

The photocurrent quantum efficiency dependence on the applied voltage in organic solar cells

Jędrzej Szmytkowski¹

Institut für Angewandte Physik, Universität Karlsruhe (TH), Wolfgang-Gaede-Str. 1,
76131 Karlsruhe, Germany

E-mail: jedrek@mif.pg.gda.pl

Received 29 May 2007

Published 15 November 2007

Online at stacks.iop.org/SST/22/1329

Abstract

We demonstrate that our recently reported model (Szmytkowski 2007 *J. Phys. D: Appl. Phys.* **40** 3352) of the photocurrent quantum efficiency in organic semiconductors explains the external quantum efficiency dependence on the electric field in organic solar cells. This effect can be explained by taking into account that the photogeneration of charge carriers occurs via the electron–hole pair dissociation and the space charge effects and recombination of charge influence the loss of photocurrent.

Organic solar cells are alternative to inorganic semiconductors due to their attractive features, such as low cost production and flexibility. Interest in such photovoltaic devices has greatly increased since the reports by Tang [1] and O'Regan and Grätzel [2]. The main efforts in these studies are concentrated on the increase of efficiency. One of the most important parameters, which is used for the characterization of solar cells, is the external quantum efficiency (EQE), also known as the incident photon-to-current conversion efficiency (IPCE). Its value describes the ratio of collected charge carriers in the external circuit per incident photons.

Recently, the influence of applied voltage on the EQE has been reported in the organic solar cells based on polymeric materials. Huynh *et al* [3] have demonstrated that the EQE depends on the reverse bias voltage in the hybrid photovoltaic cell, consisting of CdSe nanorods and organic polymer (P3HT). The EQE increases with the reverse bias, when the electric field is in the direction of the built-in field, and the tendency of saturation is observed at higher reverse voltages. The influence of the reverse bias on the EQE has also been reported for a fully polymeric solar cell based on the P3HT:PCBM layer [4] and for multilayer photodetectors based on CuPc/PTCBI [5]. The case, when the EQE increases not only for reverse but also for forward bias voltage, has been observed recently by Watt *et al* [6], both for hybrid

(nanocrystals PbS:MEH-PPV) and fully polymeric (MEH-PPV) devices.

In general, the understanding of the EQE dependence on the electric field is not clear. This effect is not observed in the conventional inorganic solar cells and Huynh *et al* [3] have shown that the standard Shockley equation [10], which is used for the inorganic devices, is not valid for a hybrid inorganic–organic system. They have explained their results qualitatively due to the assumption that photocurrent is limited by the carrier with lower mobility and is dominated by the space charge limited currents. Peumans *et al* [5] have demonstrated that the electric field dependence of the EQE can be explained by the efficient separation and transport of the free electron and hole, resulting from the dissociation of the photogenerated exciton. Riedel and Dyakonov [4], who have observed this effect only in the high energy part of the spectrum, have suggested that additional mechanisms of photogeneration occur, for example, via the photoexcitation of electrodes. Watt *et al* [6] have interpreted that under forward bias, when the electric field is in the opposite direction of the built-in field, the voltage dependence of the EQE can be explained by the influence of photoenhanced injection currents or, in the case of hybrid solar cells, by the increase of the probability of high energy photons absorbed in the nanocrystal relaxing to the band edge.

It should be noted that, in the case of dye-sensitized solar cells, the applied voltage also causes the increase of the EQE with the visible tendency of saturation [7–9]. This effect has been explained by stating that the applied potential

¹ On leave from Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, Narutowicza 11/12, 80-952 Gdańsk, Poland.

influences the charge injection efficiency [7] or accelerates the electron transfer reaction from the nanocrystalline material to the electrolyte [8].

Recently, Rappaport *et al* [11] have reported that the normalized experimental value of the EQE is comparable to the photocurrent quantum efficiency (QE), which can be defined as

$$QE = \frac{J}{J_G}, \quad (1)$$

where J is the collected photocurrent and J_G is the generation photocurrent.

In our previous paper [12], we have proposed an analytical model to describe the loss of photocurrent in organic semiconductors. Our theoretical description of QE is the enhancement of the model reported by Rappaport *et al* [11] and explains the decrease of the EQE with the intensity of light, observed experimentally for both types of organic solar cells: hybrid [3] and dye-sensitized [13]. The aim of this paper is to demonstrate that our model also explains the EQE dependence on the applied voltage. To our knowledge, only Peumans *et al* [5] have presented the theoretical calculations of this effect.

The model takes into account that the photogeneration of charge occurs in the bulk of sample via dissociation of photogenerated excitons and the space charge effects; monomolecular and bimolecular recombinations play an important role on the loss of photocurrent. The photocurrent quantum efficiency is represented by the expression [12]

$$QE = \frac{-1 + \sqrt{1 + \frac{9}{2}AP\left(\frac{1}{J_{SCL}^{(n)}} + \frac{1}{J_{SCL}^{(p)}}\right)\frac{L_n}{d}\frac{L_p}{d}}}{\frac{9}{4}AP\left(\frac{1}{J_{SCL}^{(n)}} + \frac{1}{J_{SCL}^{(p)}}\right)\left(\frac{d}{L_n} + \frac{d}{L_p}\right)^{-1}}, \quad (2)$$

where A is an electric-field-dependent parameter [11], P is the light intensity, d is the thickness of sample, $J_{SCL}^{(n)}$ and $J_{SCL}^{(p)}$ are the space charge limited (SCL) currents for electrons and holes, respectively, and L_n and L_p are the mean distances of electron and hole drifts before monomolecular recombination [14]. The parameters L_n/d and L_p/d are independent of the changing of voltage or thickness of sample (see the detailed explanation in [12]).

From the expression for the generation photocurrent $J_G = Gqd = AP$ [11, 14], we obtain the useful relationship between the parameters G and A . The field-dependent parameter G describes the photogeneration of charge carriers and q is the elementary charge. We can write that $G = \eta G_{\max}$ [15], where η is the field-dependent probability for electron-hole pair dissociation into separated charge carriers and G_{\max} is the maximum value of the photogeneration rate. The typical order of magnitude of G_{\max} is $10^{27} \text{ m}^{-3} \text{ s}^{-1}$ for polymeric materials [15].

In order to compare our theoretical calculations with the experimental results, we have manually extracted the experimental data of the EQE from figure 6 in [3]. The maximum saturation value $EQE_{\text{sat}} = 0.63$, used for the normalization, has been obtained from the fitting procedure to the experimental points.

In their experiment, Huynh *et al* [3] have used CdSe and P3HT as the electron and hole transport layers, respectively. The mobility of holes μ_p for P3HT is in the range between

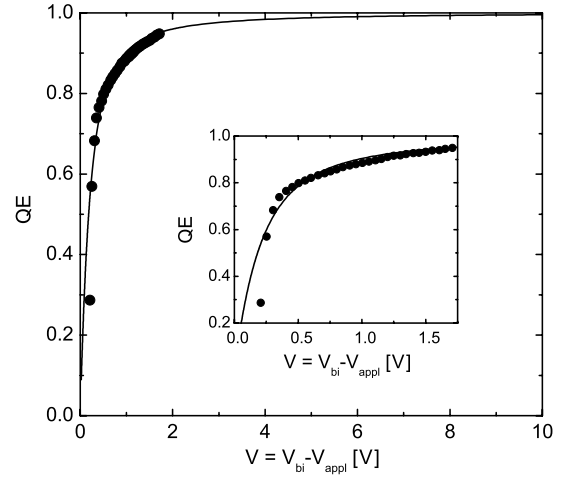


Figure 1. The photocurrent quantum efficiency as a function of the voltage. The line was calculated from equation (3) and the full circles represent the normalized experimental results of the EQE, taken from figure 6 in [3]. The inset shows the QE dependence at lower voltages. The parameters used for calculations: $G_{\max} = 9 \times 10^{27} \text{ m}^{-3} \text{ s}^{-1}$, $\eta_0 = 0.9$, $b = 25 \text{ \AA}$, $\epsilon_r = 4$, $\mu_{0p} = 1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $\beta_p = 4 \times 10^{-5} \text{ cm}^{1/2} \text{ V}^{-1/2}$, $L_n/d = 0.5$, $L_p/d = 0.5$.

10^{-4} and $10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and the exact value depends on the degree of order within the film and the regioregularity of the polymer [3]. The mobility of electrons in CdSe is several orders of magnitude greater, for example, $\mu_n = 660 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for crystalline CdSe in room temperature [19]. In the case that $\mu_n \gg \mu_p$, we can write equation (2) in the form [12]

$$QE \cong \frac{-1 + \sqrt{1 + \frac{9}{2} \frac{AP}{J_{SCL}^{(p)}} \frac{L_n}{d} \frac{L_p}{d}}}{\frac{9}{4} \frac{AP}{J_{SCL}^{(p)}} \left(\frac{d}{L_n} + \frac{d}{L_p}\right)^{-1}}. \quad (3)$$

The SCL current for holes is done by the expression $J_{SCL}^{(p)} = (9/8)\epsilon_0\epsilon_r\mu_p V^2 d^{-3}$, where $\epsilon_0\epsilon_r$ is the permittivity of material and V is the voltage. We can see that the QE given by equation (3) depends only on the SCL current of the slower carrier. It agrees well with the consideration of Huynh *et al* [3] that, in the case of the reverse bias, the photocurrent is limited by the carrier with lower mobility and is dominated by the SCL current.

The mobilities of charge carriers in organic materials are electric field dependent. We assume that the hole mobility is done by the so-called Poole-Frenkel equation $\mu_p = \mu_{0p} \exp(\beta_p F^{1/2})$, where μ_{0p} is the zero-field mobility, β_p is the parameter describing the field dependence and F is the electric field.

The probability η can be described by one of the geminate recombination theories [16]. In our calculations, we have chosen the Onsager theory [17] with the probability η written as

$$\eta = \eta_0 \int f(r, \theta) g(r) dV, \quad (4)$$

where η_0 is the electric-field-independent yield of thermalized electron-hole pairs per absorbed photons, $f(r, \theta)$ is the electric-field-dependent probability of dissociation of electron-hole pairs, $g(r)$ is the spatial distribution function, r is the electron-hole separation distance and θ is the polar angle. The function $g(r)$ can be done by the δ -Dirac, Gaussian

or exponential function [16]. In our calculations, we have implemented the analytical formula for probability η , derived by Borsenberger and Ateya [18] with the exponential function $g(r) = (1/4\pi r^2 b) \exp(-r/b)$, where b , called the dispersion parameter, describes the thermalization distance of electron–hole pairs.

The dielectric constant is equal to 3 for P3HT [20] and 9–10 for CdSe [19]. The value of ϵ_r for CdSe nanorods–P3HT device should be treated as the spatially averaged dielectric constant. Thus, we treat ϵ_r like a parameter, with the value in the range between 3 and 10.

Figure 1 presents the comparison between our calculated results obtained from equation (3) and the normalized experimental EQE results extracted from [3]. The voltage is represented by the expression $V = V_{bi} - V_{appl}$, where V_{bi} and V_{appl} are the built-in voltage and the applied voltage, respectively. For CdSe nanorods–P3HT blend solar cell with PEDOT and aluminum electrodes, $V_{bi} \cong 0.7$ V. We can see that QE increases with the voltage and saturates at higher electric fields. The agreement between the calculated and experimental data is satisfactory. The weak discrepancy at lower electric fields suggests that we cannot exclude the existence of other processes, for example the influence of bimolecular recombination on the decrease of probability η , which has been observed for Alq₃ at low voltages [21].

In conclusions, we have presented that our theoretical model of the photocurrent quantum efficiency [12] is a good method for modeling the external quantum efficiency dependence on the applied voltage in organic solar cells. This effect can be explained taking into account that the photogeneration of charge occurs in the bulk of sample and the space charge effects and recombination of charge cause the loss of photocurrent.

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