

Atomically precise graphene nanoribbons: Electronic structure, optical properties and vibrational characteristics

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Abstract

Graphene nanoribbons (GNRs) – narrow stripes of graphene [1] – are predicted to be semiconductors with an electronic band gap that sensitively depends on the ribbon width [2]. The electronic properties of GNRs also strongly depend on the arrangement of the carbon atoms in the ribbon structure. For armchair GNRs (AGNRs) the band gap is inversely proportional to the ribbon width. Zigzag GNRs (ZGNRs), on the other hand, are predicted to present spin polarized edges. Their gap opens thanks to an unusual antiferromagnetic coupling between the magnetic moments at opposite edge carbon atoms. These versatile characteristics allow the design of GNR-based structures with widely tunable electronic properties, but require highest (i.e. atomic) structural precision. With our recently developed bottom-up approach the fabrication of atomically precise AGNRs [3] can be achieved using specifically designed precursor monomers. The monomers are sublimed in ultrahigh vacuum (UHV) and deposited onto metallic substrates such as Au or Ag. Substrate catalyzed dehalogenation of the monomers induces the formation of linear polymers that are subsequently cyclodehydrogenated to form the desired GNRs. With this approach, we have fabricated ultra-narrow GNRs and related graphene nanostructures for experimental investigations of their structural and electronic properties [3-10]. For the case of $N=7$ AGNRs (7-AGNRs), the electronic band gap and dispersion of the occupied electronic bands have been determined with high precision [9].

The opening of a band gap for GNRs modifies the optical properties, showing specific absorption that contains information about electronic transitions. Optical characterization of GNRs supported on metal substrates, however, is a non-trivial task. Transmittance measurements would obviously require the use of optically transparent substrates and thus suitable transfer methods away from metallic substrates. Therefore, reflectance measurements appear more suitable for investigating the optical properties of GNRs supported on metallic substrates. We have applied Reflectance Difference Spectroscopy (RDS) [11] a spectroscopic technique that determines the difference in normal reflectivity of two orthogonal linearly polarized beams. This technique relies on the use of anisotropic materials, i.e. materials that present different optical properties in two orthogonal directions. To allow for RDS measurements of GNRs, we have aligned the nanoribbons along a single preferential direction. This has been achieved by using vicinal metallic surfaces such as Au(788). We present *in situ* RDS data acquired in UHV at different stages of the GNR fabrication process. RDS data were taken after annealing the samples at different temperatures allowing to monitor the different stages of growth: monomer deposition, monomer coupling and polymer dehydrogenation. After each annealing step, the same samples were imaged with Scanning Tunneling Microscopy (STM) to characterize the GNR structures. In addition, we have characterized the vibrational properties of the GNRs by *ex situ* Raman spectroscopy that contains valuable information about the ribbon nanostructure. All of these results will be discussed in relation to the electronic properties of the GNRs as determined from photoemission and scanning tunneling spectroscopy data.

References

- [1] A. K. Geim, *Science*, **324** (2009) 1530.
- [2] V. Barone et al., *Nano Lett.*, **6** (2006) 2748.
- [3] J. Cai et al., *Nature*, **466** (2010) 470.
- [4] M. Bieri et al., *Chem. Commun.*, (2009) 6919.
- [5] M. Bieri et al., *J. Am. Chem. Soc.*, **132** (2010) 16669.
- [6] S. Blankenburg et al., *Small*, **6** (2010) 2266.
- [7] M. Treier et al., *Nature Chemistry*, **3** (2011) 61.
- [8] S. Blankenburg et al., *ACS Nano*, **6** (2012) 2020.
- [9] P. Ruffieux et al., *ACS Nano*, **6** (2012) 6930.
- [10] L. Talirz et al. *JACS*, **135** (2013) 2060.
- [11] M. Hohage et al. *Appl. Phys. A*, **80** (2005) 1005.

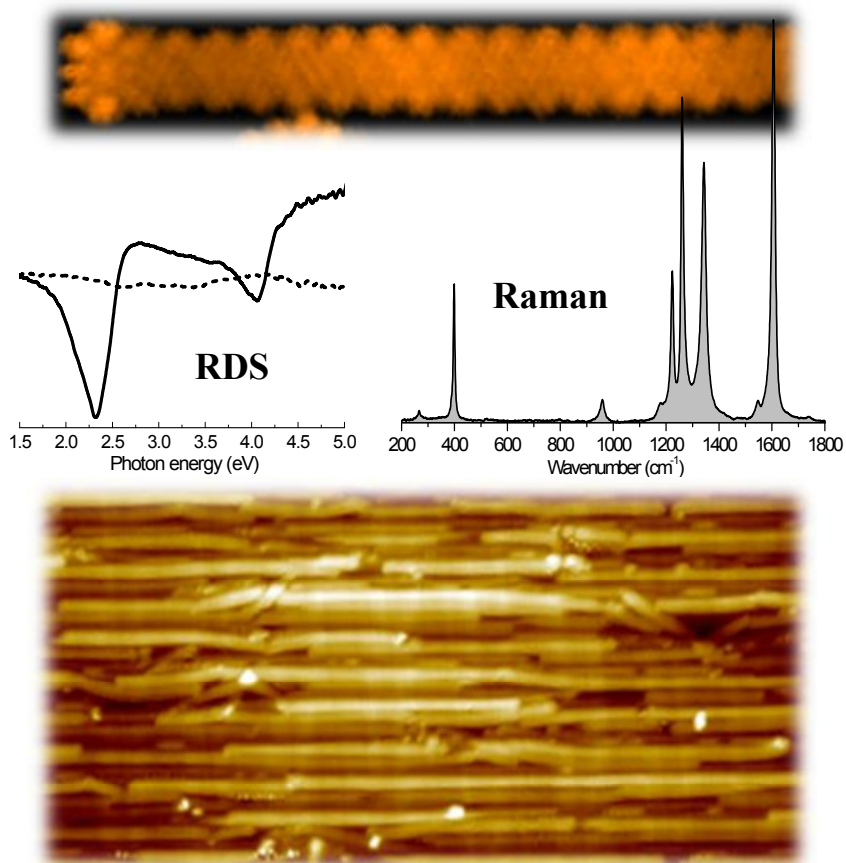


Figure. STM pictures of a 7-AGNR with one visible terminus (top) and aligned ribbons on Au(788) surface (bottom). RDS (middle, left) reveals characteristic absorption features that can be directly linked to the electronic band structure of 7-AGNRs. Raman spectroscopy (middle, right) reveals the expected intensity distribution on G- and D-modes and the width-depending characteristic radial breathing like mode (RBLM) at $\sim 400\text{ cm}^{-1}$.