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Dynamics of carrier multiplication in all-inorganic $CsPbI_3$ perovskite nanocrystals

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Carrier multiplication (CM) is a process in which a high-energy free carrier relaxes by generation of an electron-hole pair through band-to-band excitation, rather than dissipating heat by phonon scattering. CM is of interest, as it promises disruptive improvements in photovoltaic energy conversion and light detection. In general, the efficiency and the threshold energy of CM in a particular material are influenced by (i) Coulomb interactions, (ii) efficiency of carrier cooling by phonon scattering, and (iii) initial/final density of states; all these factors are strongly modified by spatial confinement and dielectric screening in nanostructures. Here we discuss dynamics of the recently reported efficient CM in colloidal $CsPbI_3$ perovskite nanocrystals (NCs) prepared by a hot-injection method. Recently, the all-inorganic cesium lead halide perovskite nanocrystals ($CsPbX_3$ NCs, X = Cl, Br, I) attract much attention due to their high outstanding optical properties and application potential[1-3]. Additionally, perovskites have been shown to have slower carrier cooling rates than conventional semiconductors, indicating potential for hot-carrier absorber layer for hot-carrier solar cells.

In general, the carrier cooling rates and mechanisms are well-established for bulk materials, while for quantum dots they are less understood. It was generally believed that for nanoscale materials cooling is considerably slowed down, due to a limited density of states. This so-called "phonon-bottleneck" effect has been shown to be countered by alternative carrier cooling processes, such as Auger-type energy transfer between electrons and holes, leading actually to increased carrier cooling rates[4]. However, this effect is suppressed in perovskite quantum dots, due to the symmetric energy dispersion and small effective mass[5].

In this study, the ultrafast carrier dynamics of $CsPbI_3$ NCs have been determined by means of transient absorption. Cubic-shaped colloidal $CsPbI_3$ NCs with an average edge length of ~10 nm were prepared through a hot-injection synthesis. The size of these NCs is of the order of the exciton Bohr diameter, putting them in the intermediate-confinement regime.
In order to determine the ultrafast carrier dynamics, a series of femtosecond white-light transient absorption experiments at varying excitation photon energies ranging from 1.9 – 4.3 eV have been employed. After photo-excitation, a bleaching feature around the bandgap energy appears due to state-filling of hot carriers that cool down to the bandedge. Fig. 1 shows dynamics of the growth of the bleach signal as function of pump photon energy. The growth time is related to the carrier cooling rate and clearly increases for photon energies up to about 4 eV. From these results we deduce the carrier energy cooling rate of ~1 eV/ps, which is about 3 times slower than for the bulk material[6].
For an excitation photon energy about 0.2 eV larger than the minimum energy required for CM (2 times the bandgap energy E_g) it can be seen that the bleach signal starts to increase faster. This indicates that carriers cool faster to their respective bandedges, which we interpret as being enabled by the CM process, opening an alternative hot carrier relaxation channel with similar or faster rate.

Therefore for high-energy pumping, the hot carrier relaxation process can phenomenologically be described by the competition between the thermal energy loss rate and the CM rate. When carriers are excited with an energy larger than the threshold for CM (4 eV), they have a limited time to undergo CM. This time is determined by the excess energy above the threshold, and the energy cooling rate. The number of carriers generated per absorbed photon can be expressed as , with k_{CM} and k_{Cool} the

carrier multiplication and excess energy cooling rates, respectively[7]. By using the values found for the CM efficiency *N* in Ref. 8, we have determined the CM time constant as 400 fs. This is much slower than what has been expected in other materials. Because of this relatively large time constant, it is also possible to see the effects in the sub-bandgap induced absorption (IA) dynamics, which is directly related to the number of carriers. It has been observed that the growth of the IA signal is longer than the excitation pulse, showing that the CM process still increases the number of carriers after the excitation pulse has finished. This is the first time that such an effect is explicitly observed, which also directly evidences the occurrence of the CM process itself.

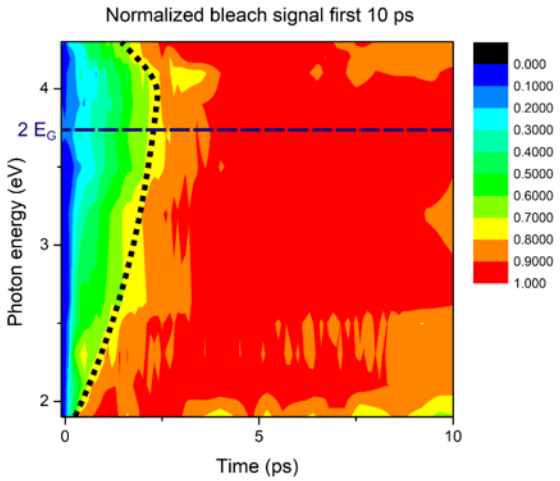

Fig. 1. Contour plot of the normalized bleach signal for the first 10 ps after photo-excitation. For photon energies up to 4 eV the growth time of the signal increases, while for still higher energies it decreases. The blue line indicates the energy of twice the bandgap.

References

1 L. Gomez *et al.* Nanoscale **9**, 631 (2017).
2 C. de Weerd *et al.* Advanced Optical Materials **6**, 1800289 (2018).
3 L. Gomez *et al.* ACS Applied Materials & Interfaces, **40**, 5984-5981 (2018).
4 E. Hendry *et al*. Phys. Rev. Lett. **96**, 057408 (2006)
5 M. Li *et al*. Nat. Comm. **8**, 3-12 (2017)
6 S. A. Bretschneider *et al*. Adv. Mater. **30**, 07312 (2018)
7 E. Rabani *et al*. Chem. Phys. Lett **496**, 227-235 (2010)
8 C. de Weerd *et al.* Nature Communications **9**, 4199 (2018).