Excited State Dynamics and Carrier Multiplication Spectroscopy in Quantum Dot and Perovskite Photovoltaic Systems.

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Multiple exciton generation (MEG) in semiconducting quantum dots (QD) is a process which produces multiple charge-carrier pairs from a single excitation. MEG is a possible route to bypass the Shockley-Queisser limit in single-junction solar cells, but it remains challenging to harvest charge-carrier pairs generated by MEG in working photovoltaic devices. However, the initial yields of additional carrier pairs may be reduced due to ultra-fast intraband relaxation processes, which compete with MEG at early times. Another process limiting the efficiency of QD photovoltaic systems is the reverse of MEG – Auger recombination. Auger type processes are also known to be responsible for the acceleration of carrier thermalisation.

In this contribution, we present an ultrafast spectroscopy study of MEG, thermalisation and Auger recombination dynamics in a set of QD and perovskite photovoltaic materials and devices.

We show that the suppression of interband Auger decay, such as biexciton Auger recombination, can achieved with the design of heterostructured core/shell QDs.[1] Particularly we address the simultaneous effect of shell growth on interband Auger recombination and intraband hot-electron cooling. Using multipulse ultrafast IR spectroscopy, we investigate how the growth of a CdS shell affects these two relaxation processes in CdSe/CdS core–shell QDs. We find that Auger losses in the biexciton state are suppressed with increasing shell thickness (fig.1), while hot-electron cooling remains unaffected. Calculations conducted within an eight-band **kp** model confirm the experimental dependence of the biexciton Auger decay on the shell thickness, and provide insights into the factors determining the cooling rate of hot carriers.

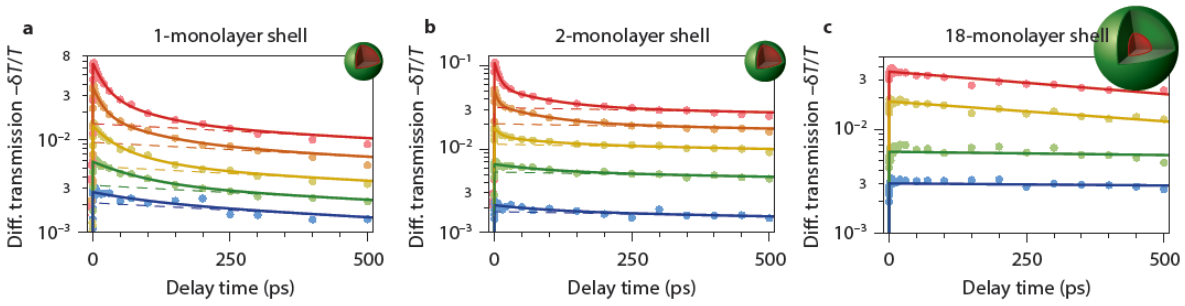

Figure 1. (a) Induced transient mid-IR absorption at the 1S-1P transition (1700 cm^{-1}) in thin-shell QDs with 1 monolayer of CdS, at fluences of the 400 nm pump of different intensity. (b) Transient absorption in thin-shell QDs with 2 monolayers of CdS. (c) Transient absorption in thick-shell QD (18 monolayers). The dashed lines are single-exponential fits to the data points between 200 and 500 ps. We fit the data of the thick-shell QDs (c) to single-exponentials.

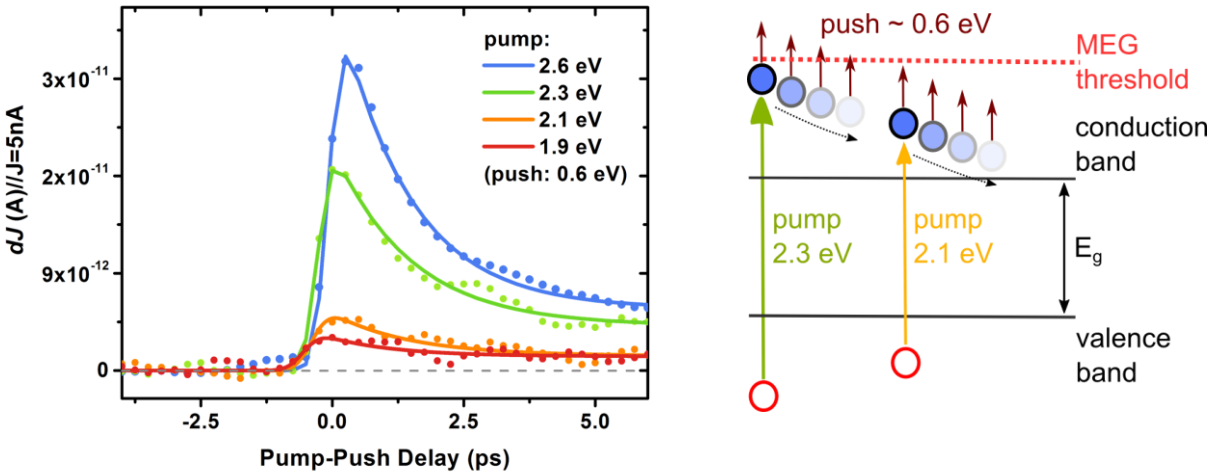

Figure 2. (left) Photocurrent response as a function of time delay between pump and push pulse. The fluence of the pump excitation was adjusted to produce 5 nA for each excitation energy. The transients were corrected for the response at negative delay times. Lines are guide-to-the-eye exponential fits convolved with the 100 fs Gaussian response function of the setup. (right) Illustration of the pump-push photocurrent experiment in a schematic band diagram.

Alternatively, Quantum dots of materials which display reduced carrier cooling rates (e.g. PbTe) can also be promising candidates to increase the impact of MEG in photovoltaic devices. We demonstrate [2] PbTe quantum dot-based solar cells, which produce extractable charge carrier pairs with an external quantum efficiency above 120%, and we estimate an internal quantum efficiency exceeding 150%. Resolving the charge carrier kinetics on the ultra-fast timescale with pump-probe transient absorption and pump-push-photocurrent measurements (fig. 2), we identify a delayed cooling effect above the threshold energy for MEG.

We also observed the effect of organic ligands on the thermalisation of charges in colloidal PbS QDs and hybrid perovskite photovoltaic materials.

References:

[1] M. Boehm et al. *Nano Lett.*, **2015**, *15* (12), pp 7987–7993

[2] F.T. Rabouw et al. *ACS Nano*, **2015**, *9* (10), pp 10366–10376