

Quantum confinement controlled photo-induced charge-transfer excitons in carbon nanotube and semiconducting nanostructure interfaces

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Formation of photo-induced charge-transfer (CT) states are the foundation of photovoltaic (PV) devices like solar cells, as it is necessary to separate the generated charges to be collected for later use (**Figure 1**). CT formation is contributed by several aspects: morphology of interface, details of electronic structure, ability of materials to interact with light and lattice vibrations. Atomistic understanding of these processes and properties paves the way for improving CT efficiency, lowering cost, and toxicity of materials for PV applications, as well as allowing design of PV materials for extreme environments. Both carbon nanotubes (CNT) and semiconducting nanowires (NW) have shown the ability to absorb light, and conduct electricity along their axial directions. This property makes both nanostructures (NS) ideal for applications in PV devices.

Unrestricted density functional theory (DFT) and Perdew Burke Ernzerhof (PBE) were used in Vienna Ab-initio Simulation Package (VASP) software as a way to characterize the optical absorption spectra, modeled in the basis of Kohn-Sham orbital pairs, occupied and unoccupied.

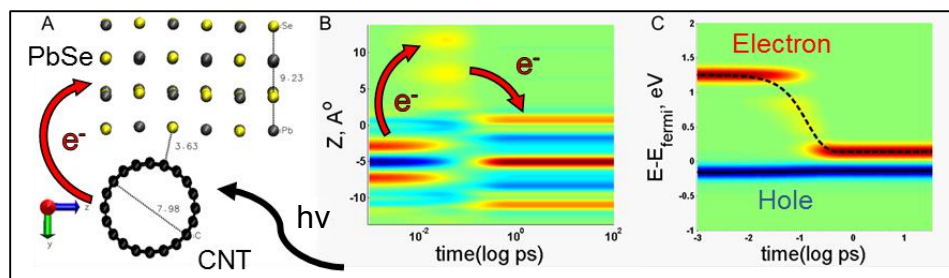


Figure 1: Panel A is the ZY plane of the 3D model of (10,0) CNT and (100) PbSe NW. Panel B is the distribution in space of the electron (red) and hole (blue) over time for the photo-induced transition HOMO-1 →

LUMO+9. Panel C is the distribution in energy of the electron and hole over time for the same transition. Panel A corresponds to B by taking femtosecond “snapshots” of the electron/hole density on A during dynamics and “compressing” it into a vertical “slice” of B. By this method, the top half of B and the bottom half of B correspond to PbSe and CNT respectively. In B, the electron moves to PbSe for approximately 10 femtoseconds before relaxing.

For each atomistic structure representing a nanointerface, the ground state properties are modeled first, then excitation by a photon, and finally the relaxation of the exciton through lattice vibrations and electron transfer. This project models the change of electronic states’ occupation over time, using atomistic computation by combination of DFT-based nonadiabatic molecular dynamics and numerical propagation of the von-Neumann equation for the density matrix. Lastly, nuclear degrees of freedom (DOF) are considered small perturbations that induce the non-radiative dissipation of energy from the electronic DOF. The rates of such dissipation are assessed by using on-the-fly non-adiabatic coupling of nuclear DOF to the electronic DOF along an ab initio molecular dynamics trajectory. This material is based upon work supported by the National Science Foundation under CHE - 1413614 "Theoretical Insights into Chemical Functionalization of Carbon Nanotubes: from Chirality Separation to Photoexcited Dynamics "