Effect of ligands and edge type on hot carrier relaxation in graphene quantum dots

Jonathan P. Trinastic[1], Iek-Heng Chu[2], and Hai-Ping Cheng[1]

[1]*Department of Physics and Quantum Theory Project, University of Florida, Gainesville, FL 32611*
[2]*Department of Physics, University of California – San Diego, San Diego, CA 92093*

Graphene quantum dots (GQDs) have many possible applications in a variety of research areas, including photovoltaics, catalysis, and sensors. Experimental research has suggested the existence of long hot carrier relaxation times on the order of 100-200 ps due to carrier-phonon interactions (Mueller et al 2011, *Nano Lett,* **11**(1), 56-60), however little theoretical work has examined phonon-induced relaxation and its size or geometry dependence in these systems. We examine hot carrier relaxation due to lattice vibrations in GQDs of varying size and edge type (armchair or zigzag), using time-dependent density functional theory (TDDFT) to calculate nonadiabatic coupling between excitations. Employing the reduced density matrix method to calculate relaxation rates, we find a 100 ps relaxation time constant for low-lying excited states in a GQD with 132 carbon atoms, matching experiment. We also find that carbon-chain ligands attached to the GQD edges significantly change the nonadiabatic coupling and reduce nonradiative recombination rates to the ground state by an order of magnitude. GQDs with zigzag edges demonstrate a significantly longer hot carrier lifetime in low-lying excited states that approach the nanosecond time scale, suggesting the possibility of engineering a phonon bottleneck through geometry modification. Acknowledgment: This work is supported by DOE/BES DE-FG02-02ER45995.