

Charge carrier generation and motion in methylammonium lead iodide perovskite films.

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Perovskite materials mostly based on $\text{CH}_3\text{NH}_3\text{PbI}_3$ are recognized as an excellent low-disorder material for efficient photovoltaic devices and currently are one of the most popular research objects in the field of photovoltaics. Perovskite-based solar cells (PSC) are an emerging, cheap photovoltaic technology, which in the last several years showed a record improvement in efficiency reaching 22%. Specially designed and fabricated perovskites also demonstrate high luminescence quantum efficiencies, therefore are also promising for light emitting devices and lasers. These materials may be fabricated by different techniques typical for organic semiconductors: processing from solutions, vacuum evaporation, crystal growth. Their electronic properties are closer to classical semiconductors: monocrystals show high carrier mobilities reaching thousands of cm^2/vs , high dielectric permittivity causes low exciton binding energies causing dispute if charge carriers are generated by direct band-to-band transitions or via exciton state like in organic materials. Mobility and exciton binding energy values are widely distributed in different reports, particularly for thin films. Thus, carrier generation and the motion character and properties in perovskite still are far from clear understood.

We analyzed charge carrier generation and motion dynamics in organo-lead iodide perovskites by employing time-resolved photoluminescence (PL) spectroscopy, transient photoconductivity and time-delayed collection field techniques. We demonstrate that photoluminescence kinetics of MAPbI_3 perovskites strongly changes with excitation intensity, that was varied over five orders of magnitude. It enabled separation of geminate and nongeminate carrier recombination processes. Geminate recombination dominates at low excitation fluence and determines the initial photoluminescence decay. This decay component is remarkably independent of the material structure and experimental conditions. On a basis of quantum mechanical numerical calculation results, we argue that the fast photoluminescence decay originates from gradual spatial separation of photo-generated weakly bound geminate charge pairs.

Combining transient photocurrent, time-delayed collection field and transient fluorescence techniques along with numerical simulations, we addressed charge carrier trapping processes in prototypical methylammonium lead iodide perovskite films. We demonstrate that carrier mobility decreases with time after their generation, particularly rapidly at low temperatures. We separate influence of energy traps and barriers and demonstrate the energy barriers, most likely formed at crystallite boundaries, rather than traps are mainly responsible for the mobility decay. Being surmountable at room temperature, these barriers still play a key role in determining carrier mobility and its decay. The suggested concept of the energy barriers moves beyond the conventional understanding of carrier mobility, diffusion, and recombination processes in hybrid perovskites.