Time-independent, high electron mobility in thin $PC_{61}BM$ films: Relevance to organic photovoltaics

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ABSTRACT

Ultrafast optical probing of electric field by means of electroabsorption combined with conventional photocurrent measurements was employed to investigate the drift and mobility dynamics of photo-generated charge carriers in the pristine $PC_{61}BM$ film and in the blend with a merocyanine dye. Electrons passed a 40 nm thick $PC_{61}BM$ film within a few picoseconds with time-independent and weakly dispersive mobility. The electron mobility is $1 \, cm^2/(V \, s)$ at $1 \, MV/cm$ and an estimate of the zero-field mobility yields $5 \cdot 10^{-2} \, cm^2/(V \, s)$. The initial electron mobility in the blend is of the order of $10^{-2} \, cm^2/(V \, s)$ and decreases rapidly. We conclude that electron motion in $PC_{61}BM$ based organic bulk hetero-junction solar cells is limited by barriers between $PC_{61}BM$ domains rather than by intrinsic $PC_{61}BM$ properties.

1. Introduction

The opportunity of solution processing and printing is an ultimate advantage of organic photovoltaics (OPV) that assures a low energy investment in the device manufacturing. Most solution processed planar and bulk hetero-junction solar cells rely on the soluble fullerene derivative [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) as an electron acceptor. $PC_{61}BM$ weakly absorbs in the visible range and has poor overlap with the solar-spectrum, thus, weakly contributes to light absorption in $PC_{61}BM$-based solar cells. Attempts to use strongly absorbing polymers [1,2] or small molecules [3] instead of fullerenes resulted in lower performance of devices. Therefore, better understanding of the features, which lie at the heart of success of fullerenes in OPV applications, could help in the development of the competitive acceptor materials and improvement of fullerene based cells.

Charge carrier mobility is one of the crucial parameters for solar cell performance. The mobility is related to the diffusion coefficient by the Einstein relation, thus it characterizes carrier motion. High mobility and, thus, fast diffusion facilitates splitting of the electron–hole pairs at the donor–acceptor interfaces [4–7] and leads to faster extraction of photo-generated charges preventing their accumulation and recombination in the active media of the solar cell. Surprisingly, the electron mobility in $PC_{61}BM$ determined by different methods significantly varies, and actual electron drift and diffusion speed on the length scale typical for solar cells is unknown. Reported electron mobility in $PC_{61}BM$ vary by three to four orders of magnitude. Early work by Mihailetchi et al. reported a value of $2 \cdot 10^{-3} \, cm^2/(V \, s)$ determined by analysis of space charge limited current (SCLC) [8]. A latter investigation by Tuladhar et al. with the SCLC technique estimated the electron mobility at $(0.8–3.3) \cdot 10^{-2} \, cm^2/(V \, s)$ in $PC_{61}BM$ films [9]. The electron mobility derived from field-effect transistor operation

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also ranges from $4.5 \cdot 10^{-3}$ cm^2/(V s) to $2 \cdot 10^{-1}$ cm^2/(V s) [10–13]. The study of PC$_{61}$BM microcrystalline powder by pulse-radiolysis time-resolved microwave conductivity provides the sum of electron and hole mobility in the range of $4 \cdot 10^{-2}$–$3 \cdot 10^{-1}$ cm^2/(V s) [14]. This may be considered as being approximately equal to the half of the electron mobility, since the hole mobility in PC$_{61}$BM is by orders of magnitude lower. The electron mobility of the order of 10^{-1} cm^2/(V s) was obtained in PC$_{61}$BM domains of PC$_{61}$-BM/MDMO-PPV blend by means of flash-photolysis time-resolved microwave conductivity technique [15]. An identical mobility value was also estimated from simulation of exciton quenching dynamics in conjugated polymer/PC$_{61}$-BM blends on the basis of Onsager–Braun model [16]. However, a much lower electron mobility in PC$_{61}$BM manifold of $3 \cdot 10^{-3}$ cm^2/(V s) was evaluated in recent photoconductivity studies of conjugated polymer APFO-3/ PC$_{61}$BM blends by time-resolved terahertz spectroscopy [17]. Ultrafast Stark-shift spectroscopy was employed by Cabanillas-Gonzalez et al. in order to reveal charge transport in thin PC$_{61}$BM films [18]. Here, the authors came to the conclusion that the carrier mobility averaged over electrons and holes dropped down from 10^{-1} cm^2/(V s) to 10^{-3}–10^{-4} cm^2/(V s) within 40 ps after photoexcitation. The work was primarily focused on demonstration of the method, therefore some additional effects related to relatively high excitation intensities, which could significantly affect the results, were not analyzed in detail. Thus, despite of numerous investigations, electron mobility values and dynamics in PC$_{61}$BM and PC$_{61}$BM-based OPV devices remains unclear, preventing clear understanding and modeling of the device performance.

In this work, dynamic Stark shift spectroscopy in combination with photocurrent measurements are employed for the investigation of the charge drift dynamics in thin films of pristine PC$_{61}$BM and in its blend with merocyanine molecule (MD376/PC$_{61}$BM blend) [19–21]. We examine the role of charge screening and show that this effect leads to qualitatively different interpretation of the electron mobility dynamics. We conclude that electron mobility is time-independent and weakly dispersive, however, strongly field-dependent in pristine PC$_{61}$BM. On the contrary, the charge mobility is substantially lower and experiences rapid relaxation in blends with organic molecules.

2. Material and methods

Experimental method is based on the measurement of the electric field-induced absorption changes (Stark effect) of organic films sandwiched between semitransparent and metal electrodes. Under reverse bias, when equilibrium carriers are extracted from the active media and their injection is negligible, the material between electrodes behaves like a dielectric medium, and the device resembles a charged capacitor. Under these conditions the applied external bias results in the homogeneously distributed electric field inside the organic layer. Excitation of the film with a short light pulse generates charge carriers, which drift and create counteracting dipoles to the built-in or applied electric field. As a result, initial strength of the

electric field decays and electroabsorption (EA) weakens until carriers are extracted from the film. Dynamics of charge drift may be reconstructed from the evolution of the observed EA. More details about the experimental technique may be find elsewhere [18,22].

Experiments were carried out on a typical femtosecond pump–probe setup based on the chirped-pulse amplified Ti:sapphire laser running at the repetition rate of 1 kHz and the output wavelength of 780 nm. Samples were excited at 390 nm utilizing the second harmonic of fundamental radiation. The p-polarized white light generated in a sapphire plate was used for probing EA of the samples in reflection configuration (see Supplementary data) at 45 degrees of the incidence angle. Square voltage pulses of reverse bias, synchronized to the laser output and having a duration of about 100 μs were applied to the sample by means of an electrical pulse generator at a frequency of 500 Hz. The measured electromodulated differential absorption (EDA) corresponded to the absorption difference between the biased and unbiased sample at a given probe pulse delay. An oscilloscope was used to measure the photocurrent through a 50 Ω load.

All devices were fabricated on quartz plates sputter-coated with indium–tin oxide (ITO). The substrates were exposed to ozone for 3 min and immediately coated with poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (HC Starck) and heat treated for 2 min at 110 °C to remove residual water. Before deposition of the active layer, the samples were annealed at 150 °C for 5 min in a nitrogen glove box. Active layers of 40 nm thickness were spin-coated from chlorobenzene solutions of PC$_{61}$BM and MD376 (15 mg/mL) at 1000 rpm in a nitrogen glove box. For blends, MD376 solution was mixed with PC$_{61}$BM solution in the 1:1 (w/w) ratio. The device fabrication was completed by thermal evaporation of aluminium.

3. Results and discussion

3.1. Pristine PC$_{61}$BM

Fig. 1 shows EDA spectra of PC$_{61}$BM film (40 nm) at different delay times. The EDA spectrum at a negative delay time corresponds to the steady state EA, and is in a good agreement with previously published data [23,24]. The electric field in the active media is the sum of the applied field and the built-in field. As determined from photocurrent measurements (not shown), the built-in field approximately equals to 0.2 MV/cm that is in agreement to the work-function difference of the electrodes of 0.8 eV. The insert of Fig. 1 shows the EA amplitude at the peak wavelength of 540 nm versus the square of electric field at the steady-state condition. The linear dependence demonstrates that the amplitude of the EA scales as the square of the field strength, indicating that observed spectral features arise due to the quadratic Stark effect [25–28].

After excitation of PC$_{61}$BM the EDA amplitude in the observed spectral range starts to decrease without a change in the spectrum. This is evidence of the electric field decay. In general, EDA data may also include a contribution from field-induced changes of the population of