

MAR16-2015-030105

Abstract for an Invited Paper
for the MAR16 Meeting of
the American Physical Society

Hole transfer dynamics from QDs to tethered ferrocene derivatives

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Quantum dots (QDs) have shown particular promise in recent years as light absorbers in solar energy conversion schemes. However, in solution junction solar devices such as QD-sensitized solar cells and photocatalytic water splitting systems, efficiencies are often limited by hole transfer from the photoexcited QD. This process is sluggish and can lead to oxidative photocorrosion of the QD material. In order to design highly efficient nanocrystal systems with hole transfer rates that out-compete these undesirable processes, a fundamental understanding of the parameters that control these rates is imperative.

We have developed a model system to study charge transfer from QDs to surface bound acceptors, to fundamentally understand the charge transfer processes for QD systems, namely electronic coupling between the donor and acceptor and the thermodynamic driving force for the hole transfer process. Specifically, we examine hole transfer from the nearly spherical CdSe-core CdS-shell QDs with photoluminescence (PL) quantum yields over 80% to ferrocene derivatives bound to the QD surface via an alkane thiol linker. In this system, we mitigate the ill-defined nonradiative charge dynamic pathways that are intrinsic to native CdSe cores, and then controllably engineer on the surface charge acceptors with well-defined oxidation potentials, spatial distribution, and quantity. By measuring the PL lifetime decay and calibrating the number of hole acceptor ligands per QD via quantitative ^1H NMR, we extracted the hole transfer rate per acceptor. This rate per acceptor could be varied over four orders of magnitude by changing the coupling between donor and acceptor through modulations in the CdS shell thickness and alkane chain length of the molecule. Furthermore, owing to the large number of acceptors on the surface, we achieve systems in which $\sim 99\%$ of the photoexcited holes are transferred to these well-defined mediators.

We further mapped the relationship between the thermodynamic driving force and hole transfer rate. We systematically tune the driving force over nearly 1 eV by varying the redox potentials of the ferrocene ligands through functionalization of the cyclopentadiene rings. Our results show a monotonic increase in rate as a function of the increasing driving force with no observed inverted region. This behavior is understood by considering the residual electron in the QD conduction band, which could exhibit intraband excitations coupled to the hole transfer, thus creating a many-state system that would eliminate the inverted region. The resulting relationship between rate and energetic driving force for hole transfer can be used to design QD-molecular systems that maximize interfacial charge transfer rates while minimizing energetic losses associated with the driving force.