Two-dimensional electronic spectroscopy of graphene nanoribbons in organic solution

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Abstract. We unravel the electronic structure of graphene nanoribbons in solution using two-dimensional electronic spectroscopy. We identify different excitons, their vibrational couplings and find that exciton diffusion or relaxation among the exciton sublevels takes place in ~ 300 fs.

1 Introduction

Graphene nanoribbons (GNRs) are nanometer-wide graphene structures that, unlike graphene itself, possess a bandgap due to quantum confinement along the ribbon width. Their optical, electronic and magnetic properties are all controllable by the width and edge structures of GNRs, making them excellent candidates for next generation semiconducting materials [1]. On the other hand, strong π - π interactions between GNRs lead to the formation of aggregates with different properties than the intrinsic ones. Chemically synthesized GNRs dispersed in organic solvents have been reported, but spectroscopic evidence of substantial aggregation remained present [2, 3].

Very recently, GNRs with armchair-edge structure with 1-1.7 nm width and variable lengths up to 60 nm were synthesized (Fig. 1). Thanks to the addition of bulky side groups very high solubility was achieved and steady state absorption, photoluminescence (PL) as well as transient absorption (TA) spectroscopies suggest that the solutions consist mainly of isolated single ribbons, even for lengths of 60 nm [4]. The linear absorption spectra of the GNRs in toluene (Fig. 1) are very broad and yet structured, suggesting that a rich electronic structure might be present.

Here we employ two-dimensional electronic spectroscopy (2DES) to study the electronic structure and dynamics of the 60 nm long GNR in solution. The 2DES setup is based on the partially collinear pump-probe geometry using a birefringent interferometer for the generation of the phase-locked pump pulse pair and employs ≈ 10 fs broadband pulses generated with visible (VIS, 530-730 nm) and near infrared (NIR, 650-1050 nm) non-collinear OPAs [5, 6].

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Figure 1. Molecular structure of the GNR and its absorption and PL spectra in toluene. The spectra are independent of the length while redshifted from the monomer. The absorption spectrum shows a convoluted structure of peaks, while the lowest main exciton peak (735 nm) is identified in the PL.

2 Results and discussion

The 2DES maps (Fig. 2) reveal that the broad absorption spectrum of the GNR consists of a series of many sharp peaks. In NIR region, we identify a diagonally stretched signal extending from 690 to 760 nm with intense exciton peak at 735 nm. There is an off-diagonal cross peak between 690 and 760 nm both of which cannot be assigned to vibration coupled transitions of the intense main lowest energy exciton at 735 nm, as there are no off-diagonal peaks connecting them to 735 nm to prove any coupling. From excitation wavelength dependent PL measurements, we also identify a relatively weak emission peak at 760 nm by 690 and 760 nm excitations. Thus the diagonally stretched feature is actually consisting of two exciton species: an intense main exciton at 735 nm and a relatively weak one at 690 and 760 nm. The weak exciton species is likely to be conformationally different from the main one.

Figure 2. 2DES maps of GNR in VIS and NIR at $t_2 = 1$ ps for parallel and perpendicular polarization combinations. At 735 nm, which exactly matches the PL peak in Fig. 1, the lowest main exciton peak is seen. The main exciton transition coupled to vibrational modes of D, G, 2D, D+G, 2G and 3D form these mesh grid-like structures. The diagonal peaks at 690, 760 nm and their cross peak are assigned to a different exciton species.

The VIS 2DES maps reveal various diagonal and off-diagonal peaks that indicate strong coupling between the main exciton at 735 nm and Raman active vibrational modes (D = 1320, G = 1610 cm^{-1} and their combinations) of graphene. Computing the expected separation

between different Raman modes and the main exciton at 735 nm, we find that the mesh grid-like structure shown in VIS is well described by vibronic coupling between the main exciton and vibrational modes which are also observed by resonance Raman. From polarization dependence, we found that intense off-diagonal peaks at $3D \rightarrow 2D$, $D+G \rightarrow G$ of the main exciton and $690 \text{ nm} \rightarrow 760 \text{ nm}$ of the weak exciton are stimulated emissions (SE), all of them shifted by energy of D mode from excitations. Broadband TA measurements featured intense oscillatory amplitude mainly coming from the D mode, further confirming the strong vibrational coupling. In connection, Raman D band intensities of GNRs are known to be sensitive to the widths, edge structures and positions of side groups that determine the exciton transitions [7]. Analogous $2D \rightarrow D$ SE peak would be also expected. However, the lack of this SE cross peak is explained by efficient energy transfer to the nearby state of weak exciton species at 690 nm, which is also confirmed by PL measurements.

The dynamic behaviours of different coordinates in the 2DES maps (Fig. 3) show that all diagonal and the off-diagonal SE peaks present a $\sim 300 \text{ fs}$ decay, in contrast to the other off-diagonal peaks (only bleach and some eventual overlapping excited state absorption). This partial decay of the SE signals is likely due to diffusion of the excitons or relaxation among the intraexcitonic sublevels which is also suggested in single wall carbon nanotube [8].

Figure 3. The fast $\approx 300 \text{ fs}$ decays shown in diagonal (left) and off-diagonal stimulated emission peaks (middle) suggest exciton diffusion or intraexcitonic relaxation.

In summary, VIS and NIR 2DES were used to unravel the excited state structure of highly soluble GNRs with 60 nm length and 1-1.7 nm width in toluene solution, revealing the presence of two different exciton species and strong vibrational coupling between the excitons and the Raman active vibrational modes of graphene. Finally, we observed exciton diffusion or intraexcitonic relaxation on the $\sim 300 \text{ fs}$ timescale.

References

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