ELECTRONIC STRUCTURE OF CHARGED NON-STOICHIOMETRIC QUANTUM DOTS

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We use density functional theory (DFT) and time-dependent DFT(TD-DFT) to explore the effect of charge on the ground and excited state properties of non-stoichiometric quantum dots CdSe QDs. The charge is introduced by two methods: (i) creating a dangling bond at the QD surface by removing a caping ligand (Cl- or H+) and (ii) electron injection to fully passivated $Cd_{28}Se_{17}Cl_{22}$ (Cd-rich) and $Cd_{17}Se_{28}H_{22}$ (Se-rich) QDs resulting in a net charge of +1 or -1. Our calculations show that ligand removal has a similar effect on the electronic structure as electron injection to the Cd-rich and hole injection to the Se-rich QD. Thus, both Cd-rich QDs with -1 charge and with a removed ligand exhibit hole trap states in the energy gap. Such trap states redshift and significantly reduce intensity of the lowest-energy optical transitions, compared to the fully passivated neutral Cd-rich QDs. As such, a coupling of bright excitons to a charge brought either by direct injection or via a dangling bond results in red-shifted optically inactive excitonic states. For Se-rich QDs, both +1 charge and a removed ligand introduce electron trap states in the energy gap, leading to the redshifted optically weak or inactive transitions. In contrast, coupling of -1 charge to optically inactive excitons in Se-rich QDs strongly increases optical activity of the lowest-energy states.