Time-Domain Modeling of Excited State Dynamics in Halide Perovskites

Oleg V. Prezhdo[a]

[a] *University of Southern California, Department of Chemistry, Los Angeles, CA 90089, USA*
prezhdo@usc.edu

Photo-induced processes play key roles in photovoltaic and photo-catalytic applications of halide perovskites, requiring understanding of the material's dynamical response to the photo-excitation on atomic and nanometer scales. Our non-adiabatic molecular dynamics techniques,[1] implemented within time-dependent density functional theory,[2-4] allow us to model such non-equilibrium response in the time domain and at the atomistic level. Considering realistic aspects of perovskite structure,[5] we demonstrate that strong interaction at the perovskite/TiO_2 interface facilitates ultrafast charge separation,[6] how dopants can be used to both decrease and increase charge recombination,[7-9] that grain boundaries constitute a major reason for charge losses,[9] that moderate humidity increases charge lifetime, while high humidity accelerates losses,[10] that hole trapping by iodine interstitial, surprisingly, extends carrier lifetime,[11] that collective nature of dipole motions inhibits nonradiative relaxation,[12] that organic cation orientation has a strong effect on inorganic ion diffusion and current-voltage hysteresis,[13] that surface passivation with Lewis base molecules decelerates nonradiative charge recombination by an order of magnitude,[14] that the experimentally observed dual (hot/cold) fluorescence originates from two types of perovskites substructures,[15] that doping with larger cations increases lattice stiffness and slows down nonradiative charge recombination,[16] why PbI_2 rich perovskites show better performance,[17] that halide composition can be used to control charge relaxation,[18] that oxidation states of halide defects strongly influence charge trapping and recombination,[19] and why perovskites exhibit unusual temperature dependence of electron and hole lifetimes.[20]

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