Ab initio Study on Excited State Properties of Pb-halide Bridged PbSe Nanoplatelets (NPL)

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Recently quasi two-dimensional (2D) semiconductor materials composed of ordered arrays of quantum dots (QDs) have attracted special attention due to their better control over photoexcited process important for photovoltaic applications, including carrier multiplication and energy relaxation mediated by phonons. In particular, PbSe 2D nanoplates (NPLs) have been recently synthesized with precisely controllable thickness via halide precursors, where $PbCl_2$ moieties attached to the (111) and (110) surfaces of QDs form intra-particle bridges, leading to the growth of the (100) face-dominated NPLs.[1] While chlorine passivation is critical to the growth and thickness control of these NPLs, its role in photoexcited dynamics is still unclear. We study phonon-mediated dynamics in these 2 nm PbSe NPLs using DFT based non-adiabatic dynamics combined with simplified trajectory surface hopping method. The energy band gap of NPLs is at L symmetry point (~0.96 eV), where it is 1.36 eV at the Γ-point. Similar as in 2-nm PbSe QDs,[2] NPLs also show roughly symmetric valance and conduction band near the bandgap edge. Orbitals associated with Pb-Cl-Pb bridging contribute only deeper to the valance band. Consequently, bridging has a significant impact on relaxation of hot holes. Our calculations show that in the case of hot electron excitation, hole relaxation rate is faster than those of electrons, while both are almost the same in symmetric excitation.

Reference:

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(2) Kilina, S. V.; Kilin, D. S.; Prezhdo, O. V. Breaking the Phonon Bottleneck in PbSe and CdSe Quantum Dots: Time-Domain Density Functional Theory of Charge Carrier Relaxation. *ACS Nano* **2009**, *3*, 93–99.