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Exciton extraction in nanocrystal solar cells

J.S. de Sousa, G.A. Farias, R.N. Costa Filho *

Universidade Federal do Ceará, Departamento de Física Caixa Postal 6030, 60440-554 Fortaleza, Ceará, Brazil

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ABSTRACT

The efficiency of exciton extraction from nanocrystals is defined as the ratio of the number of extracted excitons to the number of absorbed photons. This efficiency is studied here based on a phenomenological model parameterized by recent experimental results in CdSe nanocrystals. Several possibilities of interplay among all possible electronic transition rates (Auger recombination, impact ionization, radiative recombination and electron–hole escape) are explored showing the possibility of obtaining efficiencies above 100% when multiple exciton generation processes are taken into account.

The recent development of nanocrystals (NC's) based photovoltaic (PV) devices gave new impulse to the field of photovoltaics [1,2]. That happened mainly because of the following NC's properties: (I) the NC's bandgap can be tailored to absorb light in the whole solar spectrum; (II) the enhanced impact ionization, leading to multiple exciton generation (MEG) for each photon absorbed [3–9]; (III) the novel inexpensive chemical methods developed to grow colloidal NC's that are highly compatible with solid state device technology [10,11]; (IV) the NC's can be embedded in a semiconductor polymer film for the development of either flexible or non-flat devices, such that every surface might become a potential PV device; (V) contrary to other NC based applications, NC size homogeneity is not mandatory. Actually, a size dispersion might be useful to enlarge the absorption window. Although MEG has been experimentally obtained many times with quantum yields (QY) up to 700% [5–9], photocurrent QY's larger than 100% have not been reported so far [12]. Here, we present a phenomenological model to investigate the efficiency of exciton extraction from core–shell NC's.

There are many configurations of NC based PV devices currently under investigation [1,12]. Our model device is a variation of the configuration where small CdSe NC's (with diameters up to 5 nm) are dispersed in an organic semiconductor polymer, as shown in Fig. 1(a). The main difference relies on the fact that we consider CdSe core–shell-like NC's because covering the NC's with a thin shell of wide bandgap semiconductor prevents chemical interaction with the host material and enhances the optical absorption [13,14]. The device is illuminated by a light source with intensity I_{EX} expressed in an areal flux of incident photons. The incident photons generate e–h pairs within individual NC's. For simplicity, we consider that the only possible NC occupation states $|n\rangle$ are $|0\rangle$, $|1\rangle$ and $|2\rangle$, where n indicates the number of electron–hole (e–h) pairs. The number of NC's occupied by each state is respectively given by N_0, N_1 and N_2, in such a way that the constraint $N_T = N_0 + N_1 + N_2$ is always satisfied. Here, N_T represents the number of NC's in the device. In addition, we disregard the quantum tunneling between NCs, which can be achieved by lowering the NC density (i.e. increasing the distance among NCs). Although the charge transport through the tunnel coupling between NCs is an important and complicated transport mechanism in NC-based solar cells [15], it only changes the spatial localization of the charges without affecting the amount of NCs with 0, 1 or 2 confined excitons, which are the quantities of interest in the present manuscript.

The photocurrent generated by the NC's can be defined as the fraction of e–h pairs escaping from the NC's through the shell layer before recombining. Fig. 1(b) displays the possible electronic transitions taking place within the NC's. The decay processes from $|2\rangle$ states to $|1\rangle$ states can take place through the following processes: Auger recombination, radiative recombination (bi-exciton recombination) or out-tunneling, with the respective characteristic times of each process are given by τ_A, τ_B and τ_2. The decay channel from $|1\rangle$ states to $|0\rangle$ states can occur by either radiative recombination (mono-exciton recombination) or out-tunneling with respective characteristic times are given by τ_R and τ_1. The escape of e–h pairs is depicted in Fig. 1(c). The excitation channel from $|1\rangle$ to $|2\rangle$ states through impact ionization is also considered with τ_{ii} as characteristic time. We remark that phonons scattering does not seem to compete with the above described decay channels. The energy difference between states, above and below the threshold energy for which impact ionization takes places, does not match the NC's $\hbar\omega_{LO}$ phonon energy with nearly 3 nm of diameter [3,4]. Even though this could occur in NC's of different sizes, we disregard contributions from phonon-induced decay processes.

* Corresponding author.
E-mail address: rai@fisica.ufc.br (R.N. Costa Filho).

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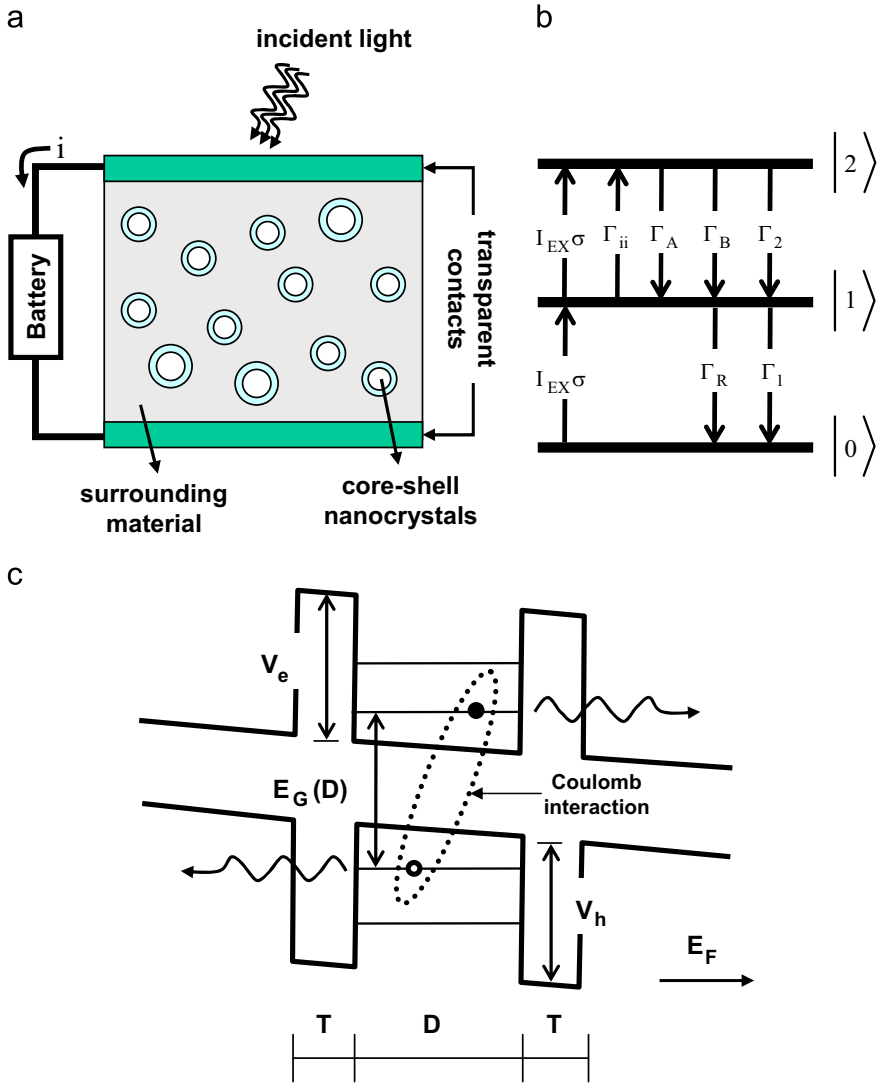

Fig. 1. (a) Idealized NC based photovoltaic device. (b) Schematics of all possible electronic transitions within an individual NC. (c) Schematics of the out-tunneling of e–h pairs from a single NC. *T* and *D* represent the shell thickness and the NC core size, respectively. The figure also shows that the NC's are subject to an external electric field E_F, which may be created by the external electrodes of the photovoltaic device.

There are other temperature related relaxation channels like thermionic emission, thermal assisted tunneling [16,17], and Poole–Frenkel effect [15], which are until certain extent, dependent on the NC size. Thus, in small NCs, the discreteness of the density of states makes the energy difference between adjacent states in the conduction and valence bands larger than the thermal activation energy k_BT even at room temperature, suppressing the occupation of excited states and thermal assisted tunneling. Moreover, the enhanced binding energy in QD's is several times larger than k_BT, so that temperature effects are not strong enough to dissociate confined e–h pairs, which suppresses thermionic emission. As for the Poole–Frenkel effect, the carriers in the ground state require energies of the order of the sum of the confinement barrier and exciton binding energies to undergo such effect. Although possible, the time characteristics of those events are extremely large, compared to other competing mechanisms. Thus, temperature related processes can be ruled out and the main contribution to the photo-generated current can be considered as arising from the out-tunneling of the e–h pairs.

A set of state-filling rate equations taking into account all above processes can be written as

$$\frac{dN_0}{dt} = -N_0 I_{EX}\sigma + N_1\left(\frac{1}{\tau_1}+\frac{1}{\tau_R}\right), \tag{1}$$

$$\frac{dN_1}{dt} = N_0 I_{EX}\sigma - N_1\left(\frac{1}{\tau_1}+\frac{1}{\tau_R}+\frac{1}{\tau_{ii}}+I_{EX}\sigma\right)+N_2\left(\frac{1}{\tau_2}+\frac{1}{\tau_A}+\frac{1}{\tau_B}\right), \tag{2}$$

and

$$\frac{dN_2}{dt} = N_1\left(I_{EX}\sigma+\frac{1}{\tau_{ii}}\right)-N_2\left(\frac{1}{\tau_2}+\frac{1}{\tau_A}+\frac{1}{\tau_B}\right) \tag{3}$$

where σ represents the average NC absorption cross-section. A similar model was used to investigate the absorption cross-section of Si NC's [18]. The photocurrent generated by the NC's is given by $i(t)=2qdN_{out}/dt$ where q is the electron charge, and the factor two accounts for the electron and hole contributions to the total current. $dN_{out}/dt = N_1/\tau_1 + N_2/\tau_2$ represents the out-tunneling rate of e–h pairs confined in the NC's. In the stationary state, the solutions of Eqs. (1)–(3) are

$$\frac{N_0}{N_T} = \frac{\Gamma_s(\Gamma_1+\Gamma_R)}{\Gamma_s(\Gamma_1+\Gamma_R)+I_{EX}\sigma(\Gamma_s+\Gamma_{ii}+I_{EX}\sigma)},$$

$$\frac{N_1}{N_T} = \frac{I_{EX}\sigma\Gamma_s}{\Gamma_s(\Gamma_1+\Gamma_R)+I_{EX}\sigma(\Gamma_s+\Gamma_{ii}+I_{EX}\sigma)},$$

$$\frac{N_2}{N_T} = \frac{I_{EX}\sigma(\Gamma_{ii}+I_{EX}\sigma)}{\Gamma_s(\Gamma_1+\Gamma_R)+I_{EX}\sigma(\Gamma_s+\Gamma_{ii}+I_{EX}\sigma)}, \tag{4}$$