

Raman fingerprints of ultra-narrow graphene nanoribbons with different geometry

Daniele Rizzo^{1,*}

Ashok Keerthi², Akimitsu Narita², Uliana Beser², Daryl McManus¹, Yinjuan Huang³, Yiyong Mai³, Xinliang Feng^{3,4}, Klaus Müllen² and Cinzia Casiraghi¹

¹School of Chemistry, Manchester University, UK

²MPI for Polymer Research, Mainz, Germany

³School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, China

⁴Department of Chemistry and Food Chemistry, TU Dresden, Germany

* daniele.rizzo@manchester.ac.uk

Bottom-up synthetic approaches based on solution-mediated cyclodehydrogenation are able to produce ultra-narrow ($\ll 10$ nm width) and structurally well-defined graphene nanoribbons (GNRs) [1-5]. The main advantage of such methods, compared to other techniques, relies on the ability to determine the precise ribbons geometry by designing the structure of the molecular precursors *ad-hoc*. For example, in addition to the traditional armchair and zigzag ribbons, cove-shaped GNRs (c-GNRs) and chevron-shaped GNRs (p-GNRs) nanoribbons have been produced [1-5]. Note that in the case of solution-mediated GNRs the edges are functionalized to provide a better solubility [1].

Therefore, ultra-narrow GNRs with very different width, edge morphology, position and type of functional groups and length, can be produced.

Raman spectroscopy is a well-established, fast and non-destructive characterization technique for various carbon nanomaterials, [6]. It is therefore expected that Raman spectroscopy could be used to fully characterise GNRs. However, the Raman

spectrum of GNRs is very complex due to the dual nature of GNRs, which are quasi-infinite in the length direction, but finite in the width direction. Therefore, GNRs with different geometry and amount of defects can show very different Raman spectra [7,8]. Here we show a detailed multi-wavelength Raman analysis of ultra-narrow c-GNRs and p-GNRs. The effect of edge morphology, position and type of functional groups and length of the ribbons on the Raman spectrum have been studied. In agreement with a previous study [8], we observed that the acoustic region of the Raman spectrum shows a characteristic radial-like breathing mode. This is particularly sensitive to the specific modification at the edges, for example it is strongly affected by the size of the functional groups and the functionalization degree of the nanoribbon. All GNRs studied also show a characteristic dispersion of the D peak, which is independent on type of functional group and length of the ribbon. Finally, effects due to changes in the lateral dimension are also discussed by comparing the Raman spectrum of ultra-narrow graphene nanoribbons with the Raman spectrum of polycyclic aromatic hydrocarbons and defective graphene.

References

- [1] Narita et al, Nature Chem., 2 (2014) 126
- [2] Vo et al., Nat. Comm., 5 (2014) 2041
- [3] Narita et al, ACS Nano, 11 (2014) 11622
- [4] Huang et al, JACS 138 (2016)10136
- [5] Cai et al, Nature 466 (2010) 470
- [6] Jorio, et al. Raman Spectroscopy in Graphene Related Systems, Wiley-VCH Verlag GmbH (2011)
- [7] Prezzi, Casiraghi, in preparation
- [8] Verzhbitskiy et al., NL, 16 (2016) 3442