Ultrafast Spectroscopy of CuInSeS Colloidal Quantum Dots: Auger Recombination, Carrier Multiplication, and Electron Transfer

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Abstract—We study size- and composition-dependent optical properties of CuInSeS quantum dots, including biexciton Auger recombination, carrier multiplication, and electron transfer to TiO2. We show that this material is promising for photovoltaic applications due to a fairly large carrier multiplication yields and efficient electron transfer, which is fast compared to nonradiative losses.

Keywords—Quantum dot; carrier multiplication; Auger recombination; electron transfer

I. INTRODUCTION

The ever-changing landscape of global energy supply and demand makes it difficult to foresee the next breakthrough technology for lower-cost and higher-efficiency renewable energy conversion or efficient means of energy storage and usage. Heterojunctions of colloidal semiconductor quantum dots (QDs), and wide-gap metal oxides are employed in a number of energy applications from light-emitting diodes and solar cells to solar fuels and CO2 reduction. The efficient separation of electrons and holes at the metal oxide/QD junction is critical to these applications, as it must outcompete various loss mechanisms such as surface trapping. Mesoporous titania (mp-TiO2) is one of the most promising and frequently investigated wide-gap (3.2 eV) metal oxide semiconductor because of its low fabrication cost, high stability, large surface-area-to-volume ratio, and attractive optoelectronic properties. Here, we investigate optical properties of CuInSeS quantum dots (CISeS) QDs and QD-sensitized mp-TiO2 films, which have recently been utilized in solar cells achieving power conversion efficiencies above 5%.

II. RESULTS AND DISCUSSION

We perform comprehensive transient absorption (TA) and time-resolved photoluminescence (PL) measurements on QDs with dimensions from 3 to 5 nm to study QD size- and composition-dependence of various excited charge-carrier processes, including biexciton Auger recombination, carrier multiplication (CM), and electron transfer (ET) to TiO2. Biexciton decay is found to be similar to that in similarly sized CdSe QDs of the same volume, which supports the conclusion on the generality of size-dependent trends in Auger recombination across QDs of various compositions. CM quantum yields approach 20% indicating that this material could, in principle, enable photovoltaic efficiencies exceeding the Shockley-Queisser limit. CM threshold though is relatively large, ~3.8 bandgaps, somewhat larger than that of previously reported PbSe and PbS QDs and quantum rods. Size-dependent ET (20-40 ns) is fairly slow, which highlights the need for efficient suppression of competing nonradiative processes that can be associated, for example, with surface traps in poorly passivated QDs. We also demonstrate the importance of having a redox electrolyte present (used in QD-sensitized solar cells for hole extraction) during ET studies in order to prevent the build-up of long-lived charges in the QDs. If the electron transfer is measured in air or argon (conditions typically used in literature studies), the measured TA and PL decay is dominated by a fast, tens of picoseconds component. This decay, however, is not due to electron transfer but rather Auger recombination of an exciton in the presence of an extra hole left behind in the QD following electron transfer to the mp-TiO2. We show that for accurate evaluation of charge transfer rates it is important to ensure a fast re-neutralization of the QDs following electron transfer, which can be accomplished by immersing film samples into the polysulfide electrolyte used in sensitized solar cells for hole extraction and transport. The PL transients measured in this case are dominated by 20-40 ns relaxation, which provides a direct measure of the ET time constant.

III. CONCLUDING REMARKS

Our measurements help understand the fundamental photophysical properties of the novel CISeS QDs. They also have important implications for applications of these QDs in sensitized solar cells and indicate directions for improving the performance of existing QD-based photovoltaic devices.

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