Thermal Quenching in II-VI Semiconductor Nanocrystals: What Causes It and How to Eliminate It

D. F. Kelley, X. Cai, K. Gong, J. E. Martin, L. S. Rohwer

Efficient down-conversion of blue light into the green and red spectral regions is necessary to facilitate the use of solid state light sources for lighting and display purposes. The luminescence from quantum dots has high quantum yield and is tunable, which makes them in many ways, ideal materials for this down-conversion. However, the II-VI quantum dots (such as CdSe, ZnSe and CdTe) typically suffer from "thermal quenching"; the reversible loss of luminescence quantum yield with increasing temperature. In this paper we show that thermal quenching has dynamic (affecting the luminescence lifetimes) and static (affecting the fraction of particles that are bright versus dark) components. We show how synthetic and surface derivatization procedures can be used to nearly eliminate both types of thermal quenching. The temperature dependence of luminescence quantum yields and time resolved luminescence decays, as well as room temperature transient absorption spectroscopy are used elucidate the quenching mechanisms. Dynamic thermal quenching is due to thermally activated trapping dynamics that occur on the same timescale as the radiative lifetime. This paper primarily focuses on static thermal quenching and several different mechanisms are considered. We show that the dominant mechanism involves thermal promotion of valence band electrons to empty chalcogenide P orbitals on the particle surfaces. This leaves a hole in the valence band and subsequent photoexcitation produces a positive trion. The trion undergoes relatively rapid nonradiative Auger relaxation, rendering the particle dark. The differences in the extents of thermal quenching between different surface compositions, different types of particles and different surface ligands can be understood in terms of the density of empty surface chalcogenide orbitals and the valence band energies. Finally, we show how these empty surface orbitals can be eliminated in core/shell/shell particles.