Carrier multiplication between interacting nanocrystals for fostering silicon-based photovoltaics

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The conversion of solar radiation into electric current with high efficiency is one of the most important topics of modern scientific research, as it holds great potential as a source of clean and renewable energy. Exploitation of interaction between nanocrystals seems to be a promising route to the establishment of third-generation photovoltaics. Here, we adopt a fully ab initio scheme to estimate the role of nanoparticle interplay in the carrier multiplication dynamics of interacting silicon nanocrystals. Energy and charge transfer-based carrier multiplication events are studied as a function of nanocrystal separation, demonstrating the benefits induced by the wavefunction sharing regime. We prove the relevance of these recombinative mechanisms for photovoltaic applications in the case of silicon nanocrystals arranged in dense arrays, quantifying at an atomic scale which conditions maximize the outcome.

A great challenge in modern science is the realization of clean, cheap and renewable energy sources, and the conversion of solar energy into electric current with high efficiency is one of the most important and promising topics. Materials engineering efforts to increase photocurrent efficiency in the visible and near-ultraviolet region are an active area of research. This is typically realized by improving light harvesting and reducing loss factors, that is, by tuning the optoelectronic properties of the system or by exploiting new schemes for photovoltaic devices. High-energy loss factors are minimized by promoting fast and non-dissipative recombination mechanisms that prevent loss thermalization processes. In this context, carrier multiplication can be used to increase solar cell efficiency.

Carrier multiplication is a carrier relaxation process that results in the generation of multiple electron–hole pairs after absorption of one single photon (carrier multiplication is also frequently termed multiple exciton generation). If favoured by the quantum confinement of the electron density, carrier multiplication can be as fast as or even faster than phonon emission, extending the portion of the solar spectrum converted into energy. The expected outcome of this process is therefore an improvement in photovoltaic performance induced by integration of nanocrystalline structures inside the solar cell device. Carrier multiplication has been studied in several low-dimensional nanosystems (PbSe and PbS, CdSe, PbTe, InAs and Si), although its origin and real relevance in quantum confined structures is still under discussion. A particular carrier multiplication scheme has recently been adopted to explain photoluminescence and induced absorption studies conducted on silicon nanocrystals (Si-NCs) organized in dense arrays (nanocrystal–nanocrystal separation of \( \leq 1 \) nm). In these experimental works, Coulomb-driven energy transfer mechanisms between neighbouring Si-NCs (termed space-separated quantum cutting, SSQC) were hypothesized to generate long-lived Auger-unaffected single electron–hole pairs scattered among several interacting nanostructures. By distributing the excitation, carrier multiplication via SSQC might therefore be one of the most suitable routes to minimizing solar-cell loss factors.

From a theoretical perspective, three different models have been implemented to describe carrier multiplication: (i) impact ionization, (ii) coherent superpositions of single- and multi-exciton states and (iii) generation of multi-excitions via virtual single excitations (second-order processes). Although each of these models has highlighted important aspects of carrier multiplication in isolated nanocrystals, none has been used to investigate how carrier multiplication is affected by the interplay between nanocrystals, largely because of the complexity of the problem. A detailed analysis of the recombination processes turned on by nanocrystal–nanocrystal interactions and their relevance to carrier multiplication dynamics is still missing. In particular, the mechanisms at the root of the experimental observations made by Timmerman et al. and Trinh et al. remain unclear and the assessment that SSQC can be sufficiently fast to influence carrier multiplication is, to date, only a reasonable assumption. In this context, numerical simulations offer the possibility of quantifying carrier multiplication events with an accuracy that complements the experimental observations.

In the present work, carrier multiplication is studied by adopting a fully ab initio scheme within density functional theory (DFT) in both isolated and interacting Si-NCs. The role played by quantum confinement is clarified by comparing carrier multiplication lifetimes calculated for isolated Si-NCs (here termed one-site carrier multiplication) with those obtained for Si bulk. Carrier multiplication events induced by nanocrystal–nanocrystal interactions (termed two-site carrier multiplication) are quantified as a function of nanocrystal–nanocrystal separation. The existence of a new effect, which stems from charge-transfer processes between nanocrystals, is proven and termed Coulomb-driven charge transfer (CDCT). A side-by-side comparison of calculated one- and two-site carrier multiplication lifetimes shows the existence of a lifetime hierarchy. The impact of nanocrystal–nanocrystal interaction on carrier multiplication dynamics is explained.
To provide a reference for later simulations, we first studied carrier multiplication in a set of isolated Si-NCs, simulating an ideal configuration comprising sparse arrays of nanocrystals where interactions between nanostructures can be neglected. By considering the surface dangling bonds as hydrogen-passivated, we obtained four isolated Si-NCs with different diameters: Si$_{35}$H$_{36}$ (1.3 nm), Si$_{42}$H$_{100}$ (1.6 nm), Si$_{42}$H$_{100}$ (1.9 nm) and Si$_{42}$H$_{172}$ (2.4 nm), with energy gaps ($E_{\text{gap}}$) of 3.42, 2.50, 2.21 and 1.70 eV, respectively. In the considered nanostructure, hydrogen passivation ensures that dangling-bond-related states are not present in the bandgap region. Carrier multiplication lifetimes were calculated by applying first-order perturbation theory (Fermi’s golden rule) to Kohn–Sham (KS) states$^{33}$, thus modeling the decay of one electron–hole pair into two electron–hole pairs as the sum of two processes: one initiated by the electron (hole spectator) and the other initiated by the hole (electron spectator). The first process leads to the formation of a negative three-carrier state termed a negative trion, and the second to a positive three-carrier state termed a positive trion$^{29}$. The carrier multiplication rate is obtained by summing over all possible final states, and its reciprocal yields the carrier multiplication lifetime. Calculated one-site carrier multiplication lifetimes ($\tau_{\text{one-site}}$) are reported in Fig. 1 as a function of the energy of the initial carrier $E_{\text{in}}$ (absolute energy scale, Fig. 1a) and of the ratio $E^*/E_{\text{gap}}$ (relative energy scale, Fig. 1b), where $E^*$ is the excess energy of the initial carrier, that is, measured from the respective band edge. The zero of the absolute energy scale is set at half gap (hence $E_{\text{in}} < 0$ for holes and $E_{\text{in}} > 0$ for electrons). Simulations show that carrier multiplication is active when $E^*/E_{\text{gap}} > 1$. In the considered energy window, carrier multiplication lifetimes monotonically decrease with respect to $|E_{\text{in}}|$ and range from tens of picoseconds to tenths of femtoseconds (Fig. 1a). Far from the activation threshold, carrier multiplication is proved to be more efficient in Si-NCs than in Si bulk, and the lifetimes seem to be independent of nanocrystal size, resulting in an almost exact compensation between the enhancement of Coulomb interaction via size reduction and a decrement of the density of final states. When vacuum states are counted, carrier multiplication lifetimes scatter across many orders of magnitude, cease to follow the typical monotonic trend, and depend upon the chosen periodic boundary conditions. The inclusion of vacuum states in carrier multiplication calculations therefore leads to non-physical conclusions, so electron-initiated carrier multiplication is energetically forbidden in the smallest considered nanocrystal. A strong dependence of carrier multiplication lifetimes on nanocrystal size is instead observed when the relative energy scale is used (Fig. 1b). This energy scale is the most appropriate for predicting possible photovoltaic applications of carrier multiplication$^{34}$, and here carrier multiplication shows clear evidence of the benefits induced by size reduction via quantum confinement.

Figure 1 | Carrier multiplication lifetimes in non-interacting Si-NCs and Si bulk. Calculated carrier multiplication lifetimes ($\tau_{\text{one-site}}$) in isolated Si-NCs and Si bulk are reported using two different energy scales. a, The absolute energy scale is adopted and lifetimes are reported as a function of energy $E_{\text{in}}$. The zero of the energy scale is set at half gap. Here, the calculated vacuum level is reported with a vertical dashed line, above which $\tau_{\text{one-site}}$ clearly scatters across many orders of magnitude. Owing to the $E_{\text{gap}}$ opening imposed by quantum confinement, the smaller the nanocrystal, the larger the energy window where one-site carrier multiplication is energetically forbidden. As a consequence, electron-initiated carrier multiplication processes that exclude unbound states are not allowed in Si$_{35}$H$_{36}$. b, The relative energy scale is adopted; that is, lifetimes are reported as a function of the ratio $E^*/E_{\text{gap}}$. Here, smaller nanocrystals yield stronger carrier multiplication. Inset: schematic of carrier multiplication decay paths (impact ionization-like). VBM, valence band maximum; CBM, conduction band minimum. According to the definition of excess energy $E^*$, the zero of the relative energy scale corresponds to the CBM (VBM), when the carrier multiplication recombination is initiated by an electron (hole).
Coulomb-driven energy or charge transfer, respectively. The depicted SSQC (in red) and CDCT (in orange) processes yield electron-initiated carrier multiplication events occurring in a pair of nanocrystals (in contrast to one-interacting nanocrystals). The energy profile of the pair of nanocrystals is electron-initiated carrier multiplication events, nanocrystal–nanocrystal interaction can also lead to non-radiative scattering processes that move one or two carriers from one nanocrystal to another, resulting in a charge transfer with the promotion of an extra electron–hole pair (CDCT, Fig. 2). Being driven by the Coulomb interaction between carriers located on separated nanocrystals, both SSQC and CDCT are expected to occur rarely in sparse arrays of nanocrystals and become relevant in the case of densely packed nanocrystals where the close proximity of nanostructures boosts the two-site components of carrier multiplication.

To shed light onto the nature of these two-site carrier multiplication processes we calculated carrier multiplication lifetimes as a function of $E_{\text{cm}}$ for two sets of interacting Si-NCs of different size, that is, Si$_{147}$H$_{100}$ × Si$_{35}$H$_{36}$ and Si$_{35}$H$_{36}$ × Si$_{147}$H$_{100}$. For each set we considered four nanocrystal–nanocrystal separations, $d = 0.4$, 0.6, 0.8 and 1.0 nm, which are close to the experimental conditions reported in refs 21–24. The results are presented in Fig. 3. Having two nanocrystals inside the same simulation box, wavefunctions are now free to delocalize over both nanostructures and a colour scale is adopted to show the percentage (termed spill-out) of localization of the initial state: red points (0%) identify carrier multiplication transitions initiated by states completely localized on Si$_{35}$H$_{36}$, and blue points (100%) refer to states completely localized on the nearby nanocrystal (Si$_{147}$H$_{100}$ or Si$_{35}$H$_{36}$). Our results indicate that, in the system Si$_{35}$H$_{36}$ × Si$_{147}$H$_{100}$ and in the considered energy window, blue points are fully associated with two-site carrier multiplication transitions, because one-site carrier multiplication is energetically forbidden inside the small nanocrystal. The other coloured points can either be associated with one-site carrier multiplication events occurring in the larger nanocrystal or be a mixture of one- and two-site processes. Varying $d$ from 1.0 to 0.4 nm (from top to bottom of Fig. 3), two-site carrier multiplication lifetimes decrease significantly by up to three orders of magnitude. In contrast, carrier multiplication processes initiated by states localized on the large nanocrystal (red points) are only weakly altered by the close proximity of nanocrystals and resemble the data obtained for the isolated Si$_{35}$H$_{36}$ (grey points). Modifications induced in the electronic structure by the change in the nanocrystal–nanocrystal separation do not therefore significantly influence one-site carrier multiplication events. In the system Si$_{293}$H$_{172}$ × Si$_{147}$H$_{100}$ (Fig. 3, where only carrier multiplication processes initiated by excited electrons are reported), one-site carrier multiplication is energetically allowed in both nanocrystals (in contrast to the previous system), and Coulomb-driven charge and energy-transfer processes can occur in any direction (from the small to the large nanocrystal and vice versa). At $d = 1$ nm, a group of points (spill-out of ~0% or ~100%) is superimposed on the carrier multiplication lifetimes calculated for the isolated nanocrystals. For these points, one-site carrier multiplication predominates. The other transitions stem from the nanocrystal–nanocrystal interaction and represent two-site events. Also in this case, when $d$ is reduced from 1.0 to 0.4 nm, two-site carrier multiplication lifetimes decrease drastically by up to three orders of magnitude, therefore proving the strong dependence of two-site events on nanocrystal proximity. It is thus possible to state that in a system of interacting nanocrystals, carrier multiplication recombinations involve both one- and two-site processes, the latter being strongly influenced by nanocrystal–nanocrystal separation. Although it is easy to recognize the kind of carrier multiplication process when wavefunctions cover just one single nanocrystal, the analysis becomes more elaborate when states are delocalized over both nanocrystals.

To estimate separately one-site carrier multiplication, CDCT and SSQC lifetimes, we have to generalize the definition of these effects to the case of states delocalized over the entire system. In this situation each carrier multiplication decay process can be split into a linear combination of one-site carrier multiplication, CDCT and SSQC with the coefficients given by weighting factors that depend on the localization of the involved wavefunctions (Supplementary Section S3). Extrapolated SSQC and CDCT lifetimes ($\tau_{SSQC}$ and $\tau_{CDCT}$) for two-site carrier multiplication processes are presented in Fig. 3. One- and two-site carrier multiplication processes were calculated for the isolated nanocrystals (in contrast to the previous system), and Coulomb-driven charge and energy-transfer processes can occur in any direction (from the small to the large nanocrystal and vice versa). At $d = 1$ nm, a group of points (spill-out of ~0% or ~100%) is superimposed on the carrier multiplication lifetimes calculated for the isolated nanocrystals. For these points, one-site carrier multiplication predominates. The other transitions stem from the nanocrystal–nanocrystal interaction and represent two-site events. Also in this case, when $d$ is reduced from 1.0 to 0.4 nm, two-site carrier multiplication lifetimes decrease drastically by up to three orders of magnitude, therefore proving the strong dependence of two-site events on nanocrystal proximity. It is thus possible to state that in a system of interacting nanocrystals, carrier multiplication recombinations involve both one- and two-site processes, the latter being strongly influenced by nanocrystal–nanocrystal separation. Although it is easy to recognize the kind of carrier multiplication process when wavefunctions cover just one single nanocrystal, the analysis becomes more elaborate when states are delocalized over both nanocrystals.
tCDCT) are reported in Fig. 4 as a function of the initial carrier energy and nanocrystal–nanocrystal separation. Our results indicate that two-site carrier multiplication lifetimes strongly decrease when E\textsubscript{in} increases or d is reduced. The results reported in Fig. 4 suggest the following lifetime hierarchy:

\[ t_{\text{one-site}} \leq t_{\text{CDCT}} \leq t_{\text{SSQC}} \]

At high energy of the initial carrier (for example, E\textsubscript{in} = 4.0 eV), when the most realistic system Si\textsubscript{293}H\textsubscript{172} × Si\textsubscript{147}H\textsubscript{100} is considered and nanocrystals are placed in close proximity, we have \( t_{\text{one-site}} \approx 0.01 \) ps, \( t_{\text{CDCT}} \approx 0.1 \) ps and \( t_{\text{SSQC}} \approx 1 \) ps. When combined with Auger recycling, this lifetime hierarchy can be used to monitor the after-pumping excited states population, thereby simulating a pump-and-probe experiment. A cyclic procedure of fast one-site carrier multiplication, two-site carrier multiplication and Auger recycling, plugged into a set of rate equations, is compatible with recent experimental evidence of quantum cutting in dense arrays of Si-NCs\textsuperscript{21–24}. The predicted time-dependent population of excited states is reported and discussed in the Supplementary Section S4, where it is shown that twice as many electron–hole pairs as the number of absorbed photons with energy above the carrier multiplication threshold appear directly after pumping (in low fluence conditions). One-site carrier multiplication is responsible for probing this double number of electron–hole pairs soon after pumping.
after short delay times ($t_{\text{on-site}} \approx 0.01$ ps), while SSQC keeps this number long-lived and subject to radiative decay only. Notably, exciton recycling mechanisms have already been hypothesized to explain energy transfer mechanisms in rare earth (Er$^{3+}$) coupled Si-NCs$^{35,36}$. To find the conditions that maximize two-site carrier multiplication processes we monitored the dependence of quantum cutting on nanocrystal proximity. For this purpose we first selected three different initial states that were close in energy ($E_{\text{in}} = 3.94$, 3.97 and 4.05 eV, respectively) and show a different localization when nanocrystal–nanocrystal separation is reduced, and we reported the SSQC lifetimes for each as a function of $d$ and the spill-out variable (Fig. 5). A strong localization onto the large nanocrystal is observed for all three initial states when $d = 1$ nm, and the SSQC lifetimes are estimated to be few nanoseconds. Whenever the initial state delocalizes over both nanocrystals, a SSQC lifetime drop is observed, showing that SSQC becomes strikingly more efficient in this regime. This occurs at $d \leq 0.8$ nm for the transition ignited by the state with $E_{\text{in}} = 4.05$ eV and at $d \leq 0.4$ nm for the state with $E_{\text{in}} = 3.97$ eV. Such behaviour is not observed when $E_{\text{in}} = 3.94$ eV because of the lack of delocalization and SSQC is slow. It is evident therefore that SSQC lifetimes have a non-trivial dependence on nanocrystal–nanocrystal separation and strongly depend on the localization of the initial state since they undergo a dramatic reduction when the initial carrier wavefunction delocalizes over the entire system. In other words, SSQC processes become fast when they cease to be simple electron–hole generation mechanisms driven by energy transfer processes between separate and independent nanocrystals and instead involve the compound system of two nanocrystals from a quantum point of view. To prove that the discussed SSQC trend is general, and not limited to the three selected states, we report in Fig. 6 the calculated SSQC lifetimes as a function of spill-out with all the nanocrystal–nanocrystal separations taken into account. The same calculations are also reported for CDCT. As previously noted, two-site lifetimes are large when the spill-out is either 0% or 100%, that is, when the initial wavefunction is strongly localized onto one single nanocrystal. In contrast, even a small delocalization of the initial wavefunction on both nanostructures is able to push up two-site Coulomb matrix elements. We observe changes of up to two to three orders of magnitude in both SSQC and CDCT lifetimes.
when the initial state ceases to be completely localized on one nanocrystal and at least 15% of the wavefunction is shared by the two nanocrystals. The most efficient two-site events are recorded when the initial carrier wavefunction extends to both nanocrystals and the spill-out parameter ranges from ~15% to ~85%, which defines the wavefunction sharing regime. These results indicate that scenarios where energy and charge transfer mechanisms occur among independent nanocrystals with wavefunctions unaffected by nanocrystal proximity ( Förster-like processes) do not provide a good description of carrier multiplication recombinations induced by nanocrystal–nanocrystal interaction (Supplementary Section S5). Only a full quantum picture of the system, considered as a whole, properly describes the carrier multiplication dynamics of two interacting nanocrystals in the considered range of separations. By favouring the creation of orbitals shared by many nanocrystals, the embedding matrix\(^{38}\) or the presence of several interacting nanocrystals (the typical condition of three-dimensional realistic systems) are expected to amplify the relevance of SSQC and CDCT in dense arrays of Si-NCs.

In conclusion, we have calculated the typical lifetimes of carrier multiplication processes occurring in both isolated and interacting Si-NCs. Simulations of carrier multiplication lifetimes in isolated Si-NCs showed that carrier multiplication benefits from size reduction via quantum confinement. When the interaction between nanocrystals is turned on, carrier multiplication recombinations are separated into one-site and two-site carrier multiplication processes, depending on whether the transitions involve only one single nanocrystal or pairs of nanocrystals. Both Coulomb-driven energy and charge transfer mechanisms were studied as a function of nanocrystal–nanocrystal separation, generalizing the common view of two separated interacting nanocrystals to a unique quantum confined structure where quantum states can spread among both nanostructures. In particular, wavefunction delocalization gives the two-site carrier multiplication dynamics a non-trivial dependence on nanocrystal–nanocrystal separation. For the first time, both SSQC and CDCT lifetimes were estimated, showing optimal efficiencies in the wavefunction sharing regime that can be favoured by the presence of several interacting nanocrystals. On the basis of \textit{ab initio} simulations, the presence of a cyclic process involving fast one-site carrier multiplication, two-site carrier multiplication and Auger recycling mechanisms has been proven to be compatible with the recent experimental observations of quantum cutting in Si-NCs based on photoluminescence\(^{21–23}\) and induced absorption experiments\(^{24}\). Thanks to the ability to generate long-lived single electron–hole pairs by distributing the excitation among interacting nanostructures, SSQC is expected to have a great impact on solar cell devices based on Si-NCs as long as the nanocrystals are arranged in dense arrays. By tailoring carrier multiplication by means of nanocrystal proximity, nanocrystal–nanocrystal interaction can therefore be used to overcome the current solar cell limitations, opening a new route to the establishment of third-generation photovoltaics.
Methods

Electronic structures were calculated from first principles within DFT in the local density approximation, adopting a pseudopotential supercell approach in reciprocal space. Quasiparticle corrections were applied to the electronic structure of Si bulk. The molecular graphics viewer VMD was used to plot the KS wavefunctions in Fig. 5. In contrast to other studies, where real-space methods are used, our methodology offers a natural description of the electronic and screening properties of both k-dispersive and low-dimensional systems, treating them on an equal footing. Carrier multiplication lifetimes have been obtained using first-order perturbation theory (impact ionization scheme), calculating the screened Coulomb matrix elements between KS states, for both isolated and interacting nanocrystals.

Dielectric screening was obtained by solving Dyson’s equation for polarizability in the random phase approximation. For pairs of interacting nanocrystals of different size, localization of the wavefunctions was obtained by introducing spill-out, which represents the probability of having the state localized onto the small nanocrystal. A general definition of one-site and two-site carrier multiplication lifetimes that takes into account wavefunction delocalization is reported in Supplementary Section S3.

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Figure 6 | Wavefunction sharing regime. Calculated two-site carrier multiplication lifetimes are reported as a function of the spill-out of the carrier initiating the carrier multiplication for the two considered sets of interacting Si-NCs: Si293H172 × Si35H36 (left panels) and Si293H172 × Si147H100 (right panels). The depicted electron-initiated lifetimes have been extracted from the results of Fig. 3 using weighting factors based on the spill-out computed for each involved state. The results prove that the efficiency of both effects is boosted when both nanostructures share at least 15% of the wavefunction of the initial carrier (spill-out from ~15 to ~85%, which defines the wavefunction sharing regime). At d = 0.4 nm, slow SSQC transitions (with lifetimes of a few nanoseconds) are induced by states of the large nanocrystal that delocalize into thegap of the small nanocrystal.
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Author contributions

M.G., I.M. and S.O. conceived the project. M.G. and I.M. designed and performed simulations with a code developed by M.G., and co-wrote the manuscript. I.M. and S.O. supervised the project. All authors discussed the results and implications and commented on the manuscript at all stages.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permission information is available online at http://www.nature.com/reprints. Correspondence and requests for materials should be addressed to M.G. and I.M.

Competing financial interests

The authors declare no competing financial interests.