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LETTER

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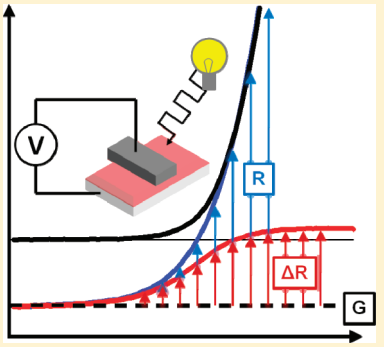
Analysis of the Relationship between Linearity of Corrected Photocurrent and the Order of Recombination in Organic Solar Cells

George F. A. Dibb,[†,‡,§] Thomas Kirchartz,[†,§] Dan Credgington,[†,‡] James R. Durrant,[†,‡] and Jenny Nelson[†,*,§]

[†]Centre for Plastic Electronics, [‡]Department of Chemistry, and [§]Department of Physics, Imperial College London, Exhibition Road, London, SW7 2AZ, United Kingdom

Supporting Information

ABSTRACT: We address the claim that the dependence of the "corrected photocurrent" (defined as the difference between the light and dark currents) upon light intensity can be used to determine the charge recombination mechanism in an organic solar cell. We analyze a poly(3-hexylthiophene):[6,6]-phenyl C61-butyric acid methyl ester (P3HT:PCBM) device using corrected photocurrent and transient photovoltage experiments and show that whereas the corrected photocurrent is linear in light intensity the charge recombination rate scales superlinearly with charge carrier density. We explain this apparent discrepancy by measuring the charge carrier densities at different applied voltages and light intensities. We show that it is only safe to infer a linear recombination mechanism from a linear dependence of corrected photocurrent on light intensity under the following special conditions: (i) the photogenerated charge carrier density is much larger than the dark carrier density and (ii) the photogenerated carrier density is proportional to the photogeneration rate.



SECTION: Electron Transport, Optical and Electronic Devices, Hard Matter

Organic photovoltaics (OPVs) present an opportunity for the low-cost manufacture of solar cells, with devices made from a polymer blended with a functionalized fullerene in a bulk heterojunction (BHJ) structure achieving power conversion efficiencies (PCEs) exceeding 7% in the literature.[1] There is therefore considerable focus on developing methods by which the loss processes limiting the efficient generation and collection of charge carriers in this class of cells may be understood and minimized. In particular, "corrected photocurrent" analyses, based on consideration of the device photocurrent as a function of voltage after subtraction of the corresponding dark current, are widely used tools to analyze the function of such devices.[2−6] Such corrected photocurrents are typically observed to scale linearly with light intensity; this observation has been widely interpreted as indicating that the dominant loss processes limiting device performance scale linearly with charge carrier density in the device. In this Letter, we address the corrected photocurrent analysis and the validity of its underlying assumptions. Additionally, we present a comparison of corrected photocurrent and transient optoelectronic analyses of the same device to demonstrate that the observation of such linear corrected photocurrents cannot be unambiguously employed to determine the order of the underlying loss pathways.

Analyses of the efficiency of organic solar cells typically consider two main classes of loss process that reduce charge collection: recombination of photogenerated excitons or charge transfer states prior to separation (geminate recombination) and recombination between pairs of dissociated electron and hole polarons, where each is generated by a different absorption event (nongeminate recombination). This latter category encompasses so-called surface recombination at the electrode interface and recombination of separated charges in the active layer. In general, the current density J at any light intensity is determined by the balance of generation and recombination according to the continuity equation

$$-\frac{1}{e}\nabla \cdot J = G - R \tag{1}$$

where G is the generation rate of dissociated charges (and therefore may be reduced by geminate recombination), R is the nongeminate recombination rate, and e is the elementary charge. The corrected photocurrent analysis used to analyze these recombination processes[2,4−6] involves calculation of the corrected photocurrent

$$J_{\mathrm{corr}}(V) = J_{\mathrm{light}}(V) - J_{\mathrm{dark}}(V) \tag{2}$$

corresponding to the difference between the current density J_{light} generated by a solar cell under illumination and the current density J_{dark} that flows in the dark at the same applied voltage, V. Several authors have found that J_{corr} scales linearly with light intensity across a range of operating voltages in various polymer:fullerene systems.[4−6] It has been suggested that this observation implies that J_{corr} is primarily determined either by a voltage-dependent geminate recombination pathway limiting G or by a

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nongeminate recombination process that scales linearly with light intensity. Whereas many authors have used the Onsager-Braun theory of field-dependent charge generation[7] to model $J(V)$ curves,[8,9] we note that in efficient polymer solar cells free charge generation has been observed to have no dependence upon voltage.[10−13] Therefore, we assume that the generation of dissociated charge carriers is voltage-independent. On the basis of these assumptions, many authors have concluded that the primary recombination pathway that determines J_{corr} is linear with charge carrier density and therefore arises from a first-order process.[4,6]

Neglecting any spatial variations of generation and recombination rates, the corrected photocurrent can be redefined using eqs 1 and 2 such that

$$J_{corr} = ed((-G + R_{light}) - R_{dark}) = -ed(G - \Delta R) \quad (3)$$

where d is the device thickness, rates are defined per unit volume, and $\Delta R = R_{light} - R_{dark}$ representing the change in nongeminate recombination rate with light intensity at a given voltage. As such, it is apparent that the corrected photocurrent analysis addresses not the overall recombination losses in the device at a given voltage and light intensity (i.e., R_{light}) but rather the difference between these loss processes present in the dark and light (ΔR). Two key assumptions underlie corrected photocurrent analyses mentioned above: (i) To draw conclusions regarding the nature of the overall recombination process from observation of J_{corr}, it is necessary to assume that ΔR scales with light intensity in the same way as R_{light}, that is, $\Delta R \propto R_{light}$. (ii) To relate studies of J_{corr} as a function of light intensity to a reaction order of a recombination process requires that the charge carrier density n within the cell is proportional to generation rate and therefore light intensity, that is, $n \propto$ light intensity. On the basis of these assumptions, one may conclude that if $J_{corr} \propto$ light intensity, then $R \propto n$. The observation that corrected photocurrent scales linearly with light intensity across the whole voltage range therefore leads to the conclusion that the dominant recombination process must be first-order with carrier density.[4,6] Below we discuss limitations to the validity of both of these assumptions.

In contrast with the conclusions of such corrected photocurrent analyses, various investigations using both electrical and optical transient techniques have provided evidence that higher order (i.e.: nonlinear) recombination processes are significant within OPV devices.[14−19] Such nonlinear behavior has been assigned to nongeminate recombination losses within the device, with these losses scaling superlinearly with charge carrier density and dominating the open-circuit voltage and the dependence of device photocurrent upon light intensity.[20−23]

In general, a nongeminate recombination process between similar densities of electrons and holes may be expected to be second-order in charge carrier density. In the presence of energetic tails of states within the active materials,[24−26] only the most mobile charges are available to recombine, resulting in the recombination rate constant being charge carrier density-dependent and in a supersecond-order dependence of recombination rate upon carrier density.[27] In simple analyses of device $J(V)$ response[21,22,28] and in detailed numerical simulations,[25,26] it has been shown that the recombination flux associated with this nonlinear recombination pathway is sufficient to explain the open-circuit voltage (V_{OC}) and fill-factor (FF) of a variety of polymer:fullerene devices.

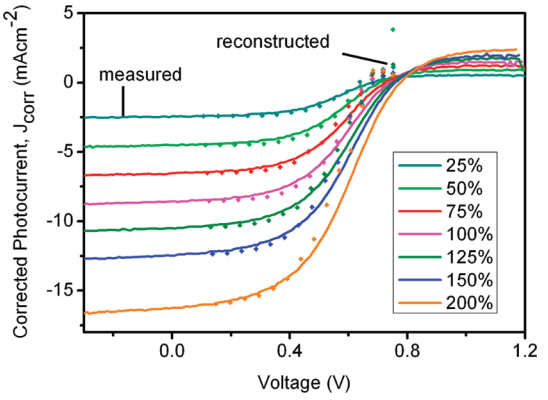

Figure 1. Comparison of the measured corrected photocurrent, J_{corr}, (solid lines) and the corrected photocurrent calculated from reconstructed dark and light curves using nongeminate recombination analysis (points) for various light intensities.

In this Letter, we reconcile observations of linear corrected photocurrents with observations of nonlinear recombination processes by comparing the measured corrected photocurrent for a poly(3-hexylthiophene):[6,6]-phenyl C61-butyric acid methyl ester (P3HT:PCBM) device with the corrected photocurrent reconstructed from the nonlinear recombination dynamics measured by transient techniques.

Because the electrical characteristics of organic cells are known to be temperature-dependent,[29,30] it is important that when performing corrected photocurrent analyses the light and dark $J(V)$ curves are measured at the same temperature. Therefore, pulsed light $J(V)$ measurements were used to ensure minimal temperature change.[5] The corrected photocurrent curves of a P3HT:PCBM solar cell measured using pulsed $J(V)$ measurements at various light intensities are shown in Figure 1 (solid lines). These can be seen to bear the characteristic S-shape and common point of convergence observed by Ooi et al.,[5] which arises from the nonzero series resistance of the device.[31,32] Figure 2a shows plots of $J_{corr}(V)$ versus light intensity for each applied voltage. Linear fits to these data show that the photocurrent scales linearly with incident light intensities across the whole operating voltage range and up to illuminations equal to twice the standard solar intensity. This shows that the P3HT:PCBM cell measured herein exhibits the same linear corrected photocurrent behavior seen by other authors, described above.

Charge extraction measurements were used to measure the total number of carriers present within the same device relative to the number of carriers present at short circuit in the dark; it is assumed that this figure is equal to the total active layer charge. Data were collected both under open-circuit conditions at a range of light intensities from dark to greater than 6 suns and at applied biases between short circuit and open circuit at fixed light intensities. Similar carrier densities to those we have reported previously for P3HT:PCBM devices were observed ,[33] with the carrier density within the active layer of the cell under open-circuit conditions varying exponentially with voltage such that $n = n_0 \exp(\gamma V_{OC})$, where in this case $\gamma = 6.9\ V^{-1}$. Transient photovoltage (TPV) measurements were performed under the same open-circuit conditions to measure the carrier lifetime. As previously, we observed an exponential dependence upon V_{OC} such that $\tau = \tau_0 \exp(-\beta V_{OC})$. We therefore conclude that the carrier lifetime within this device exhibits a power-law dependence

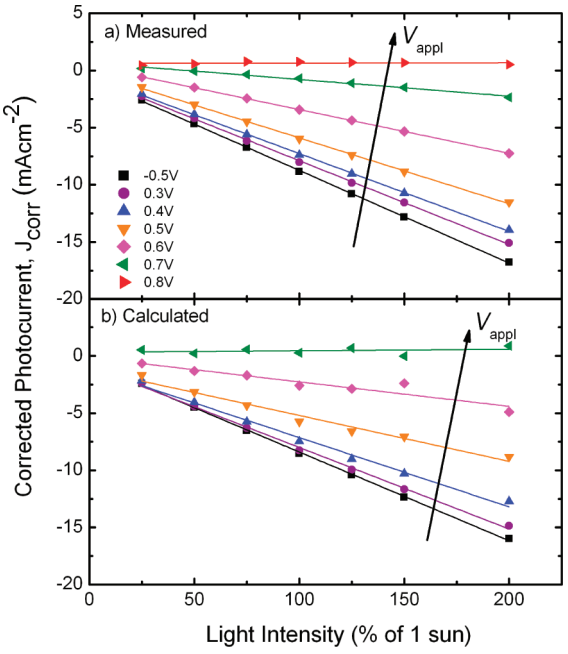

Figure 2. Plots showing the measured J_{corr} (a) and J_{corr} reconstructed from measurements of nonlinear recombination (b) as a function of light intensity (points) at various voltages, with linear fits (lines) of the data showing the linearity of corrected photocurrent with illumination intensity.

on extractable total carrier density, where $\tau \propto n^{-1.9}$, which leads to a power-law dependence of recombination rate on carrier density of order 2.9. Assuming cell neutrality, this lies within the range of values reported for P3HT:PCBM cells that have been previously reported; typically the order lies in the range of 2.5 to 3 and depends on both device architecture and microstructure.[22,28] We thus conclude that whereas our corrected photocurrents scale linearly with light intensity (Figure 2a), our transient analyses of the same device indicate a nonlinear (almost third-order) dependence of the recombination rate upon carrier density. We now go on to consider how to reconcile these two apparently conflicting observations.

We have previously proposed that the device photocurrent can be recreated from transient measurements of nongeminate recombination by subtracting a recombination current from a voltage-independent generation profile

$$J_{light} = -J_{gen} + J_{loss} \approx -J_{SC} + \frac{n}{\tau} ed \tag{4}$$

where n is the average extracted carrier density at a given applied voltage and light intensity and τ is the carrier lifetime, as determined by TPV measurements. If generation is assumed to be bias-independent, then the bias-dependent total current density $J(V)$ is calculated by subtracting J_{rec} from the short circuit current density J_{SC}.[21] By following this approach, and without the use of any fitting parameters, we find that the $J(V)$ curves of the cell studied herein are accurately reproduced, with an excellent prediction of the device V_{OC} and only a small overestimate of the device fill factor (by ~5%). (See the Supporting Information.) We note that this analysis uses only a nonlinear recombination process, with no additional loss pathways being considered.

Using light and dark $J(V)$ curves reconstructed using eq 4, we now calculate reconstructed corrected photocurrent curves, as defined by eq 2, calculated entirely from measurements of nonlinear recombination. These calculated $J_{corr}(V)$ curves are overlaid upon the experimentally measured $J_{corr}(V)$ curves in Figure 1 (points), and the plots of reconstructed J_{corr} against light intensity for various voltages are shown in Figure 2b. Figure 1 shows that these recreated corrected photocurrents are in good agreement with the directly measured ones. More importantly, Figure 2b shows that the reconstructed corrected photocurrent scales linearly with light intensity over the whole range of voltages measured, despite these reconstructions being based on a nonlinear loss pathway. It should be emphasized that the dark and light curves from which J_{corr} is calculated arise purely from an empirically measured super-second-order recombination process. We now consider how this observation may be understood by reconsidering the validity of the assumptions underlying corrected photocurrent analyses, specifically that $R \propto \Delta R$ and $n \propto G$, described above.

First of all, we examine the validity of the assumption that $n \propto G$. Consider the general case where the recombination rate has some dependence upon charge carrier density such that $R = kn^{\alpha}$ where k is the recombination rate constant and α is the order of the recombination process. Under open circuit conditions, by definition, all generated charge must recombine such that $G = R$; therefore, $n = (G/k)^{1/\alpha}$, which is only linear if $\alpha = 1$. It follows that when $\alpha > 1$, in general, the assumption that $n \propto G$ for all voltages is not valid.

Second, we examine the assumption that $R \propto \Delta R$ and therefore that the corrected photocurrent is representative of the general recombination process. To do this we consider the charge carrier densities in the device present in the light and in the dark. In the dark in forward bias, charges are injected into the cell (creating a positive current). We have previously shown that this dark current exhibits, at least for P3HT:PCBM cells, an almost identical dependence upon charge carrier density as the nongeminate recombination loss processes observed under illumination.[34] As such, we can define ΔR in eq 3 as

$$\begin{aligned} \Delta R &= R_{light} - R_{dark} \propto n_{light}^{\alpha} - n_{dark}^{\alpha} \\ &= (n_{dark} + \Delta n)^{\alpha} - n_{dark}^{\alpha} \end{aligned} \tag{5}$$

where $\Delta n = n_{light} - n_{dark}$, the difference in carrier density between light and dark at a given applied bias. The TPV results described above show that for the cell studied herein $\alpha = 2.9$. We employ a binomial expansion to re-express ΔR as

$$\begin{aligned} \Delta R &= n_{dark}^{\alpha}\left[\left(1 + \frac{\Delta n}{n_{dark}}\right)^{\alpha} - 1\right] \\ &= n_{dark}^{\alpha}\left[\frac{\alpha \Delta n}{n_{dark}} + O\left(\frac{\Delta n}{n_{dark}}\right)^{2}\right] \end{aligned} \tag{6}$$

when $\Delta n / n_{dark} \rightarrow 0$. From eqs 5 and 6, we can now straightforwardly conclude that ΔR will scale linearly with Δn regardless of the order of the recombination process if $\Delta n \ll n_{dark}$. Figure 3 compares values for Δn and n_{dark} as a function of applied voltage and light intensity determined from our charge extraction data. It can be seen that for voltages where nongeminate recombination dominates the $J(V)$ curve (i.e., close to V_{OC}) Δn is smaller than n_{dark} by up to one order of magnitude. In this limit, the additional

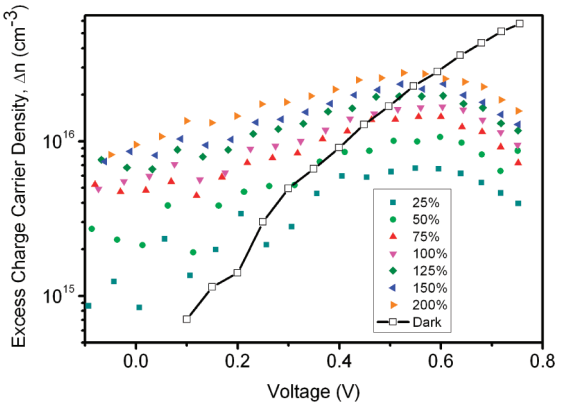

Figure 3. Excess photogenerated charge carrier density Δn measured at voltages across the operating region of the solar cell for various light intensities (points) compared with the dark carrier density n_{dark} over the same region. The comparison of these values shows the transition from a nonlinear regime where $\Delta n > n_{dark}$ to the linear regime; this transition point moves to increasing voltages for increasing light intensity.

charge carrier density generated in the light is only a small perturbation to the charge already present within the device at that applied voltage. As a consequence, the resulting change in recombination (ΔR) measured by the corrected photocurrent scales linearly with generation even when the underlying recombination pathway depends nonlinearly upon carrier density. ΔR scaling linearly with light intensity does not therefore imply that R is a first-order process.

For lower voltages, where $\Delta n > n_{dark}$ and therefore ΔR would be expected to scale nonlinearly, the recombination rate is low as the majority of charges are rapidly extracted from the cell, leaving a comparatively low average carrier density.[21] The recombination of carriers is therefore significantly smaller than their generation and $\Delta R \ll G$. Because G is linear with light intensity and the corrected photocurrent is dominated by this term, any nonlinearities in recombination are undetectable.

We can examine the breakdown of the assumptions discussed above in more detail using the experimentally determined carrier densities. Figure 3 shows that Δn does not scale linearly with light intensity over the entire voltage range and in fact becomes sublinear as the applied voltage increases past 0.3 V. (See the Supporting Information.) This is due to the nonlinear dependences of recombination and extraction upon carrier density opposing the linear generation rate. This observation clearly illustrates the limitation of the validity of the implicit assumption employed in some corrected photocurrent analyses, namely, that $n \propto G$, and in particular suggests that such analyses cannot be readily used to determine the order of loss pathways as a function of carrier density. Figure 3 also shows that as the light intensity increases, the voltage range over which $\Delta n > n_{dark}$ increases. Under sufficiently high illumination, we would therefore predict that this range will extend into the regime where recombination dominates the $J(V)$ behavior. Where this occurs, ΔR will no longer scale linearly with light intensity and the corrected photocurrent will likewise cease to scale linearly at all voltages. This corresponds with modeling of organic solar cells in the literature, which indicates that corrected photocurrent remains linear with light intensity in cells with nonlinear recombination kinetics only for light intensities less than 3 suns.[35]

In conclusion, we have demonstrated that it is possible for a cell to exhibit a corrected photocurrent that is linear with illumination intensity even if the underlying recombination process that shapes the $J(V)$ curve is nonlinear. This is true for several reasons: (i) for voltages close to V_{OC}, the additional charge carrier density generated under illumination is smaller than the carrier density present in the dark, and (ii) for a large range of voltages, $\Delta R \ll G$ meaning that the linear generation dominates the corrected photocurrent. Additionally even though ΔR may be superlinear with Δn, Δn is in turn sublinear with light intensity. Importantly, we have reconciled two methods of analysis that gave apparently contradictory results. We have shown that measurements of corrected photocurrent cannot be readily used as a test of the order of the recombination processes that determine $J(V)$ behavior. We have also shown that observation of a linear corrected photocurrent is fully consistent with a nonlinear recombination mechanism. As such, we have demonstrated some of the limitations of using steady-state measurements to determine the nature of the dominant loss mechanism within a given organic solar cell. Steady-state measurements therefore cannot unambiguously determine the order of dominant loss mechanism, and transient electrical and optical techniques combined with measurements of charge carrier density are essential for studies of recombination processes.

EXPERIMENTAL METHODS

P3HT:PCBM solar cells were made using similar procedures to those studied in previous publications,[33] with the structure ITO/PEDOT:PSS/P3HT:PCBM/Al. Under a calibrated solar simulator, the characteristics of the cell were measured to be η = 3.15%, V_{OC} = 612 mV, J_{SC} = −9.51 mA cm^{-2}, and FF = 54%.

Pulsed $J(V)$ measurements were made to minimize the influence of temperature changes between the light and dark measurements. Illumination was provided by 12 white LEDs which could be pulsed by interrupting their power supply using a fast MOSFET switch; in these measurements, the light remained on for ∼2 ms and off for ∼420 ms. The cell was held at applied bias using a Keithley 2400 source-measure unit, and the current was measured across a 50Ω resistor using a Tektronix TDS3032B oscilloscope. By measuring the current flowing during the light and dark periods it was possible to alternately measure the light and dark $J(V)$ response.

Charge extraction involves holding the solar cell at applied bias under illumination and simultaneously turning off the light source and switching the cell to short circuit. By integrating the current transient observed during this process, it is possible to infer the charge within the bulk of the cell in excess of the charge that is present at 0 V in the dark.

TPV is a small perturbation technique by which the cell is held at open-circuit under illumination. A small quantity of additional charge carriers is generated using a diffuse laser pulse, and the recombination of these charges is observed through the decaying voltage of the cell. This gives a measure of the charge recombination rate and lifetimes for the small excess carrier population, which in turn allows calculation of the bulk carrier lifetime.

ASSOCIATED CONTENT

Supporting Information. Power law behavior of recombination lifetime and charge carrier density, the strong correlation between experimental and reconstructed $J(V)$ curves. and the nonlinearity of n and Δn with light intensity. This material is available free of charge via the Internet at http://pubs.acs.org.

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