

Oxidation of PbSe Quantum Dots: Insights from First-Principle Calculations

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Extensive research has been done for the past 10 years in studying lead chalcogenides quantum dots due to their potentiality to serve as optoelectronic devices. It is known that quantum dots (QDs) exposed to air commonly demonstrate decrease in their photoluminescence (PL). However, mechanisms of QD's oxidation causing the PL quenching are not fully understood. We use density functional theory (DFT) and time dependent DFT (TDDFT) to investigate the interaction of oxygen in its molecular, atomic, and ionic forms with different surfaces of lead selenide (PbSe) QDs and its effect on the electronic and optical properties of QDs. Our calculations show that oxygen concentrations and positions at the QD facets govern an appearance of trap states at the QD's bandgap, although these states are not directly localized on oxygens. For 2-nm PbSe QDs, as the concentration of oxygen atoms at the surface increases, atomic oxygen attempts to penetrate inside the QD, substituting and shifting seleniums in the outer shell of the QD. In contrast, oxygen ions attempt to bind and then remove Pb ions from the QD's surface, resulting in Se-enriched QDs of smaller sizes, when exposed to O^{2-} at high concentrations. In both cases, excess of Se at the surface associates with the Se-localized trap states with low optical activity, which should result in PL quenching. With time, surface Se reacts with a solvent and leaves the surface, while oxygen substitutes its position at the lattice. In this case, the PbO surface shell is formed around the PbSe core that is responsible for highly optically active states at the edge of the bandgap of the QD, which increase the PL. Therefore, we proposed that the mechanism proceeded via this path after quenching to regain PL of the QD.