

Semiconductor Quantum Dots for Applications to Advanced Concepts for Solar Photon Conversion to Electricity and Solar Fuels

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In order to utilize solar power for the production of solar electricity and solar fuels on a global scale, it will be necessary to develop solar photon conversion systems that have an appropriate combination of high efficiency (delivered watts/m²) and low capital cost (\$/m²). One potential, long-term approach to attain high conversion efficiencies above the well-known Shockley-Queisser thermodynamic limit of 32% is to utilize the unique properties of quantum dot/rod (QD/QR) nanostructures to control the relaxation dynamics of photogenerated carriers to produce either enhanced photocurrent through efficient photogenerated electron-hole pair multiplication or enhanced photopotential through hot electron transport and transfer processes. To achieve these desirable effects it is necessary to understand and control the dynamics of hot electron and hole relaxation, cooling, charge transport, and interfacial charge transfer of the photogenerated carriers. These fundamental dynamics in various bulk and nanoscale semiconductors have been studied for many years using transient absorption, photoluminescence, photocurrent, and THz spectroscopy with fs to ns time resolution. The prediction that the generation of more than one electron-hole pair (which exist as excitons in size-quantized nanostructures) per absorbed photon would be an efficient process in QDs and QRs has been confirmed over the past several years in different classes of materials and their architectures. Very efficient and ultrafast multiple exciton generation (MEG), also called Carrier Multiplication (CM), from absorbed single high energy photons has been reported in Group IV-VI and Group IV semiconductors and associated solar photon conversion devices for solar electricity and solar fuels (e.g. H₂) production. Selected aspects of this

work will be summarized and recent advances will be discussed. Finally, the analogous MEG effect in molecules (called singlet fission) and its use in molecular-based solar cells will also be discussed.

We demonstrate MEG in PbS|CdS Janus-like hetero-nanostructures is enhanced over that of single-component and core/shell nanocrystal architectures, achieving 1.2 excitons per absorbed photon at 2.2 times the PbS band gap. We attribute the enhanced MEG to the asymmetric nature of the hetero-nanostructure that results in an increase in the effective Coulomb interaction that drives MEG and a reduction of the competing hot exciton cooling rate. Slowed cooling occurs through the interaction of hot-holes with a manifold of valence band interfacial states having character of both PbS and CdS, as evidenced by photoluminescence studies. We find, using transient photocurrent spectroscopy, that the MEG characteristics of the individual nanostructures are maintained in conductive arrays and demonstrate that these quasi-spherical PbS|CdS nanocrystals can be incorporated as the main absorber layer in functional solid-state solar cell architectures. Finally, based upon our analysis, we provide design rules for the next generation of engineered nanocrystals to further improve the MEG characteristics.

We also studied the optical absorption enhancement in colloidal solutions of PbS QDs upon ligand exchange from oleate to a series of cinnamate ligands. By combining experiments and *ab initio* simulations, we elucidate physical parameters that govern the optical absorption enhancement. We find that within the cinnamate/PbS QD system the optical absorption enhancement scales linearly with the HOMO/LUMO gap of the ligand and not their electron donating/withdrawing character, indicating that the ligand/QD coupling occurs equally efficient between QD VB/ligand HOMO levels and the QD CB/ligand LUMO levels. Disruption of the conjugation that connects the benzene ring and its substituents to the QD core causes a reduction of the electronic coupling between the benzene ring and the QD core electronic states. While the overall absorption enhancement is greater in the substituted benzene thiolate ligand class, we find a similar linear dependence of the absorption enhancement with ligand HOMO-LUMO gap. We

demonstrate that the optical enhancement can be used to extract the ligand binding isotherms for a given QD/ligand complex by following the absorption enhancement during ligand exchange.