

Unified Model for Exciton Diffusion and Dissociation in Organic Solar Cells

Chunhua Xiong, Jiuxun Sun,* Yao Fu, and Jingye Zhang

The performance of organic solar cells is limited by the exciton. However, the theoretical model to study the nature of the exciton is separated into exciton diffusion and dissociation. This article proposes a unified model by combining both exciton diffusion and dissociation. This model can be reduced to the classical model of exciton diffusion or dissociation. Moreover, this model quantitatively explains meaningful experimental data of the short-circuit current characteristic at different active layer thicknesses that cannot be fitted by the two classical models. In sum, this model is useful for researching the mechanism of the exciton in thin organic materials, which make some significant contributions to blend, multilayer, and A–D–A small-molecule acceptor solar cells.

Organic solar cells (OSCs) have received much attention in recent years^[1–3] because of the diversity^[4] and potential of practical applications.^[5] However, the performance, especially the power conversion efficiency (PCE), of OSCs is much lower than that of inorganic solar cells.^[6] The fundamental reason for this phenomenon is the limitation of the exciton in OSCs.^[7] Disclosure of the intrinsic state of the physical parameters of the exciton in OSCs can supply a rational mechanism for the design of materials with a promoted PCE.^[8] Therefore, many researchers^[9–11] have tried to improve the performance by studying the nature of the exciton. Classical models calculating exciton diffusion^[9] and the dissociation rate^[10] have been proposed. These two models explain most of the experimental data on the properties of OSCs, such as the current density versus voltage (JV),^[12] open-circuit voltage (V_{oc}),^[13] short-circuit current (J_{sc}),^[14] fill factor (FF),^[15] and PCEs.^[15] However, meaningful data^[12,14] on the J_{sc} at different layer thicknesses ($\approx 10^1$ nm) cannot be quantitatively expounded. Exploring a new model to explain the relationship between J_{sc} and the thickness of the active layer is urgently needed for analyzing the characteristics of blend and multilayer OSCs.

The charge-transfer (CT) state^[16] of materials determines the nature of both the diffusion and dissociation of the exciton, which limits the current density. However, almost all the recent literature separately studies exciton diffusion and the

dissociation rate. On the one hand, most experimental^[17] and theoretical^[18] works study exciton diffusion by adopting the diffusion length (L_D). L_D is a statistical parameter,^[9] corresponding to the statistical mean distance that the exciton can move before annihilation.^[19] Hess et al.^[20–22] proposed a general statistical theory and derived an ambipolar diffusion model for inorganic semiconductor lasers based on the Heisenberg equation of motion. This work is more focused on the exciton diffusion effects in OSCs. Therefore, the simplified version of the diffusion model can be safely used.^[9,23] On the other hand, most works^[24] research the dissociation

rate by introducing the exciton effect (the effect of the field- and temperature-dependent generation of free charge carriers,^[25] as shown in Equation (1)). Some reviews^[9,23] investigate both of these aspects. However, a unified theoretical model cannot be found. Therefore, modifying classical models by combining exciton diffusion and the dissociation rate is a reasonable method to predict the current density in OSCs.

In this contribution, a model combining exciton diffusion and the dissociation rate is proposed. Not only does this model explain the current density versus voltage characteristics under different illuminations but also the J_{sc} results at different active layer thicknesses can quantitatively fit the experimental data^[26] of P3HT: PCBM, which can only be qualitatively fitted^[12,14] before. Therefore, a unified method is built by combining exciton diffusion and the dissociation rate to obtain the electrical properties of OSCs.

In this modified model, the active layer (or blend layer) is divided into three parts (as shown in Figure 1). At least five points should be noted.

(i) It is assumed that all the excitons generated in the border area diffuse to the surface according to the definition of L_D . All of them will split into free electrons and holes for three reasons: 1), the injection barrier^[27] leads to strong electric fields near the electrodes; 2), the electrodes dissociate excitons via energy transfer (especially if they are metallic); and 3), large band bending occurs at the surface,^[28] which provides sufficient energy to overcome the exciton binding energy.

(ii) The free carriers generated from excitons at the surface (discussed in point i) participate in the following two procedures. The electrons (holes) participate in the current conduction at the anode (cathode), leading to an exciton current (J_{exc} , blue solid line in Figure 1; the details are discussed in Equation (3)–(5)). The holes (electrons) at the anode (cathode) return to the active layer to participate in recombination, leading to a modified boundary

Dr. C. Xiong, Prof. J. Sun, Y. Fu, J. Zhang
School of Physics
University of Electronic Science and Technology of China
Chengdu 610054, China
E-mail: sjx@uestc.edu.cn

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/pssr.201900322>.

DOI: 10.1002/pssr.201900322

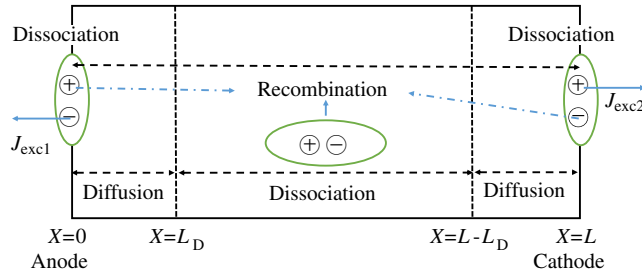


Figure 1. A schematic diagram of the theoretical model. Black dotted lines represent the region under study, and blue lines represent the carrier movement. L_D is the exciton diffusion length.

condition (blue dotted-dashed line in Figure 1; the details are discussed in Equation (6a,b)).

(iii) In the central region, it is assumed that only exciton dissociation occurs and that no exciton diffusion occurs, similar to the classical model of Koster et al.^[10] Therefore, in the region of L_D to $L - L_D$, all excitons have the probability of dissociating into electrons and holes based on the exciton effect shown in Equation (1).

$$U(x) = PG(x) - (1 - P) R(x) \quad (1)$$

where $U(x)$ is the net generation rate at different positions, P is the field-dependent probability of electron-hole pair dissociation,^[10] $R(x)$ is the recombination rate, and $G(x)$ is the generation rate of excitons at different locations.^[29]

$$G(x) = \int_0^\infty [e^{-\eta(\lambda)x} + e^{-\eta(\lambda)(2L-x)}] I_0(\lambda, T_s) \eta(\lambda) d\lambda \quad (2)$$

where $\eta(\lambda)$ is the wavelength-dependent absorption coefficient, L is the length of the active layer, $I_0(\lambda, T_s)$ is the incident photon flux of wavelength λ with light source temperature T_s , and $I_0(\lambda, T_s)$ can be approximated by Planck's black body radiation.

(iv) The recombination for all the carriers in all the regions has the same form: the Shockley-Read-Hall (SRH) recombination rate.^[30] Three parts of the carriers (point ii and point iii) participate in this procedure.

(v) This model ignores exciton-exciton annihilation due to the statistical definition of the exciton diffusion length,^[23] and some experimental data have shown an almost linear correlation between the short-circuit current and the exciton diffusion length.^[31]

This modified model is based on our previous work^[29] (which is based on Koster's dissociation model) with three significant improvements. First, the output current is the sum of the electron (J_n), hole (J_h), and exciton (J_{exc} , discussed in point ii) currents.

$$J = J_n + J_h + J_{exc} \quad (3)$$

Second, according to points (i) and (ii), the exciton current density is introduced according to the definition of the electrical current (Equation (4)). Herein, L_D is the exciton diffusion length, and N_{total0} is the total amount of excitons collected per unit time at the anode, which equals the total number of excitons generated

per unit time within the region of the diffusion length near the anode ($0 \sim L_D$). N_{totalL} has the same definition at the cathode.

$$J_{exc} = q[N_{total0} + N_{totalL}] \quad (4)$$

$$N_{total0} = \int_0^{L_D} G(x) dx, \quad N_{totalL} = \int_{L-L_D}^L G(x) dx \quad (5)$$

Third, the boundary conditions are modified as shown in Equation (6a,b) due to point (ii).

$$p(0) = N_v \exp\left(-\frac{W_{an}}{kT}\right) + N_{total0}/(\mu_p E) \quad (6a)$$

$$n(L) = N_c \exp\left(-\frac{W_{cat}}{kT}\right) + N_{totalL}/(\mu_n E) \quad (6b)$$

where $n(p)$ is the electron (hole) density, $N_{c(v)}$ is the effective density of states, k is the Boltzmann constant, T is temperature (300 K in this article), $W_{an(cat)}$ is the injection barrier at the anode (cathode), $\mu_{n(p)}$ is the electron (hole) mobility, and E is the electric field intensity. Equation (6a,b) ignores the diffusion mechanism of the reflux carrier according to ref. [32]. The remaining two boundary conditions and the recombination, Poisson and drift-diffusion equations are the same as in a previous study by Xiong et al.^[33]

To verify the rationality of this theoretical model, first the calculated J - V results are compared with experimental data at four different P_{in} : 0.5, 0.75, 1.0, and 1.4 sun (1 sun corresponds to the standard solar energy intensity, 100 mW cm^{-2}). The numerical results are calculated from the parameters of "device 1" shown in Table 1 (all the parameters in Table 1 are reasonable^[12,33-35]). The experimental data come from Shuttle et al.^[35] Figure 2 shows that the numerical results are in good agreement with the experimental data, which demonstrate that this model is well applicable to OSCs.

Furthermore, this model can solve the problem that could not be previously settled. In Figure 3, the J_{sc} results at different active layer thicknesses are compared with the other two theoretical models^[12,14] and the original experimental data.^[26] The results of this comparison are obvious, that our model is more accurate than the other two classical models.

Additionally, the border region of this model is a simplified version of the classical diffusion model. Under conditions of continuous and homogeneous generation $G = \text{const}$, it can be set $n_{exc} = Gr$.^[9] Three points need to be considered: i), an exciton can dissociate into an electron and a hole; ii), only the electron (hole) will participate in the current conduction at the anode

Table 1. The parameters of calculation ("device 1" represents the parameters of Figure 2 and "device 2" represents those of Figure 3. $L_D = 20 \text{ nm}$).

Content	T_s [K] ^{a)}	E_g [eV] ^{b)}	V_{bi} [eV] ^{c)}	$\tau_{n(p)}$ [s] ^{d)}	$\mu_{n(p)}$ [$\text{m}^2 \text{Vs}^{-1}$] ^{e)}	L [nm] ^{f)}
Device 1	3700	1.07	0.9	5×10^{-6}	2×10^{-7}	230
Device 2	6000	1.5	1.2	5×10^{-10}	4.5×10^{-8}	/

^{a)}Temperature of light source. ^{b)}Band gap. ^{c)}Built-in voltage. ^{d)}Lifetime of electron (hole). ^{e)}Mobility of electron (hole). ^{f)}Length of the active layer.

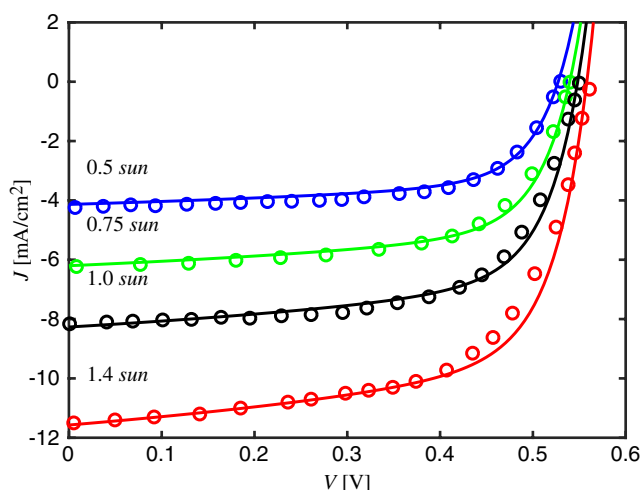


Figure 2. Verification of the model correctness. The numerical results are calculated with the parameters of “device 1” shown in Table 1. 1 sun represents 100 mW cm^{-2} .

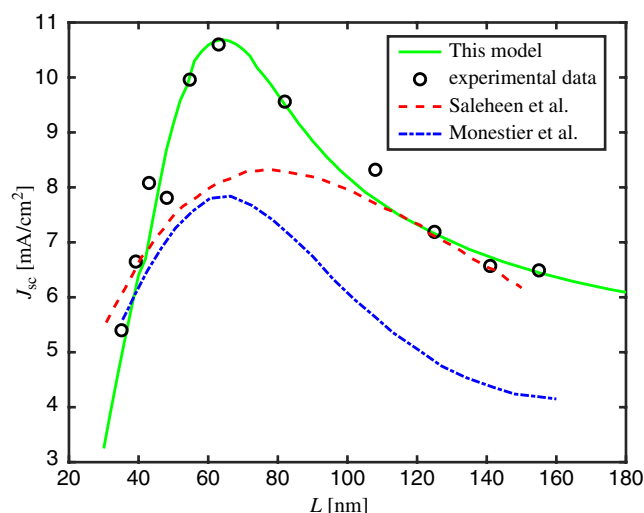


Figure 3. The J_{sc} - L characteristics. The numerical results are based on the parameters of “device 2” in Table 1.

(cathode); and iii), the hole (electron) at the anode (cathode) will return to the active layer to participate in recombination, which is the reason why the boundary conditions are modified. The exciton current can be given as $J_{exc} = qn_{exc}v$, where v is the diffusion velocity of the exciton. Therefore, $J_{exc} = qG\tau v = qGL_D$. Considering that our exciton generation rate is not constant, it is set as the integral form (Equation (4) and (5)). At the same time, $N_{total} = n_{exc}v$ is obtained, which leads to the second term on the right-hand side of Equation (6a,b).

In addition, the central area of this model can be reduced to the classical model proposed by Koster et al.^[10] when L_D is set as an infinitely small value. The classical model can explain most of the experimental data for two reasons.^[36,37] First, the L_D in previous OSCs is much smaller than that of the current

($\approx 10 \text{ nm}^{[23]}$).^[9,38] Second, the active layer of these OSCs is much thicker than L_D (almost $10^2 \text{ nm}^{[39]}$). The contribution of the exciton current density is small, which can be masked by the interfacial effects or the injection barrier. However, the numerical value of L_D is increasing year by year. At the same time, the active layer is becoming increasingly thin^[40] to meet the needs of multilayer OSCs. In this way, the importance of the model proposed in this article will be gradually reflected.

Moreover, this model can be mistaken for the model in which the exciton dissociation of CT states is more efficient near the electrodes due to band bending. However, the L_D in our model is 20 nm (average of 17 nm in previous study^[41]), which is much larger than the surface region ($\approx 1\text{--}5 \text{ nm}$).^[42]

In summary, this article proposes a modified theoretical model to research the current characteristics by combining the exciton diffusion and the dissociation rate. The model can quantitatively explain the current characteristics at different active layer thicknesses, which cannot be fitted by the two classical models. Even the classical model of exciton dissociation proposed by Koster et al. is a special case of this model. At the same time, this model is a simplified version of the classical model of diffusion. In sum, this model discloses the intrinsic state of the physical parameters of the exciton in OSCs, which can supply a rational mechanism for the design of materials with promoted PCEs.

Acknowledgements

This work is supported by the Foundation of Science and Technology on Electronic Information Control Laboratory under Grant No. JS17080706740, and by the National Natural Science Foundation of China under Grant No. 31470822 and 61703292.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

diffusion, dissociation, excitons, organic solar cells, theoretical model

Received: June 4, 2019

Revised: August 14, 2019

Published online:

- [1] J. Chen, Y. Huang, N. Zhang, H. Zou, R. Liu, C. Tao, X. Fan, Z. L. Wang, *Nat. Energy* **2016**, 1, 16138.
- [2] L. Meng, Y. Zhang, X. Wan, C. Li, X. Zhang, Y. Wang, X. Ke, Z. Xiao, L. Ding, R. Xia, H.-L. Yip, Y. Cao, Y. Chen, *Science* **2018**, 361, 1094.
- [3] C. Xiong, J. Sun, H. Yang, H. Jiang, *Sol. Energy* **2019**, 178, 193.
- [4] D. He, F. Zhao, L. Jiang, C. Wang, *J. Mater. Chem. A* **2018**, 6, 8839.
- [5] T. Usui, Y. Nakata, G. D. R. Banoukepa, K. Fujita, Y. Nishikawa, Y. Shimizu, A. Fujii, M. Ozaki, *Appl. Phys. Express* **2017**, 10, 021602.
- [6] H. Zhang, H. Yao, J. Hou, J. Zhu, J. Zhang, W. Li, R. Yu, B. Gao, S. Zhang, J. Hou, *Adv. Mater.* **2018**, 30, 1800613.
- [7] K. Yonezawa, H. Kamioka, T. Yasuda, L. Han, Y. Moritomo, *Appl. Phys. Express* **2012**, 5, 042302.

- [8] K. Feron, M. N. Thameel, M. F. Al-Mudhaffer, X. Zhou, W. J. Belcher, C. J. Fell, P. C. Dastoor, *Appl. Phys. Lett.* **2017**, *110*, 133301.
- [9] O. V. Mikhnenko, P. W. M. Blom, N. Thuc-Quyen, *Energy Environ. Sci.* **2015**, *8*, 1867.
- [10] L. J. A. Koster, E. C. P. Smits, V. D. Mihailetschi, P. W. M. Blom, *Phys. Rev. B* **2005**, *72*, 085205.
- [11] H. Long, X. Peng, K. Lin, L. Xie, J. Lu, B. Zhang, L. Ying, Z. Wei, *Appl. Phys. Express* **2019**, *12*, 052003.
- [12] M. Saleheen, S. M. Arnab, M. Z. Kabir, *Energies* **2016**, *9*, 412.
- [13] W. Tress, M. Yavari, K. Domanski, P. Yadav, B. Niesen, J. P. C. Baena, A. Hagfeldt, M. Graetzel, *Energy Environ. Sci.* **2018**, *11*, 151.
- [14] F. Monestier, J.-J. Simon, P. Torchio, L. Escoubas, F. Florya, S. Bailly, R. de Bettignies, S. Guillerez, C. Defranoux, *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 405.
- [15] S. M. Menke, W. A. Luhman, R. J. Holmes, *Nat. Mater.* **2013**, *12*, 152.
- [16] U. Hoermann, S. Zeiske, F. Piersimoni, L. Hoffmann, R. Schlesinger, N. Koch, T. Riedl, D. Andrienko, D. Neher, *Phys. Rev. B* **2018**, *98*, 155312.
- [17] O. V. Mikhnenko, R. Ruiter, P. W. M. Blom, M. A. Loi, *Phys. Rev. Lett.* **2012**, *108*, 137401.
- [18] M. T. Sajjad, A. J. Ward, A. Ruseckas, A. K. Bansal, S. Allard, U. Scherf, I. D. W. Samuel, *Phys. Status Solidi RRL* **2019**, *13*, 1800500.
- [19] P. E. Shaw, A. Ruseckas, I. D. W. Samuel, *Adv. Mater.* **2008**, *20*, 3516.
- [20] O. Hess, T. Kuhn, *Phys. Rev. A* **1996**, *54*, 3347.
- [21] O. Hess, T. Kuhn, *Phys. Rev. A* **1996**, *54*, 3360.
- [22] H. F. Hofmann, O. Hess, *Phys. Rev. A* **1999**, *59*, 2342.
- [23] S. M. Menke, R. J. Holmes, *Energy Environ. Sci.* **2014**, *7*, 499.
- [24] J. Kern, S. Schwab, C. Deibel, V. Dyakonov, *Phys. Status Solidi RRL* **2011**, *5*, 364.
- [25] L. J. A. Koster, V. D. Mihailetschi, R. Ramaker, P. W. M. Blom, *Appl. Phys. Lett.* **2005**, *86*, 123509.
- [26] G. Li, V. Shrotriya, Y. Yao, Y. Yang, *J. Appl. Phys.* **2005**, *98*, 043704.
- [27] S. R. Cowan, A. Roy, A. J. Heeger, *Phys. Rev. B* **2010**, *82*, 245207.
- [28] L. Torto, A. Cester, A. Rizzo, N. Wrachien, S. A. Gevorgyan, M. Corazza, F. C. Krebs, *IEEE J. Electron Devices* **2016**, *4*, 387.
- [29] L. Sun, J.-X. Sun, C.-H. Xiong, X.-H. Shi, *Sol. Energy* **2016**, *135*, 308.
- [30] M. Soldera, K. Taretto, T. Kirchartz, *Phys. Status Solidi A* **2012**, *209*, 207.
- [31] Y. Terao, H. Sasabe, C. Adachi, *Appl. Phys. Lett.* **2007**, *90*, 103515.
- [32] S. M. Arnab, M. Z. Kabir, *J. Vac. Sci. Technol. A* **2013**, *31*, 061201.
- [33] C. H. Xiong, J. X. Sun, D. P. Wang, Y. Dong, *J. Electron. Mater.* **2018**, *47*, 2841.
- [34] F. Laquai, D. Andrienko, R. Mauer, P. W. M. Blom, *Macromol. Rapid Commun.* **2015**, *36*, 1001.
- [35] C. G. Shuttle, R. Hamilton, B. C. O'Regan, J. Nelson, J. R. Durrant, *Proc. Natl. Acad. Sci. USA* **2010**, *107*, 16448.
- [36] Y. M. Nam, J. Huh, W. H. Jo, *Sol. Energy Mater. Sol. Cells* **2010**, *94*, 1118.
- [37] D. W. Sievers, V. Shrotriya, Y. Yang, *J. Appl. Phys.* **2006**, *100*, 114509.
- [38] O. V. Mikhnenko, H. Azimi, M. Scharber, M. Morana, P. W. M. Blom, M. A. Loi, *Energy Environ. Sci.* **2012**, *5*, 6960.
- [39] T. Kirchartz, T. Agostinelli, M. Campoy-Quiles, W. Gong, J. Nelson, *J. Phys. Chem. Lett.* **2012**, *3*, 3470.
- [40] K. Glaser, P. Beu, D. Bahro, C. Sprau, A. Puetz, A. Colmann, *J. Mater. Chem. A* **2018**, *6*, 9257.
- [41] M. C. Heiber, A. Dhinojwala, *J. Chem. Phys.* **2012**, *137*, 014903.
- [42] F. Zhao, Y. Li, Z. Wang, Y. Yang, Z. Wang, G. He, J. Zhang, L. Jiang, T. Wang, Z. Wei, W. Ma, B. Li, A. Xia, Y. Li, C. Wang, *Adv. Energy Mater.* **2017**, *7*, 1602552.