

DFT Insights into Mechanisms of Brightening of CdSe Quantum Dots by Hydrides

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Colloidal Quantum Dots (QDs) have attracted the attention of the scientific community for their unique properties, including one pot synthesis methods, abundant precursors/solvents, size-tunable optical response, and high photostability. QD's ability to harvest and emit light is extremely sensitive to their complicated surface chemistry. In experiments it was observed that QD's quantum yield increases by order of magnitude when they were treated with hydrides. However, the complicated surface chemistry makes understanding the mechanism of this enhancement unclear. We computationally investigate the effect of hydride anion (H⁻) on the geometry, the electronic structure, and optical spectra of CdSe QDs. Our density functional theory (DFT) calculations reveal that the hydrides interacting with the QD's surface result in three main structural effects: the release of hydrogen selenide, reduction of Cd, and bonding to surface Cd. The last scenario is the most pronounced in the Cd-enriched QDs and leads to a significant increase of the oscillator strength of S₁, as compared to similar QDs ligated by amine ligands. Overall, hydrides very efficient saturate both Cd- and Se-associated dangling bonds and eliminate the hole and electron trap states from the band gap of the QD.