

## Exciton-exciton annihilation and Stimulated Emission in Graphene Nanoribbons

Giancarlo Soavi<sup>1</sup>, Stefano Dal Conte<sup>1</sup>, Cristian Manzoni<sup>2</sup>, Francesco Scotognella<sup>1</sup>, Akimitsu Narita<sup>3</sup>, Xinliang Feng<sup>3</sup>, Klaus Müllen<sup>3</sup>, Giulio Cerullo<sup>1,2</sup>

1. Dipartimento di Fisica, Politecnico di Milano, Piazza L. Da Vinci 32, 20133 Milano, Italy
2. IFN-CNR, Piazza L. Da Vinci 32, 20133 Milano, Italy
3. Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany  
[giancarlo.soavi@polimi.it](mailto:giancarlo.soavi@polimi.it)

Although graphene displays extraordinary electronic properties, with its massless electrons (Dirac fermions) propagating for sub-micrometer distances in a ballistic regime without scattering, the absence of an energy-gap between valence and conduction bands is a severe limitation to its applications in electronics and optoelectronics. A possible solution to this problem is to induce a band-gap opening via quantum confinement, as for the one-dimensional Carbon Nanotubes (CNTs) and Graphene Nanoribbons (GNRs). Both systems attract great interest since they maintain the outstanding transport properties of graphene with the advantage of a sizable diameter or width-dependent band-gap. While CNTs have been intensely investigated over more than 20 years, studies on GNRs are still at their early stage and only little is known about their photophysical properties. Recent works demonstrate that, in analogy with CNTs, also in GNRs the optical absorption is dominated by excitons with high binding energy [1].

Here we apply femtosecond pump-probe spectroscopy to study the ultrafast temporal evolution of excitons in narrow (~1 nm) GNRs with cove-type edge structures, which were bottom-up synthesized in solution (THF). In particular, fluence dependent measurements for excitation at 570 nm, i.e. resonant with the first excitonic transition (inset fig. 1b), clearly highlight the appearance of a fast decay component of the ground-state bleaching (GSB) signal for increasing fluences (inset fig.1a). As for CNTs [2], this fluence-dependent ultrafast dynamics can be assigned to exciton-exciton annihilation, a mechanism that is greatly enhanced in quantum-confined systems due to relaxation of the momentum conservation and spatial confinement. Interestingly, the spectroscopic signature of this recombination process comes along with the formation of a positive differential transmission ( $\Delta T/T$ ) signal red-shifted with respect to the exciton GSB, at approximately 650 nm. This is evidenced by the change in sign of the dynamics at 650 nm (fig 1a) and the  $\Delta T/T$  spectra at 100 ps pump-probe delay (fig. 1b). Since this delayed feature is energetically far from the exciton absorption and it does not appear in the ground-state absorption spectrum, we assign it to Stimulated Emission (SE). Similar results have been obtained for nanocrystal quantum dots [3], where the optical gain has been assigned to SE of bi-excitons [4]. Extending this result to our experimental data we find that bi-excitons in GNRs should have extremely high binding energy, in the order of 240 meV, even larger than the values obtained for CNTs [5]. These results provide new fundamental insights into the photophysics of GNRs and confirm their great potential for optoelectronics and laser applications.

### References

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**Figure 1.** (a) Pump-probe dynamics of GNRs for different pump fluences at 650 nm and (inset) normalized dynamics at 600 nm. (b)  $\Delta T/T$  spectra at different pump fluences for a fixed pump-probe delay of 100 ps and (inset) ground-state absorption spectrum of the sample.

