Femtosecond spectroscopy of advanced photovoltaics : nanocrystals and perovskites

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Exciton dynamics in photovoltaic materials is a fundamentally intriguing process of vital technological importance. The course of free carrier emergence following photon absorption sets the stage for the full cycle of current generation, and means are being devised to employ excess photon energy above the fundamental band gap to enhance the efficiency of this conversion. Characterizing the dissipation mechanisms of this energy is thus very important, and ultrafast transient absorption (TA) measurements have played a central role in recording hot exciton cooling and decay. Accumulating insights highlight the diagnostic importance of signals involving near band-edge exciton transitions in following these processes both in bulk and in nano-crystalline materials, with quantitative analysis being based on effects of state filling and screening induced absorption shifts between pump and probe induced excitations.

Motivated by ongoing controversy concerning the efficiency of Multi Exciton Generation in NCs, to which we have contributed via TA measurements, a broadband femtosecond spectroscopic study of conventional PbSe core NCs was conducted in our lab to test accepted guidelines for extracting transient exciton populations and states of relaxation from TA data. The results question some widely-accepted principles of TA data analysis, such as the assumed linear bleaching of the band edge absorption with the number of relaxed excitons per NC, and the assignment of absorption induced by hot excitons just below this feature. Recent experiments on the recent breakthrough photovoltaic materials the lead halide perovskites further demonstrate the somewhat forgotten similarity of these observations to the photophysics of hot excitons in bulk semiconductor samples.

In our talk I will describe recent experiments which cover the process of exciton cooling and recombination in nanocrystals demonstrating the deviation of the recorded spectra from broadly accepted analysis paradigms. Similar experiments on lead halide perovskite films will be presented which cover in real time the appearance of free carriers and the process of carrier cooling including the coherent activation of optical phonon modes in these materials.