Hot kinetic model as a guide to improve organic and hybrid photovoltaic materials

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Despite of the great progress for the recent decade, the efficiencies of organic solar cells (OSCs) are still significantly lower than those of inorganic ones. Moreover, the record efficiency curve for OSC has been saturated for the last couple of years at ~13%. As a result, a key issue that arises is: whether there is a fundamental limit for the OSC efficiency that has been already achieved, or there are ways to overcome the stagnation.

Modeling of the OSC operation can shed light on this issue. The variety of approaches to OSC modeling is based on a kinetic approach[1-4], thermodynamic concepts[5-8], and combined or semi-empirical assumptions[8-10]. The main feature of the thermodynamic and semi-empirical models is the assumption of the (quasi)equilibrium between the photons, excitons, and free. Kinetic models, on the contrary, assume that the equilibrium in the OSC is broken mainly due to the irreversibility of the photoinduced charge transfer process[2]. Moreover, the kinetic models can take into account non-thermalized photogenerated charges, i.e., those whose energetic distribution cannot be described by a quasi-equilibrium Fermi distribution. Therefore, in the kinetic models, the equilibrium concepts such as the generalized Planck radiation law and Fermi levels splitting are inappropriate, and the OSC operation should be described by kinetic processes such as charge generation, thermalization, and recombination. Most of the OSC models are numerical because of the complexity of the processes involved into the cell operation

In this work, we propose an analytical OSC model suggesting the kinetic, i.e., non-equilibrium, nature of the OSC operation. We focus on the process of the free charge generation via hot CT states (Fig. 1). To describe the formation of a CT state from the exciton, we utilized the widely used Marcus model[11, 12] explaining CT from a donor molecule to an acceptor one. The analytical character of the model allowed us to evaluate the influence of various parameters: driving force, optical bandgap, dielectric permittivity, electron-hole separation distance in the CT state, geminate recombination, thermalization rate, reorganization energy and charge delocalization on the OSC efficiency. Our approach is applicable both for polymer and small-molecule solar cells; moreover, it can be extended to hybrid solar cells, e.g., to some types of perovskite ones.

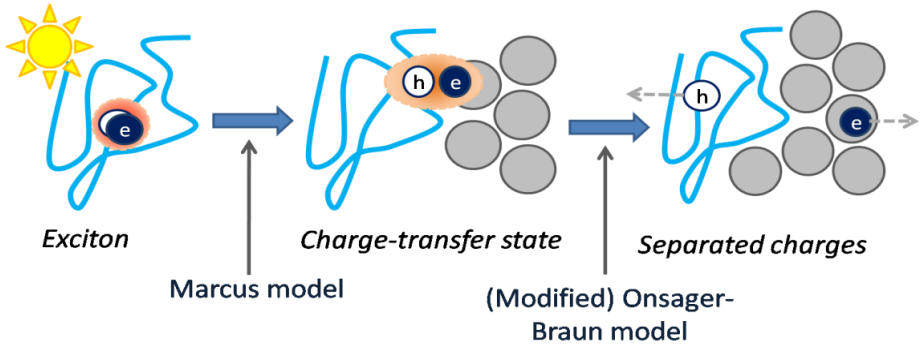

Fig. 1. Two-step model for generation of free charges in a blend of polymer donor (blue) with fullerene acceptor (grey). The first step is the formation of the CT state from an exciton, and the second one is the dissociation of the CT state into separated charges.

Fig. 2 presents experimental power conversion efficiencies of OSCs from a number of reports plotted *vs* donor E_g (points)[13]. The best cell efficiencies are observed for materials with bandgaps in the range E_g~1.5–1.6 eV, which are close to the optimal bandgaps predicted by our model and significantly larger than that within the Shockley-Queisser model.

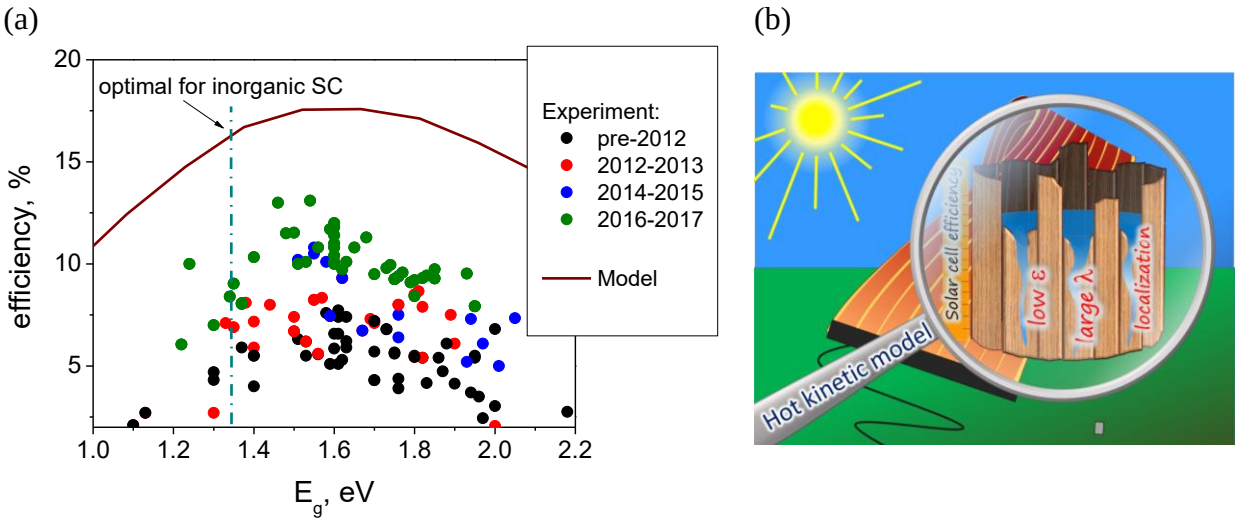

Fig. 2. (a) Power conversion efficiencies of well-performing OSCs. The line corresponds to the hot kinetic model. The vertical line shows the optimal bandgap for inorganic SCs. (b) Visualization of the results: the most promising ways to increase the OSC performance are decreasing the reorganization energy, increasing the dielectric permittivity and enhancing charge delocalization.

The proposed hot kinetic model shows that rigid semiconducting materials with low reorganization energy, high dielectric permittivity and pronounced charge delocalization are exclusively important to boost the organic solar cell efficiency toward and above 20%. The model also predicts that for state-of-the-art OSC materials, the optimal bandgaps are in the range 1.5–1.8 eV, i.e., larger than that predicted by the Shockley-Queisser model. If materials with lower reorganization energy, higher dielectric permittivity, and/or stronger intermolecular charge delocalization are developed, the bandgap reduction will be a benefit.

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