Time-Domain Ab Initio Study of Nonradiative Decay in a Narrow Graphene Ribbon

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We investigate nonradiative decay in the (16,16) armchair graphene nanoribbon (GNR) using surface-hopping with decoherence in a time-dependent Kohn–Sham scheme. The lowest singlet excitation decays within 300 ps in the ideal GNR by coupling to the 1450 cm⁻¹ disorder mode associated with edges. The C₂-insertion defect doubles the decay rate. Compared to carbon nanotubes (CNTs), GNRs are more anharmonic and show faster phonon-induced pure dephasing of electronic transitions. Defects relieve strain better and, therefore, exhibit weaker electron–phonon coupling in GNRs than CNTs. The slower nonradiative decay of GNRs compared to similar size CNTs makes GNRs better candidates for the semiconductor applications.

The isolation of a single atomic layer of graphite, or a graphene sheet, in 2004 instigated global efforts to study the synthesis, features, and device applications of this quasi-two-dimensional structure. The intense interest has led to the discovery of new physical properties, applications, including logic gates and field-effect transistors, switches, and photovoltaic systems and superconductors. Following graphene sheets, graphene nanoribbons (GNR) were synthesized. The quantum confinement and edge effects created in GNRs by reduced dimensionality generate novel properties. The (16,16) armchair GNR was chosen for the present study, as it is one of the best candidates for the semiconductor applications.

We investigate nonradiative decay in the (16,16) armchair graphene nanoribbon (GNR) using surface-hopping with decoherence in a time-dependent Kohn–Sham scheme. The lowest singlet excitation decays within 300 ps in the ideal GNR by coupling to the 1450 cm⁻¹ disorder mode associated with edges. The C₂-insertion defect doubles the decay rate. Compared to carbon nanotubes (CNTs), GNRs are more anharmonic and show faster phonon-induced pure dephasing of electronic transitions. Defects relieve strain better and, therefore, exhibit weaker electron–phonon coupling in GNRs than CNTs. The slower nonradiative decay of GNRs compared to similar size CNTs makes GNRs better candidates for the semiconductor applications.

The simulation utilizes the quantum-classical fewest-switches surface-hopping (FSSH) technique implemented within the time-dependent Kohn–Sham (TDKS) scheme and including the semiclassical correction for quantum decoherence. The method and related approaches were used previously to model electron–phonon relaxation in CNTs. The approach provides a detailed ab initio picture of the relaxation dynamics at the atomistic level and in time-domain. The FSSH-TDKS theory was implemented within the Vienna ab initio simulations package. The electronic structure was obtained using a converged plane-wave basis, the Perdew–Wang generalized gradient approximation, and projector-augmented-wave pseudopotentials. The more advanced treatments of electronic excitations, e.g., Bethe–Salpeter and multiconfiguration approaches, and phonon dynamics, e.g., multiconfiguration Hartree and quantized Hamilton dynamics, are too computationally expensive for the present systems.

The (16,16) armchair GNR was chosen for the present study, Figure 1. The GNR was cut from an infinite layer of graphene. The dangling bonds at the edges were saturated with hydrogen atoms. The GNR geometry was fully relaxed using the standard VASP procedures and including optimization of both the unit cell size in the periodic dimension and atomic coordinates.
Periodic boundary conditions were used along the length of the GNR, and 8 Å of vacuum were included in the directions perpendicular to the ribbon length to avoid fictitious interactions. Following geometry optimization, the systems were brought up to room temperature by repeated velocity rescaling. Then, microcanonical trajectories were run in the ground electronic state. The initial conditions for the TDKS-FSSH simulations were sampled from these trajectories.

To investigate the effect of disruptions to the hexagonal lattice, the 7557 defect was introduced. It involves insertion of a C—C dimer into the lattice hexagon, creating two five- and two seven-membered rings. The defect alters both the electronic and geometric structure of the GNR, Figure 1b. It causes an out-of-plane buckling of the lattice and creates a strongly localized electronic transition with the excitation energy below that of the ideal ribbon, Table 1.

Figure 2 presents a 1 ps long trajectory of the first excitation energies for the ideal (16,16) GNR and the GNR with the 7557 defect. The defect lowers the excitation energy, as expected.

The energy fluctuation is notably smaller for the defect than the ideal GNR. This is in contrast to CNTs, which showed a slightly larger oscillation of the defect energy relative to the ideal tube. The difference arises from the phonon properties of the ideal GNR and CNT rather than defects, which are roughly similar in the two materials. Less stiff than CNTs, GNRs move with a larger amplitude. The energy fluctuations seen in the defected GNR are more random than those in the ideal ribbon. This result is verified by the Fourier transforms (FT) of the autocorrelation functions of the excitation energies, Figure 3. The FT were obtained on the basis of the microcanonical ground state trajectories. A much wider range of phonon modes is seen with the defect than the ideal GNR. The latter couples almost exclusively to the disorder mode near 1450 cm\(^{-1}\), which has been detected experimentally near the edges of single graphene sheets. A weak signal is seen from the radial breathing-like modes.

## Table 1: Average Excitation Energy, Absolute Value of NA Coupling, Pure Dephasing Time, and Relaxation Time for the Ideal (16,16) GNR and the 7557 Defect

<table>
<thead>
<tr>
<th>GNR</th>
<th>excitation (eV)</th>
<th>coupling(^a) (meV)</th>
<th>dephasing (fs)</th>
<th>relaxation (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ideal</td>
<td>0.76 ± 0.079</td>
<td>0.92 ± 1.3</td>
<td>24</td>
<td>309</td>
</tr>
<tr>
<td>7557</td>
<td>0.59 ± 0.045</td>
<td>1.2 ± 1.6</td>
<td>42</td>
<td>124</td>
</tr>
</tbody>
</table>

\(^a\) The large standard deviation indicates large fluctuations in the coupling magnitude, which remains positive by definition.
Franck dephasing time of the defect corresponds to a larger localizes the phonon modes and the electronic excitation, Figure 1b. Correspondingly, the phonon-induced pure dephasing relaxation by approximately 2.5. This is due to three factors. The NA coupling in both materials is created by the $\pi$-lobes closer together and increases the overlap. Thus, the NA coupling is stronger in CNTs than in GNRs. On the other hand, the phonon-induced pure dephasing of the electronic transitions is slower in tubes than ribbons. Since ribbons are more flexible than tubes, electronic excitations of GNRs create larger geometric distortions, resulting in increased Stokes’ shifts, broader Franck–Condon progressions, wide lines, and faster pure dephasing. The fact that the dephasing in GNRs is facilitated by the anharmonic disorder mode, Figure 3, favors faster dephasing as well.

The magnitude of the NA coupling depends on the overlap of the $\pi$-electron orbitals, and therefore, it should decrease with increasing CNT diameter and decreasing curvature. On the other hand, all GNRs are relatively flat, and the overlap argument does not apply. The NA coupling may depend on the ribbon chirality. For instance, zigzag ribbons have localized edge states\textsuperscript{11} that are qualitatively different from the delocalized states of the armchair ribbons, Figure 1a. Generally, localized states create larger electron–phonon coupling. The NA coupling and other properties of localized states are relatively independent of the ribbon width, while delocalized states show strong width dependence. In particular, theoretical analyses of armchair GNRs showed strong width dependence of the band gap energy.\textsuperscript{12,13} Therefore, one may expect that fluorescence studies on ensembles of GNRs should show a broad distribution of lifetimes even for ribbons of similar widths, due to the variation of the excited state properties with ribbon chirality.

Our simulations predict that excited electronic states of narrow GNRs decay nonradiatively within hundreds of picoseconds. The results generated previously with this technique for CNTs were in good agreement with experiments.\textsuperscript{33,35} As the simulation was carried out in a vacuum, our results should be compared to suspended GNRs.\textsuperscript{9} Interactions with substrate can provide additional nonradiative decay channels and affect the pure dephasing time. Our simulation assumes that the ground state recovery occurs from the lowest energy singlet excited state. The assumption is based on the fact that the decay of higher energy singlet excitations to the lowest excitation is fast. The recent study on the ultrafast carrier dynamics in graphene showed that hot carriers relax through the (quasi-)continuum of electronic states within several picoseconds,\textsuperscript{49} helping to validate the assumption. It should be noted that the extremely small spin–orbit coupling predicted for graphene\textsuperscript{50} makes the nonradiative decay by intersystem crossing to the triplet manifold unlikely.

In conclusion, we have investigated the nonradiative decay of excited electrons in a narrow graphene ribbon with and without a common defect. The lowest excited state in the GNR decays in approximately 300 ps, or about half as quickly as in small diameter CNTs. The 7557 defect creates a local geometric distortion to the lattice and increases the decay rate by a factor of 2. The nonradiative relaxation occurs primarily via the disorder mode near 1450 cm\textsuperscript{-1} in the ideal GNR and by a wide range of modes in the defected GNR. Since all GNRs should have approximately the same NA coupling due to lack of curvature, the nonradiative decay time should scale directly with the excitation energy.

References and Notes

(20) Crespi, A. Nanotechnology 2008, 19 (26), 265401.