Probing Excitonic Effects in Chevron-like Graphene Nanoribbons

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Graphene nanoribbons (GNRs) are raising great interest as they exhibit width-tunable band-gaps, while maintaining the outstanding properties of graphene. Covalent self-assembly of suitable molecular precursors [1] is a powerful approach to obtain atomical control on GNRs width, shape and chemical composition, opening the way to a precise tuning of their properties.

Recently, we demonstrated the importance of excitons in determining the optical properties of armchair-GNRs[2]. For chevron-GNRs (chGNRs), which have less pronounced 1D character, the role of excitons is not yet established. In fact, Bronner et al. [3] explained the dominant feature observed in their EELS spectrum in terms of HOMO-LUMO gap. The absence of any excitonic feature is indeed puzzling, as they should be present in EEL-spectra, in particular for confined molecular systems[4].

In this work, we investigate the optical and electronic properties of chAGNR, comparing the results of ab-initio DFT calculations with those of RDS and EELS measurements.
chGNR were grown on Au monocrystals, following the recipe reported in literature[1]. In the case of RDS measurements chGNR were grown on the Au(788) vicinal surface, which induced their preferential alignment along the surface steps. In the case of EELS instead, chGNRs were grown on the Au(111) surface, thus obtaining a distribution of equivalent GNR-domains with six-fold symmetry[1]. The combined analysis of RDS and EELS spectra provides a full description of chGNR properties in terms of differential (RDS) and averaged (EELS) adsorbate dielectric function ε_{ads}.

For EELS, we find it crucial to optimize the experimental conditions in order to maximize the weight of the adsorbate contribution relative to that of the gold surface plasmon[5]. Both, optical and electronic spectra were analyzed applying the three-phase dielectric model. We modeled ε_{ads} with four damped harmonic oscillator located at 2.2 eV (2.3 for HREELS), 2.8, 3.4 and 4.4 eV. The experimental adsorbate dielectric function is in good agreement with theoretical results, demonstrating the fundamental role played by excitons in determining the optical and electronic properties of chGNRs.

References

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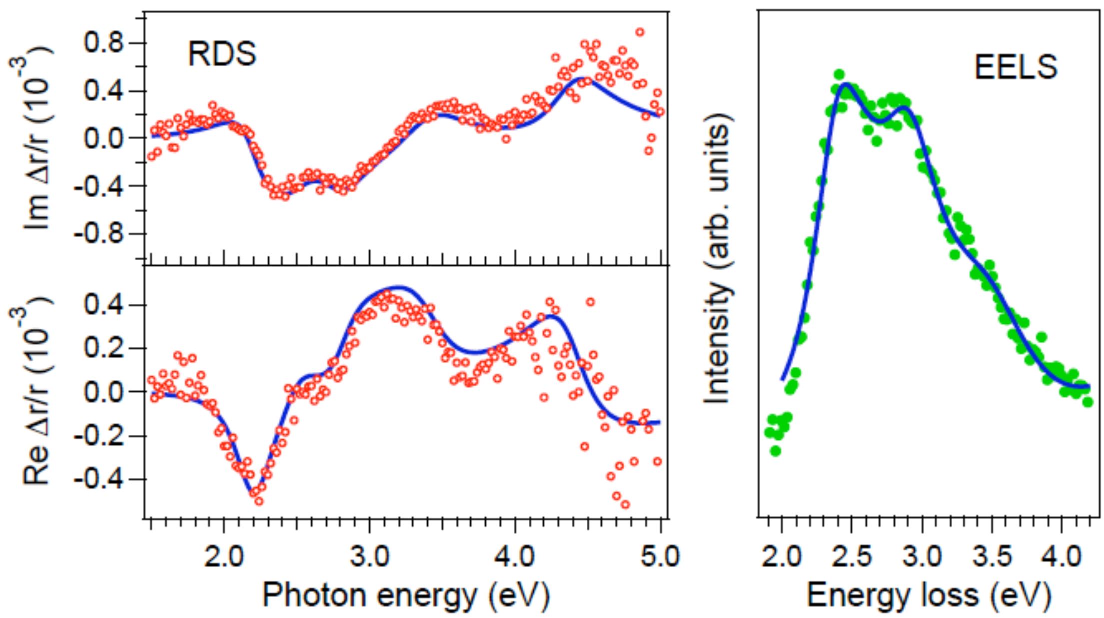

Figure 1: RDS (left panel) and EELS (right panel) measurements of chevron-type GNRs grown in the Au(788) and Au(111) surfaces, respectively. The three-phase model fitting curves are shown as solid lines.