ultrafast (within 300 fs) with a quantum efficiency approaching unity, and metastable. Similar to the first step in natural photosynthesis, this photoinduced electron transfer leads to a number of potentially interesting applications, which include sensitization of the photoconductivity and photovoltaic phenomena. Furthermore, using the conjugated polymer donors in polymer blends with another conjugated polymer acceptor, similar photovoltaic elements have been realized. Examples of photovoltaic architectures are discussed with their potential in terrestrial solar energy conversion.

1. Summary of recent advances

In the last couple of years several groups reported photovoltaic elements using conjugated polymers with incident photon to collected electron (IPCE) efficiencies of around 20% and total power conversion efficiencies around 1% for solar am1.5. Despite the low efficiency, the industrial interest in this field has been propelled by the demonstration of large-area (10×15 cm) flexible low-cost photovoltaic cells demonstrated in our group. There has also been a breakthrough by the Cambridge group using the simple lamination procedure of two polymer films to achieve an industrially attractive method for producing large-area solar cells.

2. Introduction

The flexibility of chemical tailoring of desired properties, as well as the cheap technology already well developed for all kinds of plastic thin-film applications make photovoltaic elements based on polymeric materials quite attractive.

An encouraging breakthrough for higher efficiencies is achieved by mixing electron donor-type polymers with suitable electron acceptors. To overcome the limitation of the photoinduced charge carrier generation, this dual molecule approach has been successful [1–4]. For example, in such devices, consisting of a composite thin film with a conjugated polymer–fullerene mixture, the photogeneration efficiency of charges is near 100%. In such a single-layer photoactive mixture film a 'bulk heterojunction' is formed between the electron donors and acceptors (Fig. 1). It is the photophysics between these donor–acceptor subsystems which drives the photovoltaic activity. In the following we will briefly review these interesting phenomena in a system consisting of conjugated polymers as donors and fullerenes (and derivatives of fullerenes) as electron acceptors.

Conjugated polymers in their undoped semiconducting state are electron donors upon photoexcitation (electrons promoted to the antibonding π^* band). Once the photoexcited electron is transferred to an acceptor unit, the resulting cation radical (positive polaron) species on the conjugated polymer backbone is known to be highly delocalized and stable, as shown in electrochemical and/or chemical oxidative doping studies.

Independently, the Santa Barbara and Osaka groups reported studies on the photophysics of mixtures of conjugated polymers with C_{60} [1,2,5–11]. The observations clearly showed an ultrafast reversible metastable photoinduced electron transfer from conjugated polymers onto Buckminsterfullerene in solid films. Using this molecular effect at the interface between bilayers consisting of semiconducting polymer (poly(2-methoxy,5-(2′-ethyl-hexoxy)-*p*-phenylene) vinylene, hereafter referred to as MEH-

*Corresponding author. Tel.: +43-732-2468-753; fax: +43-732-2468-770.

E-mail address: serdar.sariciftci@jk.uni-linz.ac.at (N.S. Sariciftci)

1359-0286/99/$ – see front matter
PII: S1359-0286(99)00044-3

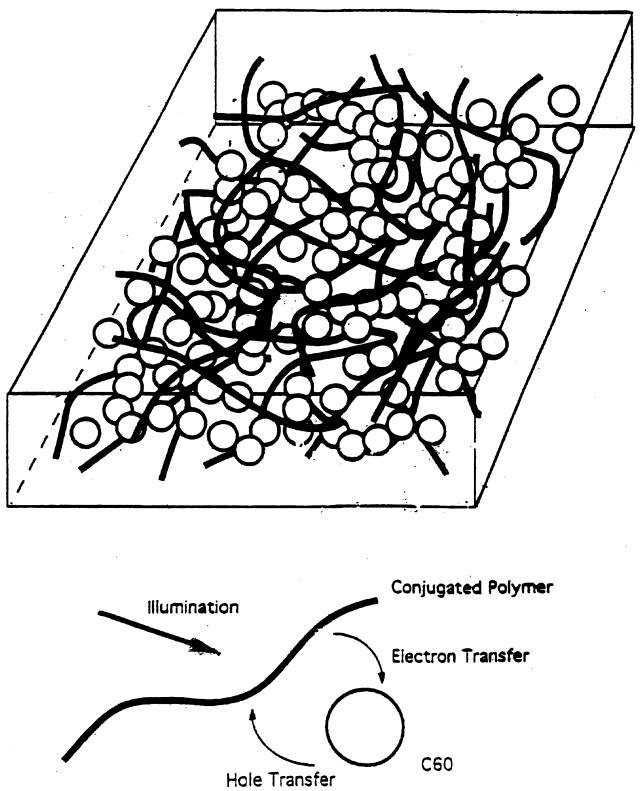

Fig. 1. Schematic illustration of a 'bulk heterojunction'.

PPV) and C_{60} films, diodes were demonstrated with rectification ratios on the order of 10^4 which exhibited a photovoltaic effect [2]. A significant improvement of the relatively low collection efficiency of the D–A bilayer was achieved by using phase-separated composite materials through control of the morphology of the phase separation into an interpenetrating network ('bulk heterojunction'). The power conversion efficiency of solar cells made from MEH-PPV–C_{60} composites was subsequently increased by two orders of magnitude to approximately 3% for monochromatic irradiation into the absorption band [3]. The Cambridge group with a parallel approach using acceptor-type conjugated polymers in composite with MEH-PPV has also realized efficient polymeric photovoltaic devices [4].

2.1. Ultrafast photoinduced electron transfer from conjugated polymers onto C_{60}

The optical absorption spectrum of a MEH-PPV–C_{60} film is a simple superposition of the two components without any indication of interaction between the two materials in the ground state. The strong luminescence of MEH-PPV, however, is quenched by a factor in excess of 10^3 [1] indicating the existence of a rapid quenching process, e.g. subpicosecond electron transfer [12]. The strong quenching of the luminescence of another conjugated polymer poly(3-octylthiophene) (P3OT) reported by Morita et al. [8] is also consistent with efficient photoinduced electron transfer. Thus, the quenching of luminescence has been observed in a number of conjugated polymers in composite with fullerenes, indicating this to be a general phenomenon for the non-degenerate ground state conjugated polymers [5].

To investigate the excited state with spin selective spectroscopic methods, photoinduced absorption detected magnetic resonance experiments were performed in conjugated polymer–C_{60} composites giving evidence for a complete quenching of the MEH-PPV triplet–triplet absorption signal at 1.35 eV. Instead a strong spin equal to a 1/2 signal dominates, indicating charged polarons as photoexcitations on the polymer donor [13]. This confirms that the photoinduced electron transfer occurs on a time scale sufficiently fast to quench the intersystem crossing to the triplet state.

Direct observation of the photoinduced electron transfer from conjugated polymers onto C_{60} is shown using subpicosecond photoinduced absorption (PIA) studies. Upon adding C_{60} to P3OT, the PIA spectrum, decay kinetics, and intensity dependence all change dramatically [14–16]. At 1 ps after photoexcitation by a 100 fs pump pulse at 2.01 eV, the PIA spectrum for P3OT–C_{60} (1%) already shows a single broad long-living PIA band with virtually no evidence of the features seen in pristine P3OT at 1.9 and 1.2 eV. This ultrafast (<1 ps) formation of the PIA band at 1.55 eV again demonstrates that the electron transfer occurs on a subpicosecond time scale.

The admixture of 1% of C_{60} into conjugated polymer matrix results in an increase of initial photocurrent by an order of magnitude. This increase of the photocarrier generation efficiency is accompanied by the successive increase in lifetime of the photocarriers upon adding more and more C_{60}. Thus, the ultrafast photoinduced electron transfer from the semiconducting polymer onto C_{60} not only enhances the charge carrier generation in the host polymer but also serves to prevent recombination by separating the charges and stabilizing them [17]. The composite films exhibit a remarkably enhanced photoconductivity over the broad spectral range from the near infrared to the ultraviolet. This observation is in full agreement with the photoinduced electron transfer phenomenon which leaves metastable positive polarons on the polymer backbone after the electron transfer, i.e. '*photodoping*'.

Definitive evidence of charge transfer and long-lived charge separation is obtained from light-induced electron spin resonance (LESR) experiments [1]. The ESR signal upon illuminating the P3OT–C_{60} composites with light of $h\nu = E_{\pi-\pi^*}$ where $E_{\pi-\pi^*}$ is the energy gap of the conjugated polymer (donor), two photoinduced ESR signals can be resolved; one at $g = 2.00$ and the other at $g = 1.99$ [1]. The higher g value line is assigned to the conjugated polymer cation (polaron) and the lower g value line to the C_{60}^- anion. We have further investigated the LESR of conjugated polymer–fullerene composites on the saturation

behaviour of the signal. These saturation experiments show clearly that the LESR signal assigned to positive polarons on the conjugated polymer backbone (high *g* value) has a different saturation behaviour, e.g. different relaxation mechanism compared to the fullerene anion signal which is not saturating at all (rapid relaxation on the fullerene balls [18]). We can safely conclude from these studies that the photoinduced radicals in these polymer–fullerene composites are independent from each other and dissociated completely.

2.2. Conjugated polymer–C_{60} heterojunction photodiodes

From the energy band diagram (Fig. 2) it is clear that the heterojunction formed at the interface between a semiconducting polymer and a C_{60} thin film should function as a diode with a rectifying current–voltage characteristic (analogous to a p–n junction, however with a different mechanism based on molecular redox properties). In reverse bias, electron injection into the semiconducting polymer and electron removal from C_{60} are energetically unfavorable. This inherent polarity of the device results in very low reversed bias current densities. On the other hand, electron injection into C_{60} and electron removal from the semiconducting polymer are energetically favorable, thus resulting in relatively high current densities under forward bias. Analogous arguments for molecular diodes were first proposed by Aviram and Ratner years ago for Langmuir-Blodgett D–A structures [19]. Thus, two kinds of photodiodes have been fabricated: bilayer heterojunction devices and single-layer 'bulk heterojunction' diodes (Fig. 3).

The current–voltage characteristics of a heterojunction device consisting of successive layers of ITO–MEH-PPV–C_{60}–Au shows an exponential turn-on up to 500 mV in forward bias; the rectification ratio is approximately 10^4.

The current–voltage characteristic of the device changes dramatically upon illumination by visible light and shows the photovoltaic effect with an open circuit voltage (V_{oc}) around 0.5 V, and the short circuit current density (J_{sc}) is 2.08×10^{-6} A cm^{-2} with 10 mW illumination resulting in a power conversion efficiency of 0.04%.

Although the quantum efficiency for photoinduced charge separation is near unity for a D–A pair, the conversion efficiency in a bilayer heterojunction device is limited:

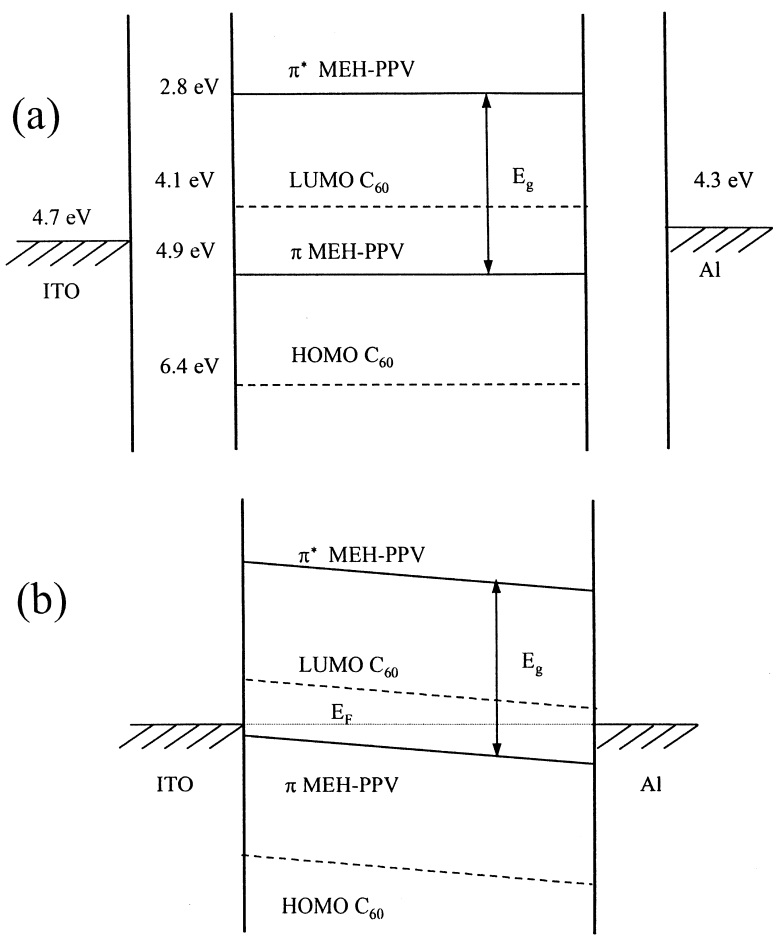

Fig. 2. Schematic energy band diagram of the bulk heterojunction consisting of conjugated polymers and fullerenes: (a) open circuit; (b) short circuit condition.

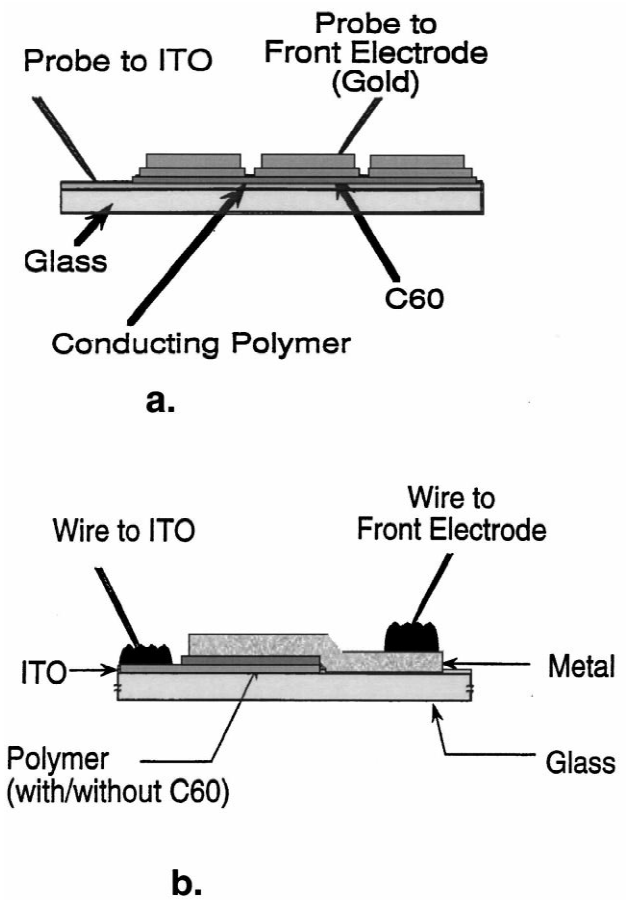

Fig. 3. Device architectures used in the fabrication of plastic solar cells: (a) bilayer heterojunctions; (b) single-layer bulk heterojunction devices.

1. Due to the molecular nature of the charge separation process, efficient charge separation occurs *only* at the D–A interface; thus, photoexcitations created far from the D–A junction recombine prior to diffusing to the heterojunction.
2. Even if charges are separated at the D–A interface, the photovoltaic conversion efficiency is limited by the carrier collection efficiency; i.e. the separated charges must be collected with minimum losses.

2.3. The 'bulk heterojunction' concept

A semiconducting polymer with asymmetric contacts (a low work function metal on one side and a high work function metal on the opposite side, metal–insulator–metal MIM diodes) functions as a 'tunneling injection diode'; such devices have been described by Parker [20]. A schematic cross-sectional view of such devices is displayed in Fig. 3.

For photovoltaic cells made with pure conjugated polymers, energy conversion efficiencies were typically 10^{-3}–10^{-2}%, too low to be used in practical applications [21–23]. Thus, as noted above, with the addition of only 1% C_{60}, the photoconductivity of MEH-PPV+C_{60} increases by an order of magnitude over that of pure MEH-PPV. Consequently, interpenetrating phase-separated D–A network composites would appear to be ideal photovoltaic materials [3,6]. Since any point in the composite is within a few nanometers of a D–A interface, such a composite is a 'bulk D–A heterojunction' material (see Fig. 1).

Important progress has been made toward creating 'bulk D–A heterojunction' materials [3,4,24,25]. Recent reports on polymer–polymer devices with up to 4.8% power conversion efficiencies at the absorption wavelengths led to considerable improvement of the general efficiencies of these types of photovoltaic cells [25]. In their report, Granström et al. use a well known technique from polymer processing which facilitates the melt-blending of two different polymer layers under applied pressure, i.e. lamination [25]. The different stoichiometry of the two layers creates a gradient for hole conducting and electron conducting components in the bulk heterojunction.

2.4. Flexible large-area plastic solar cells

To fully utilize the potential of the conjugated polymers as plastic photoactive materials as well as to investigate the device technology problems of upscaling, we realized, at the University of Linz, large-area (6×6 cm and 15×10 cm) photovoltaic elements on flexible ITO coated plastic (PET) substrates. A picture of such an element is shown in Fig. 4. The schematic cross-section of such devices is displayed in Fig. 3. Devices with an open circuit potential of ≈0.7 V, a short circuit current of ≈1 mA cm^{-2} and a filling factor FF≈0.35 under an illumination of 10 mW cm^{-2} at 488 nm can be routinely fabricated (Fig. 5). The stability of such devices without any protection is extremely poor. It is imperative that the photovoltaic elements have to be protected from ambient air. The comparison of lifetimes of such a large-area photovoltaic cell (fabricated in air and under arbitrary conditions without precautions ensuring dust-free and/or oxygen-free conditions), unprotected or protected with a special coating, clearly show that protection against air oxygen increases the lifetime considerably.

3. Conclusion

The excellent photosensitivity and relatively high energy conversion efficiencies obtained from bulk heterojunction materials are promising. Further optimization of device performance can be achieved by optimization of the device physics:

1. Optimize the choice of metallic electrodes to achieve good ohmic contacts on both sides for collection of the oppositely charged photocarriers.

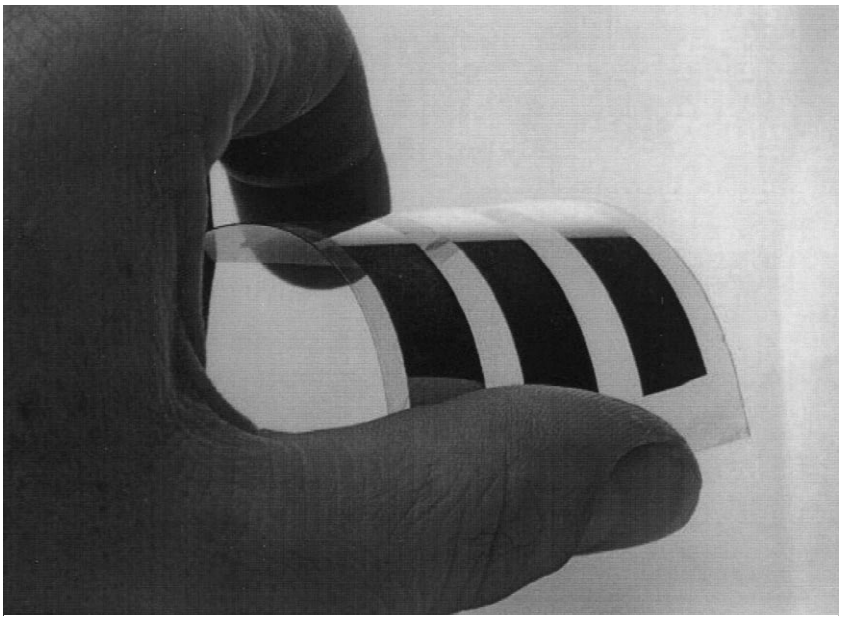

Fig. 4. Picture of a fully flexible large-area plastic solar cell (6×6 cm).

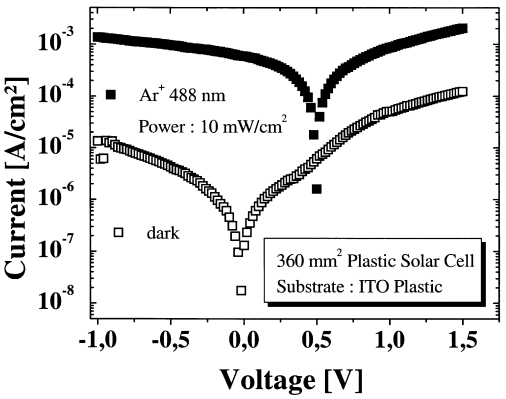

Fig. 5. Current–voltage characteristic of the large-area polymeric photovoltaic devices.

2. Optimize the choice of the D–A pair (the energetics influences the open circuit potential).
3. The band gap of the semiconducting polymer should be chosen for efficient harvesting of the solar spectrum.
4. Optimize the network morphology of the phase-separated composite material, thereby maximizing the mobility of the charge carriers within the different components of the bulk heterojunction.

References

[1] Sariciftci NS et al. Photoinduced electron transfer from conducting polymers onto Buckminsterfullerene. Science 1992;258:1474.
[2] Sariciftci NS et al. Semiconducting polymer Buckminsterfullerene heterojunctions: Diodes, photodiodes and photovoltaic cells. Appl Phys Lett 1993;62(6):585.
[3] Yu G et al. Polymer photovoltaic cells: Enhanced efficiencies via a network of internal donor–acceptor heterojunctions. Science 1995;270:1789.
[4] Halls JJM et al. Efficient photodiodes from interpenetrating polymer networks. Nature 1995;376:498.
[5] Sariciftci NS, Heeger AJ. Photophysics, charge separation and device applications of conjugated polymer/fullerene composites. In: Nalwa HS, editor, Handbook of organic conductive molecules and polymers, John Wiley, 1996, pp. 414–50.
[6] Sariciftci NS. Role of Buckminsterfullerene in organic, photoelectric devices. Prog Quant Electr 1995;19:131.
[7] Sariciftci NS, Heeger AJ, US Patent No. 5 331 183, University of California, USA, 1994.
[8] Morita S, Zakhidov AA, Yoshino K. Doping polythiophenes with fullerenes. Sol State Commun 1992;82:249.
[9] Morita S et al. Photoconductivity in poly3-octylthiophene with C60. Jpn J Appl Phys 1993;32:L1173.
[10] Morita S et al. Doping of poly(phenylenevinylene) derivatives with C60. J Appl Phys 1993;74(4):2860.
[11] Fujii A, et al. Organic photovoltaic cell with donor-acceptor double heterojunctions, Jpn J Appl Phys Pt 2, 1996;35(11A) L1438–L1441.
[12] Smilowitz L et al. Photoexcitation spectroscopy of conducting polymer–C60 composites. Phys Rev 1993;B47:13835.
[13] Wei X et al. Absorption-detected magnetic-resonance studies of photoexcitations in conjugated-polymer/C-60 composites. Phys Rev B, Condensed Matter 1996;53(5):2187–90.
[14] Kraabel B et al. Ultrafast photoinduced electron transfer in conducting polymer–Buckminsterfullerene composites. Chem Phys Lett 1993;213(3–4):389.
[15] Kraabel B et al. Ultrafast spectroscopy on photoinduced electron transfer from semiconducting polymer to C60. Phys Rev 1994;B50:18543.
[16] Kraabel B et al. Subpicosecond photoinduced electron-transfer from conjugated polymers to functionalized fullerenes. J Chem Phys 1996;104(11):4267–73.
[17] Lee CH et al. Sensitization of photoconductivity of conducting polymers by C60. Phys Rev 1993;B48:15425.
[18] Dyakonov V et al. Photoinduced charge carriers in conjugated polymer–fullerene composites studied with light induced electron spin resonance. Phys Rev 1999;B59:8019.

[19] Aviram A, Ratner MA. Molecular diode. Chem Phys Lett 1974;29:277.
[20] Parker ID. Tunneldiodes of conjugated polymers. J Appl Phys 1994;75(3):1656.
[21] Yu G, Zhang C, Heeger AJ. Dual function of conjugated polymer devices. Appl Phys Lett 1994;64(12):1540.
[22] Yu G, Pakbaz K, Heeger AJ. High efficiency photonik devices made with semiconducting polymers. Appl Phys Lett 1994;64(25):3422.
[23] Antoniadis H et al. Photovoltaic effects at polymer/metal interface. Polymer Preprints 1993;34(2):490.
[24] Yu G, Heeger AJ. Charge separation and photovoltaic conversion in polymer composites. J Appl Phys 1995;78:4510.
[25] Granstrom M et al. Laminated fabrication of polymeric photovoltaic diodes. Nature 1998;395:257.