Supporting Information

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SI Text

Analytical Model to Describe the Charge Density and Its Dependence on Cell Voltage and Light Intensity for Various Conditions. ***Approach.*** The photovoltaic device is modeled as a p-type region with boundary conditions

$$n(0) = n_0\left[\exp\left(\frac{\alpha eV}{k_B T}\right) - 1\right], \qquad J_n(d) = 0,$$

where $n(0)$ is the electron charge density in the semiconductor at the cathode interface, n_0 and α are constants, e is the electronic charge, V is the applied voltage, k_B is Boltzmann's constant, T is temperature, $J_n(d)$ is the electron current at the anode, and d is the device thickness.

Disorder is included by introducing a tail in the density of states through the value of α, ($\alpha < 1$), as we have proposed previously (1).

The continuity equation for electrons is solved analytically for the case $J = e(\mu Fn + Ddn/dx)$, a uniform generation profile G (proportional to light intensity I), recombination $R = n/\tau$, where τ is the carrier lifetime, and the electric field $F = (V_{BI} - V)/d$, where V_{BI} is the built-in potential due to the difference between the work functions of the electrodes. The spatially averaged electron density $\bar{n}$ and total current density J are determined as a function of light intensity and applied voltage for the following regimes:

1. Diffusion only ($F = 0$) with no disorder
2. Drift and diffusion using a built-in potential $V_{BI} = 0.7$ V and no disorder
3. Diffusion only ($F = 0$) with disorder
4. Drift and diffusion using a built-in potential $V_{BI} = 0.7$ V with disorder

To obtain analytical solutions nonlinear recombination is neglected, which will affect the curvature of the light intensity dependence of charge density $\bar{n}(I)$, and the mobility is treated as constant rather than as charge density dependent, which will lead to the sublinear dependence of charge density on light intensity observed (see ref. 2).

Below we compare plots of the determined charge density as a function of light intensity $\bar{n}(I)$ and applied voltage $\bar{n}(V)$ for the different conditions 1–4 with and the experimental charge density data provided in the paper in Fig. 2. The key features of the experimental charge density data that we are trying to reproduce are (*i*) the charge density is both voltage and light intensity dependent, (*ii*) at low voltages (near short-circuit) the charge density follows an approximately exponential dependence on voltage, (*iii*) the charge density in the dark follows a relatively weak dependence on voltage, and (*iv*) $\bar{n}(I)$ is strongly dependent on voltage.

Case 1: Diffusion only, no disorder ($\alpha = 1$). Comments: Unlike the experimental data, in the diffusion only regime with no disorder, the charge density remains independent on applied voltage until close to the open-circuit voltage. Also, the charge density in the dark follows a much stronger dependence on voltage than is observed experimentally, which suggests disorder is likely to be present.

Case 2: Drift diffusion, no disorder ($\alpha = 1$, $V_{BI} = 0.7$ V). Comments: In the case of drift, we find that the charge density is strongly dependent on voltage, resulting in an approximately exponential dependence on charge density in good agreement with the experimental data. However, similarly to the diffusion only case, the dependence of charge density in the dark on voltage is too strong.

Case 3: Diffusion only, with disorder ($\alpha = 0.3$). Comments: Introducing disorder for the diffusion only case, we find that under light conditions the charge density becomes voltage dependent. However, this effect arises directly from the dark charge density, and at relatively high light intensities, the charge density becomes much higher than in the light resulting in it to be independent on voltage. Introducing disorder, however, leads to the charge density in the dark to follow a weaker dependence on voltage as observed experimentally, and it also reproduces the behavior of the $n(I)$ at for different applied voltages.

Case 4: Drift diffusion with disorder ($\alpha = 0.3$, $V_{BI} = 0.7$ V). Comments: For the case of both drift and disorder we find that we are able to recreate the same behavior of the experimental charge density data, both in the light and in the dark. It is therefore the conclusion of this work that the charge density data determined are most consistent, for the analytical study presented herein, with a drift-diffusion regime in the presence of disorder. Under these conditions, the plots of $n(I)$ for different voltages are not parallel, thus the charge density is not given by the sum of dark and light components. This implies superposition of dark and photocurrent is not expected to apply.

Conclusions. Conventional semiconductor theory describing the diffusion only case with no disorder is unable to reproduce both the voltage and light intensity dependence of charge density. Inclusion of an electric field is able to explain the voltage dependence of charge density, but not the light intensity dependence. Disorder can explain the light intensity dependence of charge density and to a small extent the voltage dependence of charge density. The best resemblance of the experimental charge density data is found for the case of both an electric field and disorder conditions.

1. Nelson J (2003) Diffusion-limited recombination in polymer-fullerene blends and its influence on photocurrent collection. *Phys Rev B* 67:155209.

2. Shuttle CG, Hamilton R, O'Regan B, Nelson J, Durrant JR (2010) Measurement of charge density dependence of carrier mobility in an organic semiconductor blend. *Adv Funct Mater* 20:698–702.

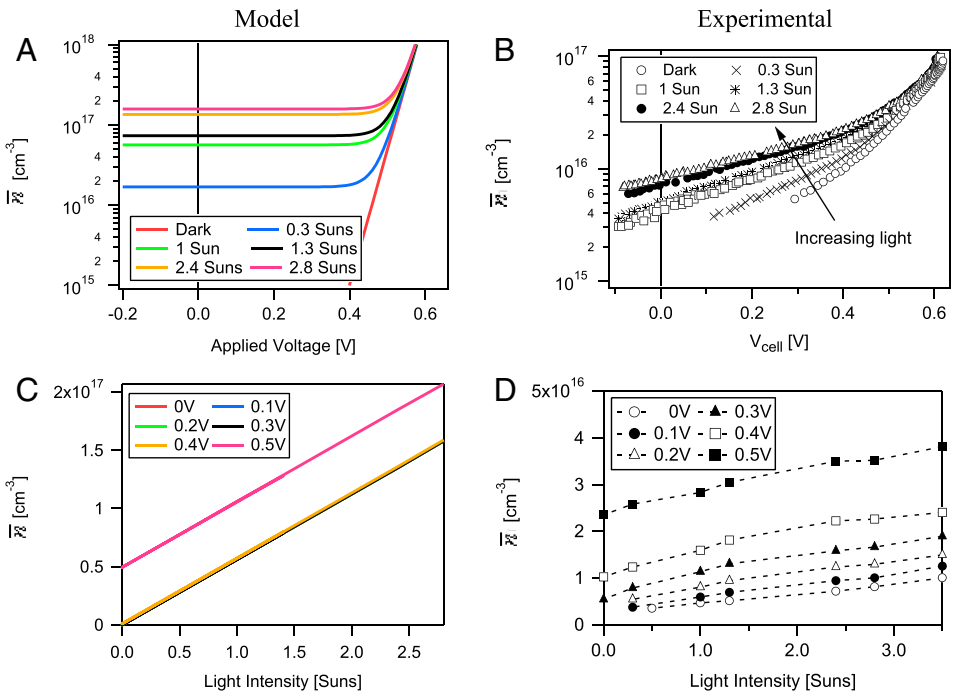

Fig. S1. Model calculations (*a*, *c*) assuming diffusion only with no disorder ($\alpha = 1$) versus experimental data (*b*, *d*). (*a*, *b*) Charge density versus voltage. (*c*, *d*) Charge density versus light intensity.

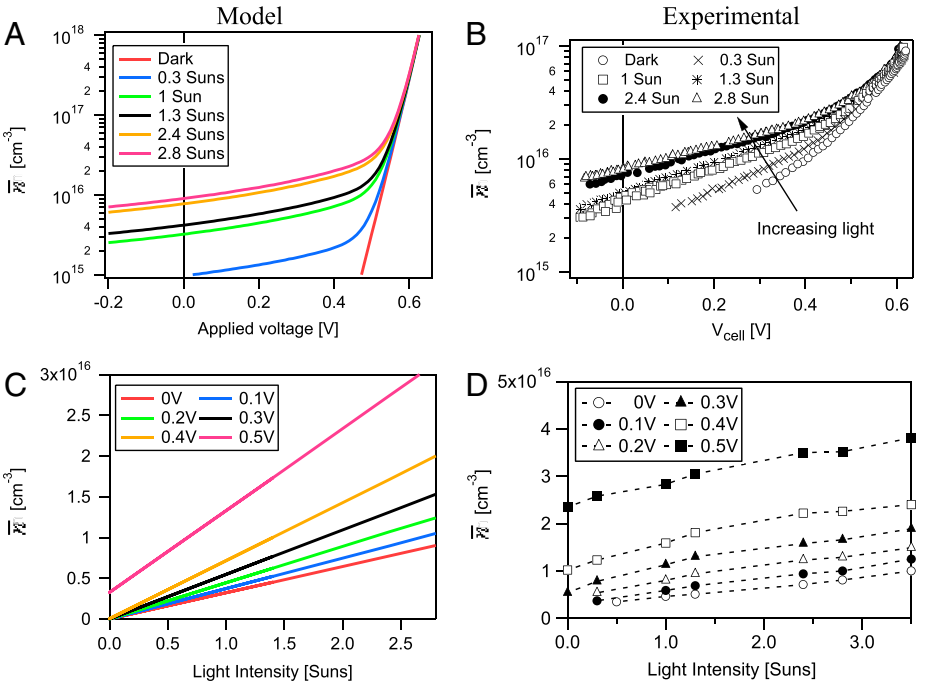

Fig. S2. Model calculations (*a*, *c*) assuming drift diffusion with no disorder ($\alpha = 1$, $V_{BI} = 0.7$ V) versus experimental data (*b*, *d*). (*a*, *b*) Charge density versus voltage. (*c*, *d*) Charge density versus light intensity.

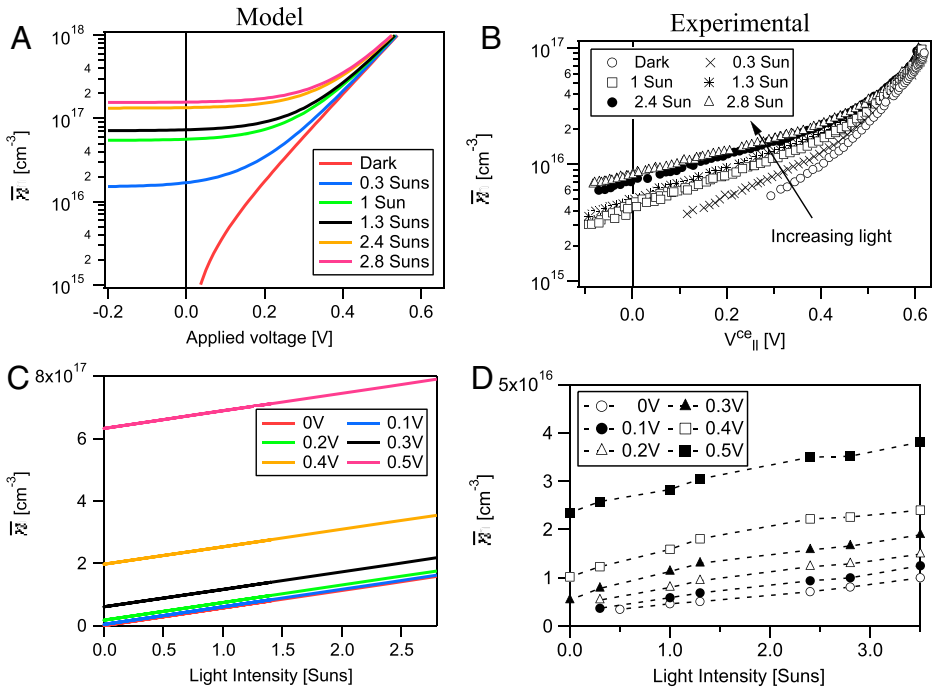

Fig. S3. Model calculations (*a*, *c*) assuming diffusion only with disorder ($\alpha = 0.3$) versus experimental data (*b*, *d*). (*a*, *b*) Charge density versus voltage. (*c*, *d*) Charge density versus light intensity.

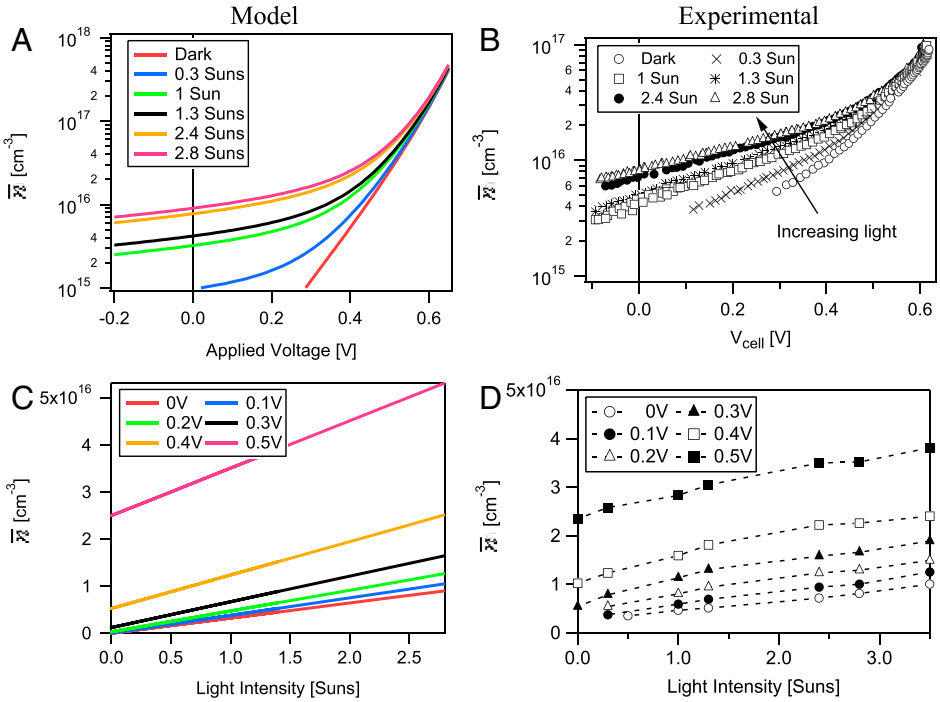

Fig. S4. Model calculations (*a*, *c*) assuming drift diffusion with disorder ($\alpha = 0.3$, $V_{BI} = 0.7$ V) versus experimental data (*b*, *d*). (*a*, *b*) Charge density versus voltage. (*c*, *d*) Charge density versus light intensity.