Giant suppression of Auger electron cooling in charged semiconductor nanocrystals

Marco Califano

Institute of Microwaves and Photonics,

School of Electronic and Electrical Engineering,

University of Leeds, Leeds LS2 9JT, United Kingdom

Abstract

This letter presents a detailed study of the electron relaxation lifetimes from the excited p-like state into the ground s-like state via Auger cooling in positively and negatively charged CdSe nanocrystals, where the dependence of Auger cooling rates on size, temperature and carrier-carrier interaction effects is investigated. A nearly two-orders-of-magnitude reduction of Auger rates is found in small nanocrystals populated by two electrons and one hole at room temperature. This effect increases with decreasing temperature leading to a total lifetime increase of up to 4 orders of magnitude for $T \sim 10$ K. Such a giant suppression of Auger cooling rates appears to be a general property of semiconductor nanocrystals. A similar reduction of Auger rates at room T is found in negatively charged PbSe nanocrystals as well.

PACS numbers: 71.15.-m, 71.55.-i

Understanding and manipulating carrier dynamics in nanomaterials is of paramount importance for their device application. An excellent example is the quantum cascade laser [1] where accurate design of the width and composition of the component quantum wells, leads to an impressive level of control over sub-band populations, carrier dynamics and emission energies. All this however comes at the expense of a fabrication process involving expensive high precision growth of the semiconductor structure and a lengthy processing of the wafer. Semiconductor nanocrystals (NCs), in contrast, are inexpensive, easy to produce through chemical synthesis and can be manufactured in large quantities. Furthermore, due to their chemical flexibility, they can easily be ordered in 3D superlattices, prepared as close-packed films or incorporated with high densities into sol gel, glasses or polymers. NCs with sizes smaller than the excitonic Bohr radius (strong confinement regime) offer wide tunability of their electronic and optical properties coupled with strong Coulomb interaction between the charge carriers forced to coexist within a small volume due to spatial confinement. In CdSe colloidal NCs, the intraband transition energies between the p-like and the s-like conduction states are of the order of hundreds of meV, and can be tuned by varying the NC size to cover most of the infrared (IR) energy window. Since the CdSe bulk optical phonon energy is $\hbar\omega_{LO} = 26$ meV, according to the adiabatic approximation, the p-like state should have a very long lifetime, as the multi-phonon emission process associated with its decay has a small probability which decreases as the number of phonon emitted increases (this limitation is known as the phonon bottleneck). This is in contrast with the experimental observation of sub-picosecond lifetimes [2]. The absence of a phonon bottleneck has been explained [3, 4] in terms of an Auger-like process whereby the electron excess energy is transferred to the photogenerated hole which is excited to deep valence levels. The hole then undergoes a fast relaxation (with typical times ≤ 1 ps) to the band edge through the denser valence band energy ladder. This hypothesis, although still controversial, has gained increasing evidence culminating with the very recent direct observation of electron-to-hole energy transfer by Hendry and co-workers [5], where time-resolved luminescence and terahertz spectroscopy revealed that the rate of cooling of the photoexcited hole depended critically on the electron excess energy. Whilst such a fast relaxation would benefit devices based on *interband* lasing (emitting or absorbing in the visible range), it is detrimental to applications exploiting *intraband* transitions, such as IR sources and detectors.

Auger cooling (AC) rates have been shown to depend on: (i) the NC size [2, 4] (the

observed lifetimes increased with size remaining however in the sub-picosecond range for NC radii up to 40 Å); (ii) the surface termination (i.e., the nature of the capping groups) [2, 6, 7] (a lifetime increase of up to 2 orders of magnitude in charge-separated, pyridine-capped dots was observed by Sionnest and co-workers [6], whereas the increase observed by Klimov *et al.* [2, 7] in pyridine-capped dots was of only about one order of magnitude); (iii) the NC temperature [6] (only a weak dependence was observed).

A detailed theoretical investigation into the effects of (i) and (iii) on Auger electron relaxation rates in CdSe NCs in the presence of a single additional unbalanced spectator carrier delocalized within the dot (i.e., not trapped in a surface state), is presented using the formalism developed in Ref. [4]. The electron relaxation in the different configurations is schematically presented in Fig. 1. Four CdSe NCs with sizes $R_1 = 10.3$ Å, $R_2 = 14.6$ Å, and $R_3 = 19.2$ Å, and $R_4 = 28$ Å, are considered, spanning the regimes from very strong to intermediate confinement, and a PbSe NC with $R = 15.3$ Å for comparison. The Auger rates are calculated as [4]:

$$1/\tau_i = \frac{\Gamma}{\hbar} \sum_n \frac{| < i|\Delta H|f_n > |^2}{(E_{f_n} - E_i)^2 + (\Gamma/2)^2}, \tag{1}$$

where $|i>$ and $|f_n>$ are the initial and final Auger electronic states, E_{f_n} and E_i are their eigen-energies, and ΔH is the Coulomb interaction. For $T \neq 0$ a Boltzmann average is calculated over the initial states. The single-particle energy levels ε_i are calculated using the plane-wave semiempirical pseudopotential method described in Ref. [8], including spin-orbit effects.

If carrier-carrier interaction effects are neglected (single-particle, SP, approximation), the presence of an additional spectator electron in the conduction band minimum (CBM, the e_s state in Fig. 1) leading to a reduction of the number of available final states by a factor of 1/2 compared with the neutral NC, results in a decrease of the Auger relaxation rate $1/\tau(2e, 1h)$ by the same amount. Similarly, the presence of a hole in one of the two h_s states in Fig. 1, by doubling the number of final states, yields an electron relaxation rate $1/\tau(1e, 2h)$ twice as large as in a neutral NC. Both effects are shown in Figs. 2 (b) and (c) (circles), which also illustrate the very weak temperature dependence exhibited by the SP lifetimes.

When the interactions between carriers are taken into account within the configuration interaction (CI) formalism [9], however, large departures from the above intuitive predictions

are found (see Fig. 2 (b) and (c), squares). The AC lifetimes of a negatively charged dot show a size-dependent increase, compared with the neutral configuration, of about two orders of magnitude for the smallest NC, and of a factor of ~ 10 for the largest dot considered. Furthermore they also exhibit a huge temperature dependence, further increasing by 2-3 orders of magnitude, depending on the NC size, from room temperature to $T = 10$ K, with lifetimes of the order of hundreds of ps already at $T = 100$ K (see Fig. 2 (a), squares). The presence of an additional hole leads instead to less dramatic effects on the AC lifetime, both in terms of magnitude and in terms of temperature dependence (see Fig. 2 (c) and (d)). The rest of this work will therefore concentrate on the more intriguing $\tau(2e, 1h)$.

The very different behaviour between SP and CI results may seem artificial but a simple argument can provide a qualitative explanation for it. The three particles in the initial Auger state (e_s, e_p, h_s) can be in either of 8 spin configurations, in four of which the electrons spins are aligned and in the remaining 4 have opposite direction. The two electrons in the final Auger state (e_s, e_s, h_n) are both in the CBM, therefore they have opposite spins. Transitions between initial states with aligned electron spins and final states with opposite spins would require a spin flip and the corresponding matrix elements in (1) will be small, as Coulomb interactions do not change spin, yielding long lifetimes. On the other hand, transitions not requiring the electron spin to flip can have large matrix elements with correspondingly short lifetimes. The difference between SP and CI results is due to the different nature of multi-particle states in the two approaches. With no interparticle interactions taken into account, the SP initial state consists of a multiplet of 8 degenerate levels each of which is a pure spin state with the electrons having either the same or opposite spin; the CI initial states are instead only two-fold degenerate and, most importantly, resulting from a superposition of different excitonic configurations, are not pure spin states, but receive all large contributions from spin-aligned configurations (such contribution is calculated to be 43% in the case of the lowest energy multiplet). The two electrons in the final Auger state have opposite spins in both SP and CI approaches, the only difference being that, again, in the SP description the states are pure spin states (i.e., they are contributed to 100% by a single spin configuration), whereas CI states receive contributions from many different states, all of which have, however, two electrons with opposite spins (the hole can be in different spin and "orbital" configurations). It is now clear why the two approaches yield such different lifetimes: Auger SP rates contain matrix elements of transitions between pure

spin states with same electron spins, for each initial state energy, whereas CI matrix elements only couple mixed-spin (opposite and aligned) initial states with pure opposite spins final states for all transition energies. The large temperature dependence of the CI rates shown in Fig. 2(a) and (b) originates from the large contribution of spin-aligned configurations to the lowest energy initial state mentioned above, leading to a small rate at low temperature, whilst higher energy levels receive larger contributions from opposite-spin configurations, yielding larger transition rates, which are dominant at room temperature. This is illustrated in Fig. 3. The same arguments can of course not be applied to the case of a NC populated by a single electron-hole pair, as in that configuration there is no restriction on the spin of the particles in the final states. As a consequence CI and SP yield similar AC lifetimes [4].

The first question that needs to be addressed now is whether configuration (a) in Fig. 1 is realistic, i.e., can be achieved in laboratory. Experimentally there are two different ways to excite an electron to the p state: (i) by resonantly photoexciting it *directly* into the excited p state [5] (or to a state above it), or (ii) by photoexciting it first to the ground (s) state and then *re-exciting* it using an IR pump pulse [6, 7]. If an unpaired ground state electron is present during procedure (i), it will have a low probability of absorbing the pump photon and will remain in the s state. The configuration considered here will be achieved *directly* (or after relaxation of the high-energy electron-hole pair, in the case of a larger photoexcitation energy). If procedure (ii) is applied, then, for high enough IR pump fluences, the spectator electron may be excited to the p level together with the photogenerated electron. We calculate a very short lifetime for this configuration, with one of the electrons decaying via AC to the s state in times of the order of tens of fs, bringing the system in the desired long-lived configuration.

The next question that needs to be considered regards the alternative decay channels expected to be most effective. Due to the presence of the additional electron, another relaxation mechanism, namely Auger recombination (AR), where an electron-hole pair recombines non radiatively via energy transfer to a third particle (the electron in the present case), which is excited to high energy states, becomes possible. AR was both experimentally observed [11] and theoretically predicted [4] to occur on time scales of the order of *tens* of ps at room temperature when two electrons and two holes are present, and is therefore expected to provide an upper limit to the lifetime of the p electron. The fact that only one hole is present here (which together with the two electrons forms a negative trion instead of the neutral

bi-exciton investigated in Refs. [11] and [4]), is of no consequence since, as mentioned above, the recombination process is a three-particle process and there is a simple relationship [4] between the lifetime of the state with 2 electrons and 2 holes and that of the states with 2 electrons and 1 hole and 1 electron and 2 holes. The important difference, however, is that both measurements and theoretical calculations for AR were done in a configuration where the two electrons and the two holes occupy the band edge (i.e., are in the respective s states). This turns out to be a fundamental difference with the configuration assumed in the present work, where one of the electrons occupies the excited p level. In fact our calculated AR lifetimes in this case are of the order of *hundreds* of ps at room temperature, therefore larger than the corresponding AC decay times. This means that AC is more efficient than AR, and our calculations show that p state electron lifetimes of the order of ~ 100 ps are achievable in negatively charged NCs at temperatures lower than 150 K (see Fig. 2(a)). A slow relaxation component with lifetimes about two order of magnitude longer than the fast component, representing less than 10% of the total bleaching signal for TOPO- or thiol-capped samples, was indeed observed in CdSe NC at room temperature [6], but was attributed to decay in charge-separated quantum dots. However, a similar slow background was also subsequently observed [7] in ZnS-capped NCs, where electron-hole charge separation is inhibited, and was explained in terms of accumulation of electrons in some long-lived state. In the light of the results presented here it may alternatively be interpreted as having been due to a fraction of the NCs being negatively charged. In fact it is not uncommon for NC ensembles to contain some percentage of charged dots. Furthermore the lifetimes of such slow decay measured in Ref. [6] at 80 K are of the order of a few hundreds of ps, in very good agreement with our results in that temperature range (Fig. 2(a)).

Finally the generality of the predicted suppression of AC rates found in CdSe NCs is investigated by calculating p electron Auger lifetimes in PbSe NCs with $R = 15.3$. PbSe and CdSe NC have fundamentally different crystal and electronic structure, therefore there are no *a priori* simple arguments suggesting any similarity in this effect. A similar increase in the AC lifetime is found in the presence of a spectator electron in the s state at room temperature [12] (see Fig. 2b empty squares), suggesting this effect to be a general property of semiconductor NCs.

In summary, negatively charged CdSe semiconductor NCs with an unpaired electron in the s state exhibit a 3-4 orders of magnitude reduction of AC rates at low T with a long

lived excited electron state lasting ~ 100 ps at temperatures as high as 150 K in small dots.

I'd like to thank A. Franceschetti and A. Zunger for supplying many codes used in this work and for their comments on the manuscript. I also gratefully acknowledge the Royal Society for financial support.

[1] J. Faist, F. Capasso, C. Sirtori, D. L. Sivco, A. L. Hutchinson, M. S. Hybertsen, A. Y. Cho, Phys. Rev. Lett. **76**, 411 (1996).

[2] V. I. Klimov, J. Phys. Chem. B **104**, 6112 (2000).

[3] Al. L. Efros, V. A. Kharchenko, and M. Rosen, Solid State Comm. **93**, 281 (1995).

[4] L.-W. Wang, M. Califano, A. Zunger, and A. Franceschetti, Phys. Rev. Lett. **91**, 056404 (2003).

[5] E. Hendry, M. Koeberg, F. Wang, H. Zhang, C. de Mello Donega, D. Vanmaekelbergh, and M. Bonn, Phys. Rev. Lett. **96**, 057408 (2006).

[6] P. Guyot-Sionnest, M. Shim, C. Matranga, and M. Hines, Phys. Rev. B **60**, R2181 (1999).

[7] V. I. Klimov, A. A. Mikhailovsky, D. W. McBranch, C. A. Leatherdale, and M. G. Bawendi, Phys. Rev. B **61**, R13 349 (2000).

[8] L.-W. Wang and A. Zunger, Phys. Rev. B **51**, 17 398 (1995).

[9] A. Franceschetti, H. Fu, L.-W. Wang and A. Zunger, Phys. Rev. B **60**, 1819 (1999).

[10] As in Ref. [4], AC lifetimes are calculated as a function of the electron *sp* energy splitting $\Delta^e_{sp} = \varepsilon^e_p - \varepsilon^e_s$. The values displayed here and referred to in this work represent averages over a range of Δ^e_{sp} corresponding to a 10% dispersion in the NC size.

[11] V. I. Klimov, A. A. Mikhailovsky, D. W. McBranch, C. A. Leatherdale, and M. G. Bawendi, Science **287**, 1011 (2000).

[12] The temperature dependence in this case is however much weaker (the lifetimes increasing by a factor of 2 between T=300 K and T=10 K) compared to that found for CdSe NCs.

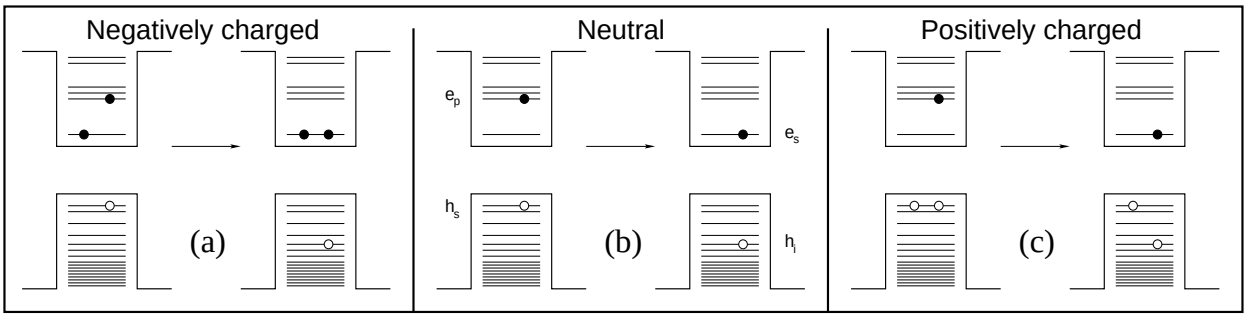

FIG. 1: Schematics of Auger decay in the multi-particle configurations considered in this work: (a) negative trion X^-, (b) neutral exciton X, (c) positive trion X^+.

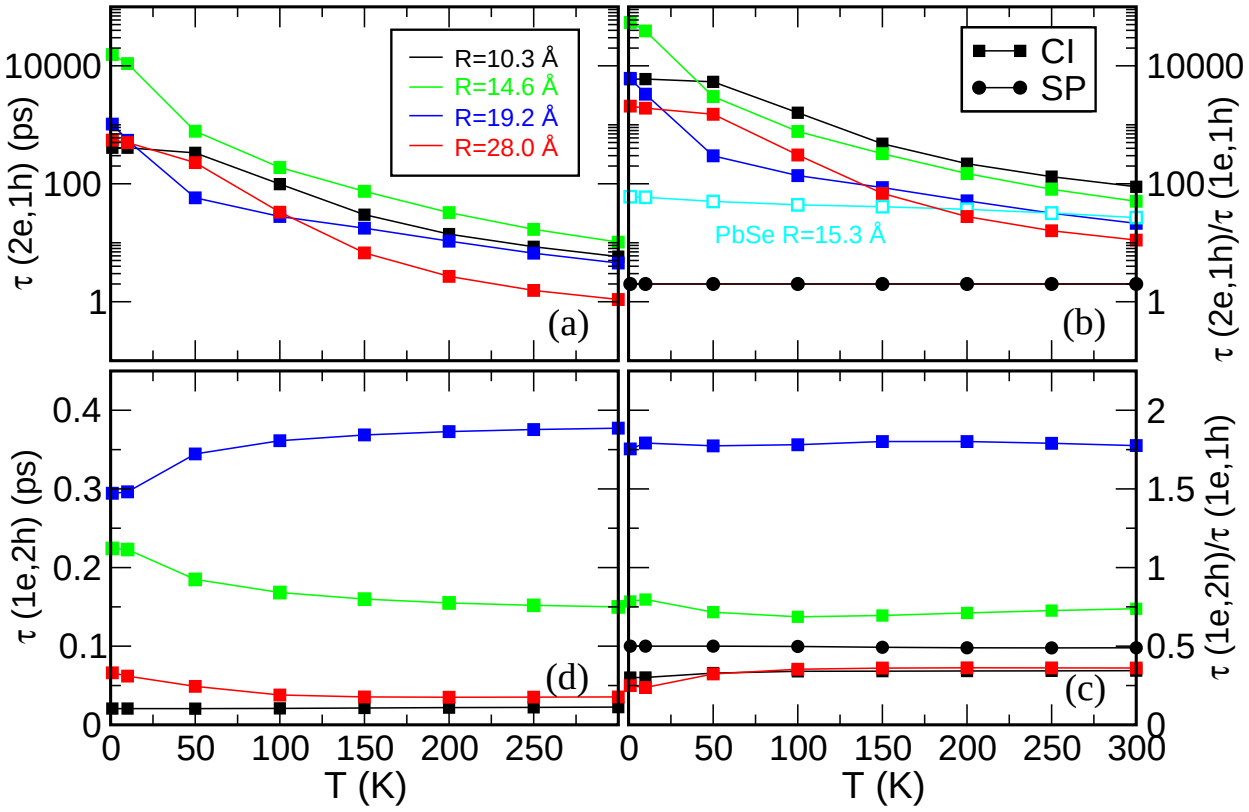

FIG. 2: (Color online): The lifetimes of negatively (a) and positively (d) charged CdSe NCs [10] and their relative increase [(b) and (c), respectively], compared to that of neutral NCs, in the configuration interaction (CI, squares) and single-particle (SP, circles) approaches, as a function of temperature (T) for all sizes considered. All SP curves overlap in (b) and (c). In (b) our calculated CI lifetime as a function of T for a PbSe NC with R=15.3 Å is shown for comparison (empty squares).

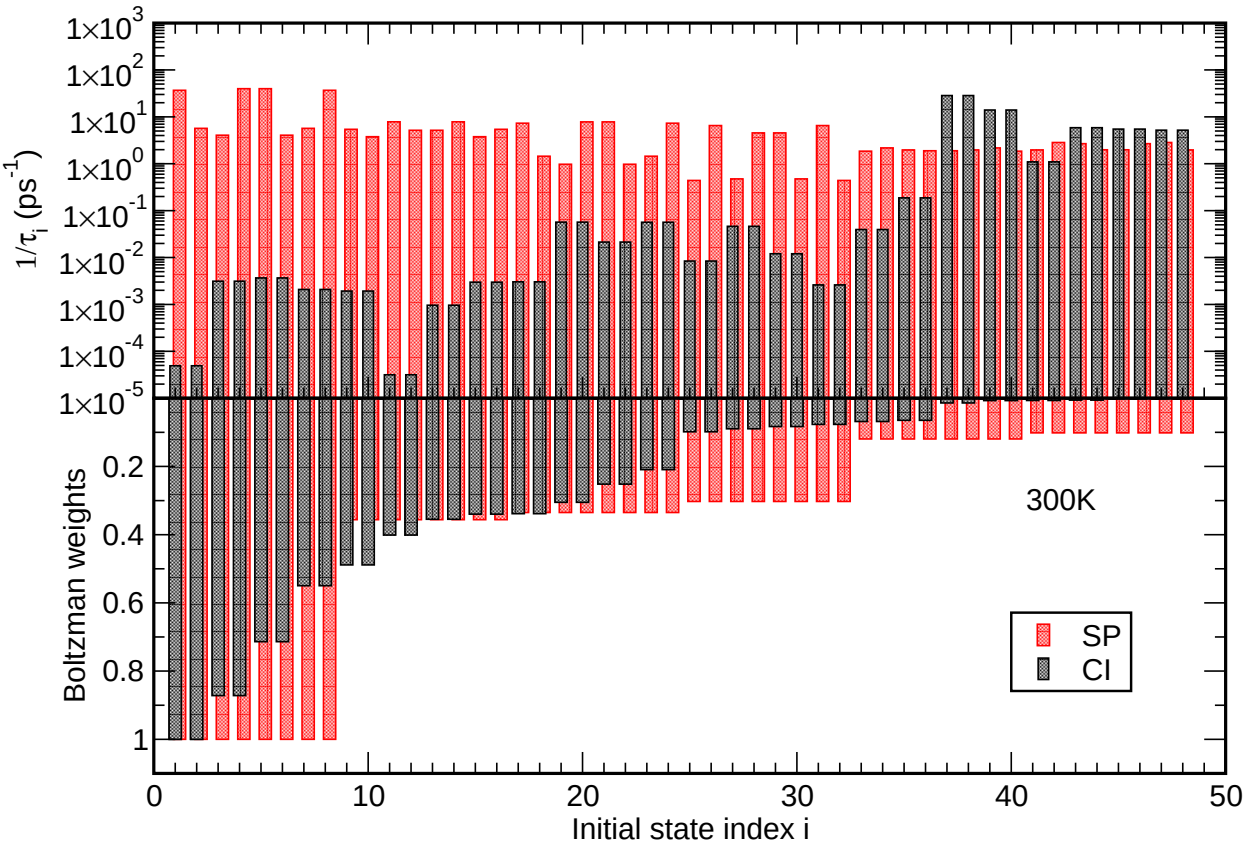

FIG. 3: (Color online) Comparison between the rates $1/\tau_i(2e, 1h)$ (upper panel) in Eq. (1), and the Boltzmann factors at T=300 K (lower panel) calculated, for each initial state i, within the CI and SP approaches (the two sets of results have been offset along the x axis for clarity), for a CdSe NC with $R = 14.6$ Å. The only appreciable Boltzmann weights at T=10 K are those with value =1 at room temperature.