Modeling Charge Transfer over Organic/Inorganic Interfaces in Nanocomposites

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Attaching dye molecules to the surface of the quantum dots (QDs) has potential to improve efficiency for both solar-to-electrical and solar-to-chemical energy conversion processes. In both types of applications, the charge transfer from the photoexcited QD to the molecule play a crucial role. Applying DFT-based non-adiabatic molecular dynamics (NAMD) and the Fewest Switching Surface Hopping (FSSH) methods, we have revealed ultrafast hole transfer (~10 fs) from the CdSe QD to the Ru(II) dye, following by a slow component (~100 fs) associated with the redistribution of population throughout QD states. The ultrafast interfacial QD-to-dye hole transfer is rationalized by strong non-adiabatic couplings between the QD surface states and the high frequency vibrational modes of isocyanide ligands in the dye. We also have studied the effect of the complex heterostructures of Janus QDs, where a half of the QD is made from CdSe and another half is from PbSe forming an interface along a specific crystalline direction. Our calculations show that the Pb-enriched (111) crystalline direction of the interface enhances optical response of the QDs. The hole transfer is found to be very sensitive to the polarity of the environment, rather than the ways of dye's attachment to the surface. Our calculations also explain the role of surface ligands in electron transfer from photoexcited PbS QDs to perylenediimide acceptors: The experimentally detected rate variation by over a factor of 4 stems from both ligand-induced changes in the free energy for charge transfer and electrostatic interactions that alter perylenediimide electron acceptor orientation on QD surfaces. Overall, our calculations provide atomistic insights into QD-to-molecule charge transfer, giving researchers an additional handle for enhancing QD photocatalysis by means of the QD interfaces and QD-molecule engineering.