Cation-Dependent Hot Carrier Cooling in Halide Perovskite Nanocrystals

Lead halide perovskites (LHPs) nanocrystals (NCs), owing to their outstanding photophysical properties, have recently emerged as a promising material not only for solar cells but also for lighting and display applications. The photophysical properties of these materials can be further improved by chemical engineering such as cation exchange. Hot carrier (HC) cooling, as one of the key photophysical processes in LHPs, can strongly influence performance of LHPs NCs based devices. Here, we study HC relaxation dynamics in LHP NCs with cesium (Cs), methylammonium (MA, CH₃NH₃⁺), and formamidinium (FA, CH(NH₂)₂⁺) cations by using femtosecond transient absorption spectroscopy. The LHP NCs show excitation intensity and excitation energy-dependent HC cooling. We investigate the details of HC cooling in CsPbBr₃, MAPbBr₃, and FAPbBr₃ at three different excitation energies with low excitation intensity. It takes longer time for the HCs at high energy to relax (cool) to the band edge, compared to the HCs generated by low excitation energy. At the same excitation energy (350 nm, 3.54 eV), all the three LHP NCs show fast HC relaxation (<0.4 ps) with the cooling time and rate in the following order: CsPbBr₃ (0.39 ps, 2.9 meV/fs) > MAPbBr₃ (0.27 ps, 4.6 meV/fs) > FAPbBr₃ (0.21 ps, 5.8 meV/fs). The cation dependence can be explained by stronger interaction between the organic cations with the Pb-Br frameworks compared to the Cs. The revealed cation-dependent HC relaxation process is important for providing cation engineering strategies for developing high performance LHP devices.