

Blend-Based Photovoltaic Devices

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Abstract

We present two approaches for the fabrication of efficient photovoltaic devices. In the first one, the active layer is a bipolar material made by doping of an inert polymer with donor and acceptor molecules. In the second approach, inorganic nanoparticles are dispersed in a conjugated polymer. Photovoltaic measurements are presented for both systems.

Keywords: photovoltaic devices, donor-acceptor blends, organic-inorganic composites.

Introduction

There is a long standing interest towards the development of organic photovoltaic devices for applications in solar energy harvesting and photodetectors¹. The main driving force is the potentially low device fabrication cost which is associated with the processability of organic materials. Apart from ease of processing, organic materials offer optoelectronic properties that can be tuned over a large range via chemical synthesis and even be tailored to fit specific applications. This unique feature has been exploited to help understand and dramatically improve the properties of photovoltaic devices. As a result, the power conversion efficiency in the solar cell configuration (electrical energy produced per incident optical energy), which was as low as 10⁻⁵% in the early seventies is by now larger than 1%.

The mechanism of operation of organic photovoltaic cells is very simple: In a single layer configuration, the organic layer is sandwiched between two metal electrodes with different work functions. Illumination of the organic semiconductor with light of the proper wavelength creates free electrons and holes. The built-in potential which is established due to the difference in the Fermi energy of the two metals forces these carriers to drift towards opposite sides. When connected to the proper electrical circuit, photovoltaic devices function as photodetectors that generate an electrical current proportional to the incident light intensity, or as solar cells that provide electrical power to an external circuit.

The single layer device configuration suffers from two main shortcomings: First, the yield of free charge generation in pristine organic materials is typically very low, therefore, only a very small portion of the absorbed

photons contribute to the generation of free carriers. Second, organic materials usually exhibit monopolar charge transport (only one of the carriers appears to be mobile, indicating that the other one is severely trapped or suffers from an intrinsically low mobility). As a result, the less mobile carrier accumulates in the bulk of the organic creating a space charge field that degrades the device performance. Bilayer devices, which are the equivalent of a p-n semiconductor junction, are designed to tackle this problem to some extent, but their active volume (which is confined next to the organic/organic interface) is very small for efficient operation.

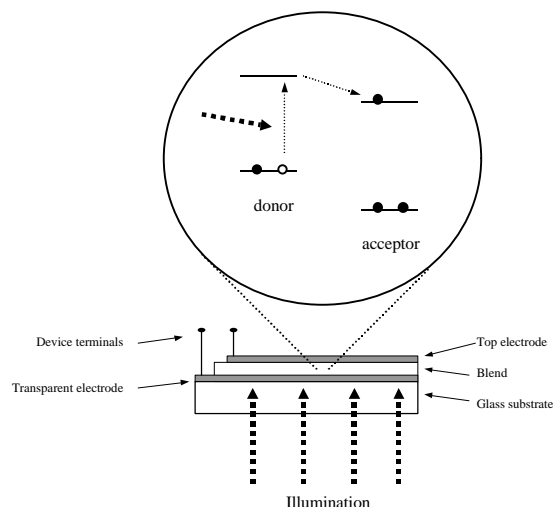


Figure 1. Blend-based photovoltaic device.

Recently, blend-based cells have been proposed as a novel type of device with potentially high efficiency. Their operation is based on a single active layer which is a blend of donor and acceptor-like moieties. Examples include polymer-small molecule² and polymer-polymer³ blends that are prepared by casting from a common solution, as well as blends of two small molecules⁴ prepared by coevaporation. The principle of operation of this type of device is shown in figure 1. The blend is sandwiched between two different metal electrodes that create the built-in potential. Upon excitation of a donor moiety, photoinduced electron transfer from the lowest unoccupied molecular orbital (LUMO) of the donor to the LUMO of a neighboring acceptor takes place, which leaves a free hole in the donor and a free electron in the acceptor. A similar result is attained upon

the excitation of an acceptor. Once separated, the two charges drift in different phases thereby minimizing their chance of recombination and allowing the individual optimization of both mobilities. Provided there are two interpenetrated percolating pathways, both charges can be efficiently collected at the electrodes.

In this paper we present two approaches towards the preparation of efficient blend-based organic photovoltaic devices. In the first one, small molecules are doped into an inert polymer matrix to create a bipolar donor-acceptor blend. In the second approach, inorganic nanoparticles are dispersed into a conjugated polymer. We discuss the device preparation and preliminary photovoltaic characterization data.

Experimental

The small molecule-based devices were fabricated and characterized at Xerox. TTA was used as the donor (hole transport species) and carboxyphenyl naphthaquinone as the acceptor (electron transport species). These molecules, shown in figure 2, were chosen for their solubility at a useful weight percent loading, apart from their electrical properties. Blends were made with various amounts of donor and acceptor as well as combined with other dopants. Typical weight percentages were 29% and 18% wt. donor and acceptor respectively. The binder polymer was a polyvinyl butyral (PVB).

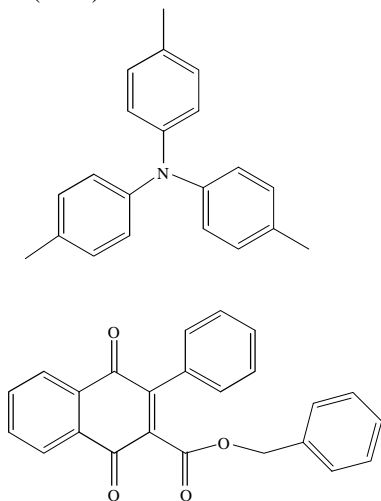


Figure 2. Chemical structures of TTA (above) and carboxyphenyl naphthaquinone (below).

Films of 1 micron thickness were spin-cast onto Al coated polyimide sheets from a solution of 13.3% in wt. solids, at speeds up to 1500 rpm for 30 seconds. The resulting films were cross-sectioned for transmission electron microscopy and confirmed to be uniform within 10 nm. Top semi-transparent electrodes, 1.2 cm diameter, of Au were then sputtered onto the films, to a thickness of ca. 15 nm. Current voltage characteristics were measured by a Keithley 237 high voltage source-measure unit. White light illumination was provided by a fluorescent tube. All

material/sample preparation and measurements were performed in ambient conditions, within a temperature range of 21-23°C and relative humidity ranging from 35-68%. Results were reproduced over a period of 3 weeks.

The nanoparticle-based devices were prepared and characterized at Cornell. Amorphous silica nanoparticles (100 nm diameter) coated with n-octylsilane were synthesized in house and mixed with regioregular poly(3-octyl thiophene) (P3OT-figure 3) into a toluene solution. The devices were made by spin casting the solution on ITO covered glass substrates at 3000 rpm for one minute. The resulting film thickness was of the order of 100 nm. The device fabrication was completed by the deposition of 20 nm thick Ca cathodes, overcoated with 20 nm Al. The active device area was 3mm². The electrical characteristics were measured with a 236 Keithley source-measure unit and illumination was provided by a tungsten filament lamp. All device fabrication and characterization was carried out inside a nitrogen glove box with less than 1 ppm oxygen and moisture contents.

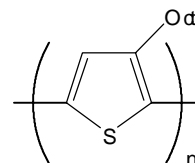


Figure 3. Chemical structure of poly(3-octyl thiophene).

Results and Discussion

Small molecule-based devices

Typical current-voltage characteristics in the dark and under illumination from a small molecule based-device are shown in figure 4.

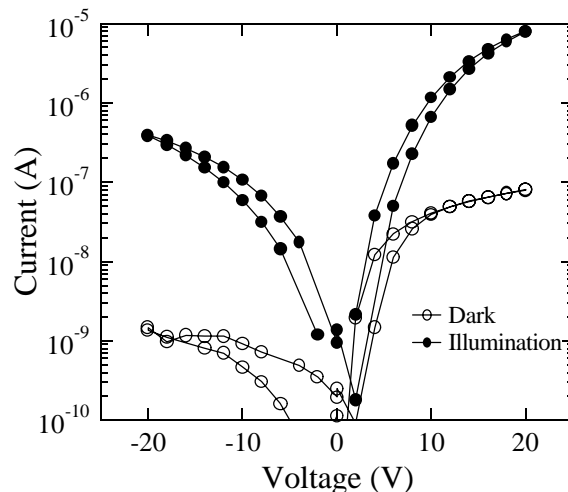


Figure 4. Current-voltage characteristics from a small molecule-based device.

In the dark the device behaves like a diode with the forward current (Au positive) reaching 0.1 μ A at 20V.

Under reverse bias the current is practically equal to the noise floor of our setup. Upon illumination with approximately 50 mW/cm^2 , the reverse current increases for more than two orders of magnitude at -20V , indicating that the device acts as a photodetector. The current also increases in the forward bias, indicating that in the dark, the current is injection limited. Due to the white light illumination, only a very rough estimate of the device efficiency can be made. At -20V , the quantum efficiency is found to be of the order of 10^{-4} . Considering the facts that the dopant concentration and the device thickness are not optimized and the top Au contact is not very transparent, this is a very promising figure.

It is worth noting that the device characteristics remained unaltered after a period of two weeks (the data shown in figure 4 is from the first device, prepared two weeks ago). There is also negligible hysteresis under repeated cycling, which indicates that the blend offers truly bipolar transport with no substantial trapping of carriers. We are currently working on optimizing the dopant concentration and layer thickness to improve device efficiency.

Nanoparticle-based devices

Following the pioneering work by the Grätzel group⁵, who prepared photovoltaic devices using dye sensitized mesoporous TiO_2 , TiO_2 nanoparticles were added in conjugated polymers to increase their photovoltaic efficiency⁶. The mechanism of operation of this type of device is similar to the donor-acceptor blends: upon excitation of the conjugated polymer (which acts as a donor), the electron transfers to a neighboring nanoparticle, leaving a free hole in the polymer. Since TiO_2 has a large electron mobility and most conjugated polymers transport holes, the blends offers bipolar transport.

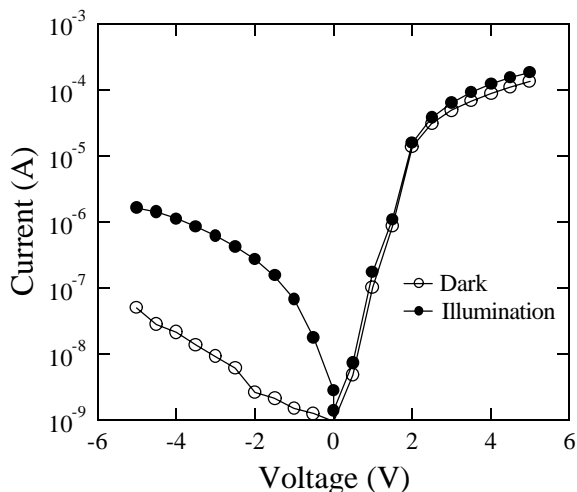


Figure 5. Current-voltage characteristics from a nanoparticle-based device.

We have used a variety of nanoparticles dispersed in poly(3-octyl thiophene) and found that apart from the

electron transfer and transport, there is an additional contribution from the nanoparticles. In figure 5, typical current-voltage characteristics in the dark and under illumination from a device containing 10% wt. SiO_2 nanoparticles are shown. In the dark, the usual diode behavior is observed, with a rectification of more than 3 orders of magnitude at 7V . Under illumination the reverse current increases more than an order of magnitude, indicating a substantial contribution from the photo-generated carriers.

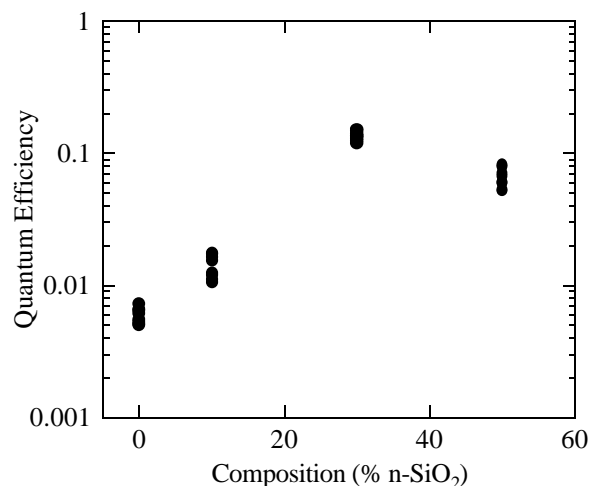


Figure 6. Dependence of efficiency on nanoparticle concentration.

In figure 6, the dependence of the quantum efficiency at -7V on the SiO_2 nanoparticle concentration (in % v/v) is shown. Compared to pristine P3OT, the material with 30% nanoparticles has an efficiency that is more than an order of magnitude larger.

The addition of nanoparticles does not change the electronic properties of P3OT. The normalized optical absorption spectra of the pristine and the nanoparticle-containing material are identical. Photoinduced electron transfer is also unlikely to take place, since the conduction band (E_c) of SiO_2 (at -1 eV below the vacuum level) is higher than the LUMO of P3OT (at -3 eV below the vacuum level). Therefore, there must be another mechanism that is responsible for the increased efficiency of the nanoparticle devices.

Adding nanoparticles in P3OT causes an increase in the optical density, as scattering from the nanoparticles increases the effective optical path length. Therefore, light that would be transmitted through a pristine P3OT sample is now being absorbed. Addition of too many nanoparticles, however, will deteriorate the electrical properties of the blend, since there will be too little P3OT to sustain efficient charge transport. The maximum in the efficiency in figure 6 represents the balance between scattering and transport. We are currently working on quantifying these effects.

Conclusions

In conclusion, we demonstrated two novel approaches towards blend-based photovoltaic devices. The first approach involves blends of donor and acceptor molecules in an inert polymer matrix. The second approach involves addition of nanoparticles in conjugated polymers. Both approaches offer several degrees of freedom that can be optimized to yield efficient photovoltaic devices.

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Biography

Malliaras studied Physics at the Aristotle University (Greece) and did his doctoral research in the University of Groningen (the Netherlands), on photorefractivity in polymers. Before joining the faculty at Cornell in July 1998, he was a post doctoral fellow at the University of Groningen ('96) and the Center for Polymer Interfaces and Macromolecular Assemblies (CPIMA), at the IBM Almaden Research Center ('97-'98). His research focuses on the design, fabrication, characterization and computer modeling of organic optoelectronic devices such as light emitting diodes and photovoltaic cells. He is a member of the American Physical Society and the Materials Research Society.