Influence of the Surface of a Nanocrystal on its Electronic and Phononic Properties

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Over the past thirty years, it has been consistently observed that surface engineering of colloidal nanocrystals (NC) is key to their performance parameters To gain insight into the origins of these improvements, we investigate the effect of the surface termination on the electron-phonon coupling in lead sulfide (PbS) NCs. We perform *ab initio* molecular dynamics (AIMD) on experimentally-relevant sized NCs constructed with thiol or Cl, Br, and I anion surfaces. Analysis of the time-dependent evolution of the electronic energies and wavefunctions extracted from the AIMD indicate a suppression of the thermal broadening of optical transitions and multi-phonon mediated electronic transitions going from thiol to halide termination. Analysis of the phonon density of states and electronic wavefunctions indicate that the suppression of electron-phonon coupling upon halide termination stems from a reduction of the overlap of the electronic wavefunctions with large thermal displacement phonon modes resulting from the NC surface. Our work helps to explain why electron-phonon interactions are crucial to charge carrier dynamics in NCs and how surface engineering can be applied to systematically control their electronic and phononic properties.