

# Multiple Exciton Generation and Carrier Dynamic in Electronically coupled PbSe Semiconductor Nanocrystals

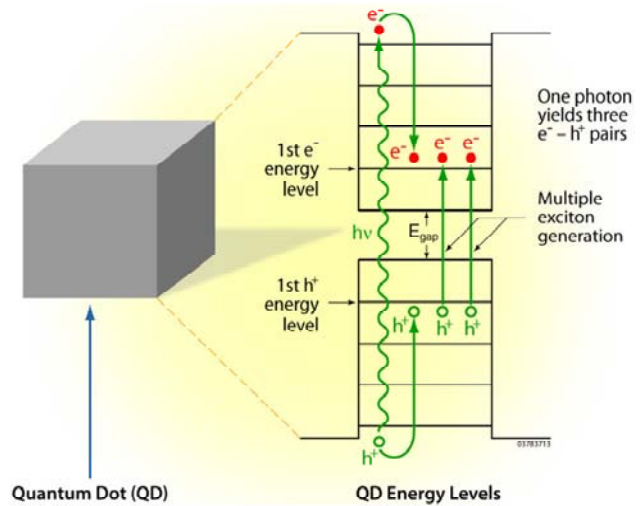
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Multiple exciton generation (MEG) is a process that occurs in semiconductor nanocrystals where one highly energetic photon produces multiple charge carriers and can significantly enhance solar energy conversion efficiencies. Using ultrafast transient absorption spectroscopy we studied MEG in two series of chemically-treated PbSe nanocrystal (NC) films. We find that the average number of excitons produced per absorbed photon varies between 1.0 and 2.4 ( $\pm 0.2$ ) at a photon energy of  $\sim 4E_g$  for films consisting of 3.7 nm NCs, and between 1.1 and 1.6 ( $\pm 0.1$ ) at  $h\nu \sim 5E_g$  for films consisting of 7.4 nm NCs. The variations in MEG depend upon the size of the NCs and the chemical treatment used to electronically couple the NCs in each film. The single and multi-exciton lifetimes also change with the chemical treatment: biexciton lifetimes increase with stronger inter-NC electronic coupling and exciton delocalization, while single exciton lifetimes decrease after most treatments relative to the same NCs in solution. These results imply that a better understanding of the effects of surface chemistry on film doping, NC carrier dynamics, and inter-NC interactions is necessary to build solar energy conversion devices that can harvest the multiple carriers produced by MEG. Our results show that the MEG efficiency is very sensitive to the condition of the NC surface as well as to NC size, and suggest that the wide range of MEG efficiencies reported in the recent literature may be a result of uncontrolled differences in NC surface chemistry.

We have developed a simple, ITO/PbSe-NC/metal photovoltaic cell via a Schottky junction at the back electrode that produces a large short-circuit photocurrent ( $> 20 \text{ mA cm}^{-2}$ ) and solar conversion efficiencies of  $\sim >2\%$ . The PbSe NCs films are chemically treated using 1,2-ethanedithiol (EDT) to produce highly photoconductive films that yield EQEs of 65% across the visible and up to 25% in the infrared region of the solar spectrum, with IQEs approaching 90%. A layer-by-layer technique is used to deposit the films and produces smooth, high quality, reproducible films. We have measured the  $n$  and  $k$  of our layer-by-layer PbSe nanocrystal films and constructed an optical model in order to understand the optical generation rate in our devices.

We discuss limitations of our device structure in observing MEG photocurrents and report progress towards overcoming those limitations. These encouraging results provide incentive to study and understand the carrier dynamics in these films.



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