Hyperspectral Analysis of Ultrafast Hot Carrier Dynamics in Pb-chalcogenide Nanocrystals: a Case for Slow Cooling

Pieter Geiregat[1,2], **Arjan Houtepen**[2], **Michiel Aerts**[2], **Christophe Delerue**[4], **Zeger Hens**[1,*] and **Dries van Thourhout**[3]

[1]Department of Inorganic and Physical Chemistry, University of Ghent, Krijgslaan 281, 9000, Gent, Belgium (*E-mail: zeger.hens@ugent.be)

[2]Deparment of Chemistry, Opto-electronic materials section, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

[3]Department of Information Technology, University of Ghent, Sint-Pietersnieuwstraat 41, 9000, Gent, Belgium.

[4] IEMN, Département Institut Supérieure d'Electronique et du Numérique, UMR CNRS, 8520 Lille, France

Lead-chalcogenide (PbX, X=S,Se,Te) nanocrystals are thought to be good candidates for next-generation photovoltaics as they show multiple-exciton generation (MEG), a mechanism first proposed by Nozik et al. for nanoscale systems and experimentally verified in the past decade for many other material systems. Typical ultrafast measurements investigating MEG take place in the near-infrared region of the spectrum, i.e. near the band-gap transition. Since MEG in PbX nanocrystals requires high-energy carriers obtained through short wavelength photo-excitation (typically 3Eg or more, where Eg is the band gap of the semiconductor material), it is worth looking at the band structure and carrier dynamics of PbX materials in that high energy range. We studied the behavior of hot carriers (i.e. with excess energy to the band gap) using hyperspectral transient absorption spectroscopy, where we obtain a 2D map (time and wavelength (energy)) of the carrier cooling in an energy region relevant to the MEG process, i.e. above the MEG energy threshold. Carrier cooling plays an important role in the MEG process and was used e.g. to explain differences in MEG efficiency between PbS and PbSe[1]. Recent phenomenological models attempt to predict MEG based on this competition between MEG and carrier energy loss. Identifying mechanisms that could slow down carrier cooling is thus of great importance in understanding the efficiency of MEG itself. At higher energy, a special critical point in the Brillouin zone for PbX materials is the sigma-point. It is not an energy minimum, but a saddle point where quantization effects take place as evidenced by Houtepen et al.[2] for PbSe nanocrystals. If carriers cool to the sigma point after being created through photo-excitation at higher energies, a momentum change (i.e. a flip of the carrier k-vector) would be required to leave the sigma point and continue cooling to the band gap in the L-point. Such an event could slow down the cooling process, which could make it relevant for the MEG efficiency. A clear trace of this slowdown would be a carrier accumulation in this sigma point which could be evidenced by an occurrence of a 'bleach' feature, i.e. a reduction of the sigma-point absorption through carrier occupation. Using excitation energies above and below the sigma point for different sizes of PbS nanocrystals, we show that carriers indeed accumulate in the sigma point, giving rise to a very fast (300 femtosecond) accumulation and depletion (250 fs) on timescales relevant to the MEG process. We present the details of this work and stress the importance of future detailed studies of the MEG mechanism in the spectral regions where the relevant carrier dynamics take place, i.e. in the UV-VIS. Such new fundamental studies can help to identify the reasons for the high MEG efficiencies obtained in current materials and ease the search for new materials in the future.

References

1. Stewart, J. T. *et al*. Comparison of carrier multiplication yields in PbS and PbSe nanocrystals: the role of competing energy-loss processes. *Nano Lett*. **12,** 622–8 (2012).

2. Koole, R. *et al*. Optical investigation of quantum confinement in PbSe nanocrystals at different points in the Brillouin zone. *Small* **4,** 127–33 (2008)