# Impact Ionization Can Explain Carrier Multiplication in PbSe Quantum Dots

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## ABSTRACT

**The efficiency of conventional solar cells is limited because the excess energy of absorbed photons converts to heat instead of producing electron–hole pairs. Recently, efficient carrier multiplication has been observed in semiconductor quantum dots. In this process, a single, high-energy photon generates multiple electron–hole pairs. Rather exotF7 (ABSTRApiec4e0 0 19 Tmaismple)-32hav. served324(Rropouscri324()-40ABSTRAarr**

Thus, the II and AR processes are described by the same transition matrix elements $\langle X|W|XX\rangle$

states (Figure 1e and f). Finally, the electron and the hole relax via electron/hole cooling, leading to a ground-state exciton (Figure 1g). In this Letter, we focus on the II and AR processes.

We consider a nearly spherical $Pb_{260}Se_{249}$ quantum dot 3.1 nm in diameter. The dot is obtained by cutting out a Se-centered sphere from bulk PbSe (rocksalt lattice structure, lattice constant $a_0 = 6.12$ Å). All Pb and Se surface atoms are passivated using ligand-like atomic pseudopotentials (centered along the direction of the dangling bonds), that are fitted to remove surface states from the dot band gap. The single-particle energies, $\epsilon_i$, and wave functions, $\psi_i$, are then obtained by solving the single-particle Schrödinger equation

where $\hat{V}_{SO}$ is the nonlocal spin−orbit operator and $V(\boldsymbol{r}) = \sum_{\boldsymbol{R}} v(\boldsymbol{r} - \boldsymbol{R})$ is a linear superposition }j /F2 1 Tf 0.83748 TD[()-449()0(s)-449(u)-449(l(}Tj /F19 1 Tf 0.333-449(lin. [2T2o(enen)Tj 0 -88649(electron/ace)-469(ator

Figure 2b reveals the existence of very different densities of final states for the II and AR processes of eqs 1 and 2, suggesting the possibility of different transition rates. However, the density of final states is not by itself a reliable indicator of the actual II and AR transition rates, because some transition matrix elements in eqs 1 and 2 may vanish as a consequence of the selection rules enforced by the two-particle character of the Coulomb interaction. For example, to first order the II process can occur only if one of the two electrons (or one of the two holes) in the final XX configuration occupies the same single-particle level as the electron (or the hole) in the initial X configuration (see Figure 1). Figure 2c shows that indeed a large fraction (>98%) of the transition matrix elements $\langle X|W|XX\rangle$ vanish as a result of this many-body selection rule. Thus, it is important to take into account the existence of many-body forbidden transitions to obtain accurate estimates of the II and AR rates.

We have calculated the II and AR rates by identifying the transition matrix elements that are zero (many-body forbidden), and assuming that the non-zero matrix elements are approximately constant. We have averaged the II and AR rates over the initial states in a narrow energy window (20 meV), to account for (i) the electronic dephasing of the initial state, which we assume to occur on a very fast time scale, and (ii) the statistical nature of ensemble measurements. The ensuing transition rates are shown in Figure 3. Remarkably, we find that the AR rate (XX → X) is almost constant as a function of energy. This is a consequence of the fact that the nearly linear increase of the density of final states (X) with energy (Figure 2b) is compensated by the increasing fraction of transition matrix elements that vanish (Figure 2c). The II rate (X → XX), however, increases rapidly with energy, overtaking the AR rate already at $\sim 2.1E_{\mathrm{g}}$ (Figure 3). For $\hbar\omega = 3E_{\mathrm{g}}$, we find that the II rate is over 2 orders of magnitude faster than the AR rate, thus explaining the observed[5,6] asymmetry between AR and II lifetimes.

The II lifetime can be estimated from the calculated ratio between the II and AR rates (Figure 3). The experimental AR lifetime (extrapolated to the size of the PbSe dot considered here) is approximately 6 ps,[5] which gives, from our calculations, an estimated II lifetime $\tau^{\mathrm{II}} \approx 0.01$ ps at $\hbar\omega = 3E_{\mathrm{g}}$3.862l57sms762(the)-31 Tf 0.5 0 TD f5 0[(our)-255r0(elec4171 486.518 454.088 Tm (II)Tj /F6 1 Tf 9.

from Figure 4, the XX-producing absorption spectrum has a well-defined energy threshold at $\hbar\omega_{\mathrm{th}} \approx 2.2E_{\mathrm{g}}$, indicating that carrier multiplication can be initiated by photons of this energy. We note, however, that for $\hbar\omega = 2.2E_{\mathrm{g}}$ only about $^{1}/_{4}$ of the absorbed photons are potentially useful for II (ratio between the XX-producing absorption spectrum and the full absorption spectrum in Figure 4). This reduces the carrier-multiplication efficiency compared to $\hbar\omega = 3E_{\mathrm{g}}$. Our calculated carrier-multiplication threshold is in agreement with the experimental observations of Ellingson et al.,[6] without the need, however, to invoke optically forbidden transitions. We find that the low-energy threshold is due instead to the asymmetry between the valence-band and conduction-band densities of states (Figure 2a), which allow optical transitions where the excess energy of the electron is significantly larger than that of the hole.

Our calculations show (Figure 3) that, for energies above $\sim 2.2E_{\mathrm{g}}$, the intrinsic II rate ($X \rightarrow XX$) is much faster than the AR rate ($XX \rightarrow X$). However, the II decay channel competes with other radiative (e.g., electron−hole recombination) and nonradiative (e.g., electron/hole phonon-assisted cooling) decay paths for the photogenerated exciton. Radiative recombination times in PbSe quantum dots are rather long (>1 ns). Nonradiative intraband relaxation times ranging between 0.25 and 6 ps have been reported in the literature.[19,20] For exciton energies just above threshold ($\hbar\omega \approx 2E_{\mathrm{g}}$), intraband relaxation is faster than II, leading to relatively small[6] or negligible[7] carrier multiplication efficiencies. For $\hbar\omega \approx 3E_{\mathrm{g}}$, however, II is significantly faster than any competing decay processes and represents the main decay channel for an electron−hole pair of that energy (Figure 1). For even higher excitation energies, multiple carrier generation can occur through a chain process, whereby the bi-exciton generated by the II process decays into a tri-exciton, and so on. The physical reason for the ultrafast II decay rate lies in the very sharp increase of the multi-exciton DOS with energy (see Figure 2b). This is likely to be a common feature of many semiconductor quantum dots, suggesting that ultrafast II rates can be expected in other materials as well. Indeed, efficient carrier multiplication has been reported recently in CdSe,[7,8] PbS,[6] and PbTe[21] quantum dots.

In summary, we have proposed that the impact ionization mechanism can explain carrier-multiplication phenomena recently observed in PbSe colloidal nanocrystals and that no alternative models are required to explain existing experimental observations of (i) ultrafast carrier-multiplication rates (<200 fs)[5,6] and (ii) low-energy carrier-multiplication thresholds ($\hbar\omega < 3E_{\mathrm{g}}$).[6] In the case of 3.1-nm-diameter PbSe quantum dots, our pseudopotential calculations predict a II threshold $\hbar\omega_{\mathrm{th}} \approx 2.2E_{\mathrm{g}}$ and a II lifetime smaller than 20 fs for $\hbar\omega \geq 3E_{\mathrm{g}}$.

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