

Raman fingerprints of atomically precise graphene nanoribbons: insights from ab-initio simulations

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Graphene nanoribbons (GNRs) are attracting increasing attention as highly promising candidates for nano- and opto-electronics. This interest has been boosted by the possibility to achieve ultra-narrow and structurally well-defined GNRs by bottom-up techniques, where the precise structural pattern is dictated by molecular precursors. While atomically precise GNRs on a metallic substrate can now be produced by advanced and well-established techniques [1], liquid-phase processable GNRs with atomically precise edges have been only recently obtained by solution-mediated methods [2]. Such systems are characterized by cove-shape morphology, where a C ring periodically decorates the zigzag edge. In addition, the solubility is provided by functionalizing the edges with long alkyl chains. The characterization of these novel nanostructures is, however, at the early stages. In particular, they show peculiar Raman spectra [2], above all in the low-energy region, which cannot be easily interpreted in light of the previous studies on ideal armchair- and zigzag-edged GNRs [3].

Here we present a theoretical investigation of the vibrational properties of such cove-shaped GNRs, and compare our result with multi-wavelength Raman spectroscopy data [4]. Simulations were performed using a first-principle plane-wave pseudopotential implementation of Density-Functional Theory (DFT) and Density-Functional Perturbation Theory (DFPT), as available in the Quantum ESPRESSO package [5]. Raman intensities were calculated using the second-order response method [6], within the Placzek approximation. We find that both the edge geometry and the functional groups influence the Radial-Like Breathing Mode (RLBM), which is significantly redshifted with respect to the case of the zigzag backbone, in agreement with experimental observations [2,4]. The cove-shape morphology of the edge is instead mainly responsible for the activation of the D peak, which is not present in purely zigzag GNRs [3,7].

References

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[7] This research was supported by the Federal Ministry for Education and Research of Germany (Alexander von Humboldt Foundation Sofja Kovalevskaja Award), the ESF project GOSPEL (Ref. No. 09-EuroGRAPHENE-FP-001); the Italian Ministry of Research through the national projects PRIN-GRAF (Grant No. 20105ZZTSE) and FIRB-FLASHit (Grant No. RBF12SWOJ). Computer time was granted by PRACE at the CINECA Supercomputing Center (Grant No. PRA06 1348), and by the Center for Functional Nanomaterials at Brookhaven National Laboratory (U.S. DoE, Office of Basic Energy Sciences, contract No. DE-SC0012704).