

Extracting Charge Carriers from Colloidal Quantum Dots: Challenges and New Perspectives

Nanometer-sized inorganic semiconductor crystals, better known as “quantum dots”, offer a high potential for many opto-electronic applications, but have so far been successfully applied mostly in light-emitting schemes, where advances in surface passivation have served to limit non-radiative recombination processes. Whereas the solid-state formalism is very well suited to describe the photophysics of quantum dots idealized as perfect particle-in-a-spherical-box models, there are challenges associated with understanding the behavior of quantum dots as electron donors and/or acceptors, a regime quite clearly outside the realm of the idealized infinite potential barrier at the surface of the quantum dot. In other words, in applications involving interfacial charge transfer between the semiconductor confined band states and outside redox-active species (photovoltaics, photocatalysis, etc...), such approaches where the colloidal quantum dots are effectively insulated from their surroundings cannot be used, and the complexity associated with surface states needs to be explicitly addressed. Our research program aims at characterizing this behavior in detail by designing molecular electron- acceptors that are tuned for specific single-electron-transfer regimes. One interesting scheme involving interfacial charge-transfer reactions is the dye-sensitized solar cell (DSSC) setup, where quantum dots are used as sensitizers for wide bandgap semiconductors such as TiO_2 . A popular approach relies on the solution-based sulfide/polysulfide redox couple to close the circuit between the QD-sensitized photoanode and the counter electrode, which yields stable cells under working operation. Unfortunately, this redox system also severely limits the efficiency of QD-DSSCs by cutting the open-circuit potential to more than half the optimal value that could be extracted from cadmium chalcogenide QDs. Here we report the interaction between a variety of stable nitroxide free radicals and II-VI chalcogenide quantum dots. These free radicals are shown to act as efficient quenchers of the intrinsic photoluminescence of colloidal quantum dots, an effect directly associated to efficient hole transfers from the photoexcited QDs to the free radicals, suggesting the potential that these compounds could offer as redox couples substitutes in QD-DSSCs. By changing the structure and functionalization of these radicals, different aspects of electronic charge transfer can be monitored, including a wide tunability of the interfacial charge-transfer rate constants, from sub-picosecond to tens of nanoseconds. We also show the role that inhomogeneously distributed surface traps play in interfacial photophysics of colloidal quantum dots, and how reasonable physical models can be obtained to describe the photophysical behavior of the QD-radicals pairs.

