Ultrafast spectroscopy helps optimize third-generation quantum dot solar cells

Nikolay S. Makarov1, Qianglu Lin2, Hunter McDaniel1, Kirill A. Velizhanin3, Claudiu M. Cirloganu1, Lazaro A. Padilha1, Weon-Kyu Koh1, Nobuhiro Fuké1, Istvan Robel1, Jeffrey M. Pietryga4, Victor I. Klimov1

1Center for Advanced Solar Photophysics, Los Alamos National Labs, Los Alamos, New Mexico, USA
2Department of Chemical Engineering, New Mexico State University, Las Cruces, New Mexico, USA
3Theoretical Division, Los Alamos National Labs, Los Alamos, New Mexico, USA
4Materials & Energy Technology Laboratories, Sharp Corporation, Nara, Japan
makarov@lanl.gov

Abstract—We apply femtosecond transient absorption (TA) and photoluminescence (PL) spectroscopies to study optical properties of various colloidal quantum dots (QDs) relevant to processes such as carrier multiplication (CM), up-conversion (uC) of infrared radiation, and electron transfer (ET) to mesoporous titania. These studies are conducted in the context of applications of QDs as active layers in solar cells. We observe fairly slow (20-40 ns) ET in CuInSe2 QDs, which highlights the need for efficient suppression of deleterious nonradiative processes associated, for example, with surface trapping in poorly passivated QDs. CM quantum yields can be optimized in engineered core/shell PbSe/CdSe QDs to approach 60-80% at ~3 bandgaps, indicating that these QDs could enable photovoltaic efficiencies exceeding the Shockley-Queisser limit, a process that reduces the thermalization losses and increases the efficiency of third-generation solar cells by harvesting of low-energy solar photons.

Keywords—Quantum dot; electron transfer; up-conversion; carrier multiplication; Auger recombination;

I. INTRODUCTION

Every hour the sun delivers to the earth the amount of energy which can, in principle, satisfy the global needs of the humanity for the entire year. Currently available solar technologies, however, have limited efficiency, which is one of the major factors preventing their wide spread use. Two mechanisms for losses – hot carrier loss and transparency loss affect light harvesting on the blue and red sides of the energy gap of the active absorbing material in solar cell, respectively. Photons below bandgap “leak” through a regular solar cell and do not contribute to the power conversion. Photons well above bandgap excite hot charge carriers which undergo rapid cooling, or thermalization, such that only an electron-hole exciton result in charge separation and thus contribute to photocurrent. Hot-carrier losses can be reduced using CM – a process where Coulombic collisions of hot photexcited carriers with electrons within the valence-band excite them across the energy gap, generating additional electron-hole pairs. The transparency loss can be mitigated using stacked cells with different gaps (multi-junction cells). Another interesting approach is uC whereby two low-energy, sub-bandgap photons are converted into higher-energy, above-bandgap exciton, which, in principle, can boost the power conversion efficiency above 50%.

II. RESULTS AND DISCUSSION

To overcome the limitations of the existing photovoltaics, we explore CM, uC, and ET in various groups of colloidal QDs using TA and time-resolved (TR) PL spectroscopies. First, we explore excitation fluence-dependent TA dynamics to deduce size- and composition dependence of the Auger recombination biexciton lifetimes. We find the biexciton lifetimes to be almost independent on QDs composition and scale linearly with the QDs volume, which points to generality (material independent volume scaling) of Auger lifetimes in QDs. Then, we combine analysis of TA and TR PL dynamics to study CM in various monocomponent QDs, alloyed QDs, and especially engineered core/shell nanostructures. We show that for the monocomponent and alloyed QDs, CM is similar across various types of nanomaterials, and is mostly defined by a competition between the non-CM cooling rates of hot carriers and CM lifetimes. Significant improvements in CM can be achieved using especially engineered core/shell QDs with slower thermalization. Similar core/shell QDs allow for efficient Auger-uC, a process relying on Auger recombination, whereby two low-energy excitons are converted into a single high-energy hot exciton. Thanks to reduced rates of intra-band relaxation, the shell-localized excitons recombine radiatively, resulting in the up-converted photoluminescence – a convenient way to observe and characterize the uC. Finally, we study size-dependent ET in QD-sensitized mp-TiO2 films, and show that while this process appears to be fairly slow, high electron extraction efficiency can still be achieved in well-passivated QDs thanks to long lifetimes of neutral excitons.

Our study demonstrates that the use of CM and Auger-uC in the especially engineered core/shell nanostructures represents a promising approach for enhancing photoconversion efficiency of third-generation solar cells by allowing for lower thermalization losses and more efficient harvesting of low-energy solar photons.