Multiexciton dynamics in colloidal nanorods and nanosheets

M. Aerts[1], L.T. Kunneman[1], F.C.M. Spoor[1], J.M. Schins[1], T. Bielewicz[2], C. Klinke[2], M. Tessier[3], H. Heuclin[3], B. Dubertret[3], and L.D.A. Siebbeles[1]

[1] Optolectronic Materials, Department of Chemical Engineering, Delft University of Technology, The Netherlands
[2] Institute of Physical Chemistry, University of Hamburg, Germany
[3] Laboratoire de Physique et d'Etude des Matériaux, CNRS, Université Pierre et Marie Curie, Paris, France

Second order Auger recombination of electron-hole pairs in CdSe nanoplatelets.

We have determined the Auger recombination kinetics of electrons and holes in colloidal CdSe-only and CdSe/CdS/ZnS core/shell nanoplatelets by time-resolved photoluminescence measurements.[1] Excitation densities as high as an average of 18 electron-hole pairs per nanoplatelet were reached. Auger recombination can be described by second-order kinetics. From this we infer that the majority of electrons and holes are bound in the form of neutral excitons, while the fraction of free charges is much smaller, see Fig. 1. The biexciton Auger recombination rate in nanoplatelets is more than one order of magnitude smaller than for quantum dots and nanorods of equal volume. The latter is of advantage for application in lasers, light-emitting diodes and photovoltaics.

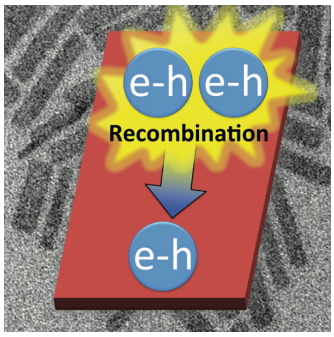

Fig. 1. Electron-hole pairs in CdSe nanosheets behave as neutral excitons that decay via seond order Auger recombination.

Carrier multiplication in PbS nanosheets.

The generation of two or more electron-hole pairs for the absorption of a single energetic photon is of interest for development of highly efficient (up to 44%) solar cells. The efficiency of this carrier multiplication (CM) process depends on several factors, including the competition with cooling, the Coulomb interaction between the hot charge carrier and the trion and the final trion density of states. All these factors might change depending on nanocrystal dimensionality. Previously carrier multiplication has been investigated in lead chalcogenide quantum dots (0D), nanorods (1D) and bulk (3D).[2-4]

We investigated the efficiency of carrier multiplication in two-dimensional PbS nanosheets of 3 to 6 nm thickness using ultrafast optical pump-probe spectroscopy.[5] The efficiency of carrier multiplication in nanosheets is much higher than for quantum dots, nanorods and bulk material. For the thinnest nanosheets the CM efficiency (per unit excess photon energy normalized to the band gap) largely exceeds that of quantum dots and nanorods and is close to the maximum attainable value of 1, see Fig. 2.

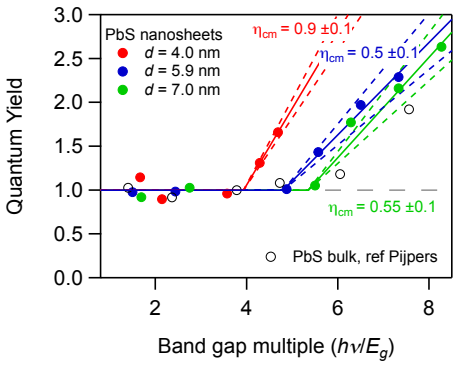

Fig. 2 Quantum yield versus band gap multiple for three PbS nanosheet samples with thicknesses as indicated.

We find efficient bimolecular exciton-exciton Auger recombination, indicative of bound e-h pairs. The high CM efficiency, the confinement-induced band gap, and high photoconductivity make thin PbS nanosheets very attractive for application in photovoltaic devices.

Cooling and Auger recombination of charges in PbSe nanorods.

The cooling and Auger recombination of electron-hole pairs in PbSe quantum dots (QDs) and a series of nanorods (NRs) with similar diameter and varying length was studied by ultrafast pump-probe laser spectroscopy.[6] Hot exciton cooling rates are found to be independent of nanocrystal shape. Auger recombination occurs via cubic third-order kinetics of uncorrelated charges in the QDs and NRs with length up to 29 nm. On increasing the NR length to 52 nm, a crossover to bimolecular exciton decay is found, see Fig. 3. This suggests a spatial extent of the one-dimensional exciton of 30-50 nm, which is significantly smaller than the value of 92 nm for the three-dimensional exciton diameter in bulk PbSe. The Auger decay time increases with NR length, which is beneficial for applications in nanocrystal lasers as well as for generation of free charges in photovoltaics.

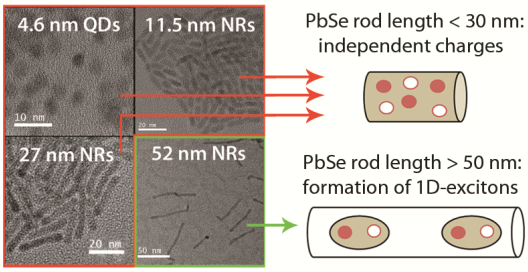

Fig. 3. In longer nanorods electron-hole pairs behave as excitons.

References

(1) Kunneman, L. T.; Tessier, M. D.; Heuclin, H.; Dubertret, B.; Aulin, Y. V.; Grozema, F. C.; Schins, J. M.; Siebbeles, L. D. A. *J. Phys. Chem. Lett.* 2013, *4*, 3574.
(2) Midgett, A. G.; Luther, J. M.; Stewart, J. T.; Smith, D. K.; Padilha, L. A.; Klimov, V. I.; Nozik, A. J.; Beard, M. C. *Nano Lett.* 2013, *13*, 3078.
(3) Padilha, L. A.; Stewart, J. T.; Sandberg, R. L.; Bae, W. K.; Koh, W.-K.; Pietryga, J. M.; Klimov, V. I. *Nano Lett.* 2013, *13*, 1092.
(4) Pijpers, J. J. H.; Ulbricht, R.; Tielrooij, K. J.; Osherov, A.; Golan, Y.; Delerue, C.; Allan, G.; Bonn, M. *Nature Phys.* 2009, *5*, 811.
(5) Aerts, M.; Bielewicz, T.; Klinke, C.; Grozema, F. C.; Houtepen, A. J.; Schins, J. M.; Siebbeles, L. D. A. *submitted for publication.*
(6) Aerts, M.; Spoor, F. C. M.; Grozema, F. C.; Houtepen, A. J.; Schins, J. M.; Siebbeles, L. D. A. *Nano Lett.* 2013, *13*, 4380.