Edge functionalization of graphene nanoribbons for electronic applications

Francisco J. Martin-Martinez, Stijn Fias, Gregory Van Lier, Frank De Proft and Paul Geerlings

Vrije Universiteit Brussel (VUB), Research Group General Chemistry (ALGC), Pleinlaan 2, B-1050, Brussels, Belgium
fmartinm@vub.ac.be

Graphene nanoribbons (GNRs) have come into the picture as promising candidates for the design of electronic devices, due to their finite width and distinct electron confinement. As a matter of fact, the lateral quantum confinement in GNRs opens a band gap in a useful range for electronic and solar cells applications, with a sufficient on/off ratio for semiconducting devices. According to previous studies on GNRs, widths below 3 nm should be reached to obtain band gaps that fall in the same range of the current worldwide-used semiconductors materials like Si or GaAs. [1] Furthermore, a periodicity in the band gap exists as the width of the GNR is increased,[2] and the aromaticity distribution along the GNR could be crucial to understand the basic electronic properties of the GNRs.

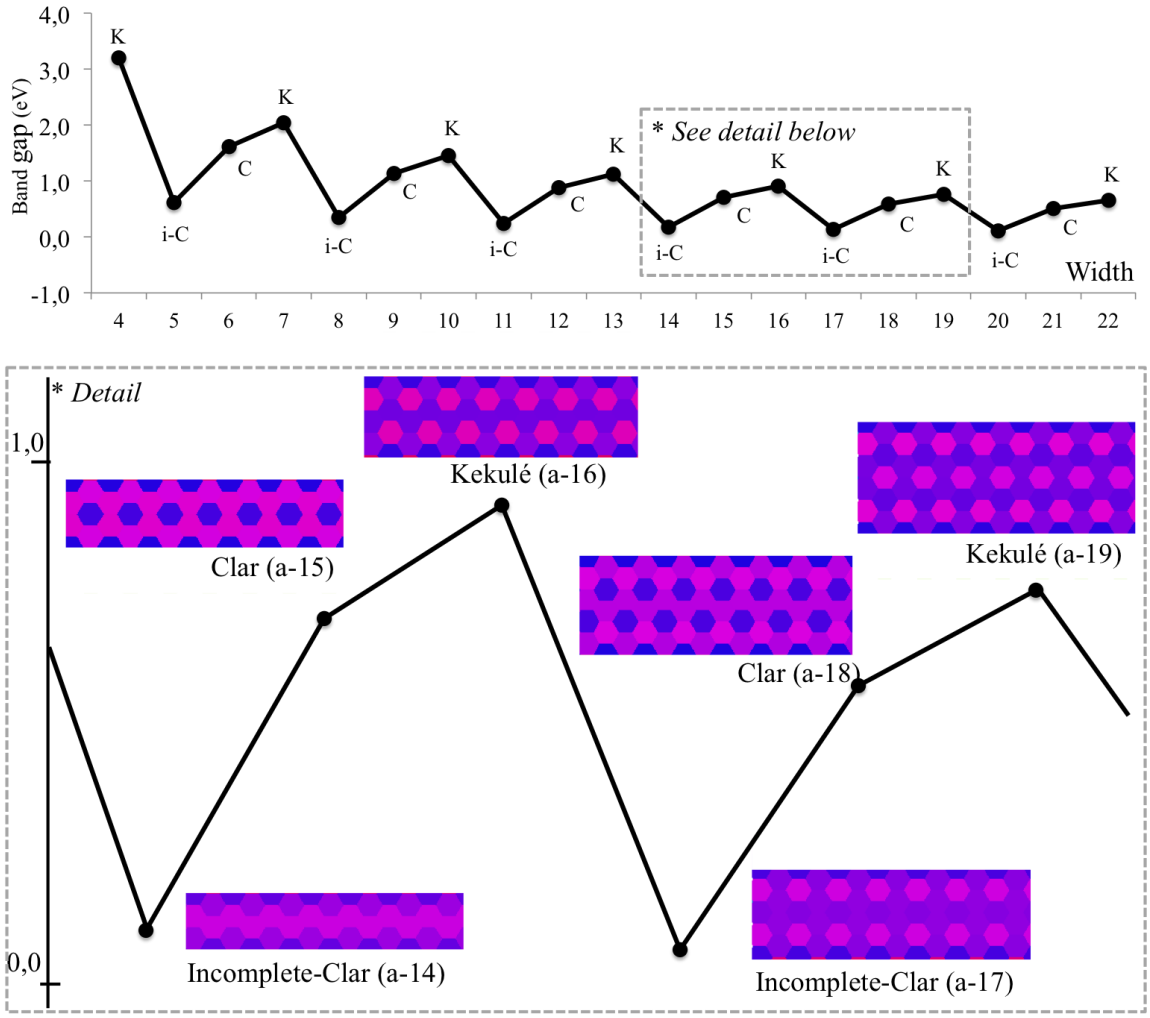
As already described in literature, three different types of aromaticity patterns have been found for armchair GNRs depending on their width. [3] In this work we study the aromaticity of GNRs using the Six Centre Index [4] (SCI) and the Mean Bond Length (MBL) geometry descriptor. [5] These patterns are similar to the patterns of armchair carbon nanotubes depending on the length.[6],[7] Each pattern appears periodically every three steps as the width of the GNR is increased, closely related to the same periodicity found in the energy band gap. [8] The reasons for the appearance of such patterns are proposed within the framework of the Clar sextet theory.

Fluorine, Oxygen and Hydrogen edge functionalization are considered in order to perform a rational tuning of both the aromaticity patterns and the band gap. Even more, a way to induce aromaticity patterns and therefore suitable band gap in zigzag GNRs is shown. The close relation between aromaticity distribution and electronic properties of these materials is demonstrated and the possible application for electronics is discussed.

References

[1] Barone, V.; Hod, O.; Scuseria, G. E. Nano Lett. **6** (2006) 2748.
[2] Son Y-W.; Cohen, M. L.; Louie, S. G. Phys. Rev. Lett. **97** (2006) 216803.
[3] Baldoni, M.; Sgamellotti, A.; Mercuri, F. Org. Lett. **9** (2007) 4267.
[4] Bultinck P.; Fias, S.; Ponec, R. Chem. Eur. J. **12** (2006) 8813.
[5] Martin-Martinez, F. J.; Melchor, S.; Dobado J. A. Org. Lett. **10** (2008) 1991.
[6] Matsuo, Y.; Tahara, K.; Nakamura, E. Org. Lett., **5** (2003) 3181.
[7] Martin-Martinez, F. J.; Melchor, S.; Dobado J. A. Phys. Chem. Chem. Phys. **13** (2011) 12844.
[8] Martin-Martinez, F.J.; Fias. S.; Van Lier, G.; De Proft, F.; Geerlings, P. Chem. Eur. J. *in press* (2012).

Figure



Band gap of GNRs depending on the width, and detail of the relation between the periodicity in the band gap and the aromaticity patterns. Only the central part of the ribbon is represented here.