Chiral graphene nanoribbon inside carbon nanotube: *ab initio* study

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Though graphene is currently receiving significant attention because of the unique physical properties it exhibits, the absence of an electronic band gap in this material remains one of the main obstacles hindering its application in electronic devices. One of the most effective solutions for introducing an energy gap between the conduction and valance bands of graphene is to shape it into strips of fixed width – graphene nanoribbons (GNRs). Formation of GNRs with well-defined, atomically smooth edge is essential for controlling their electronic properties. However, as discovered very recently, this is possible only by assembly of these nanostructures inside carbon nanotubes [1]. We study structure and electronic properties of a sulfur-terminated zigzag GNR (S-ZGNR) synthesized recently inside a single-walled carbon nanotube (SWNT) using calculations in the framework of dispersion-corrected density functional theory.

Two mechanisms that allow for the relatively wide GNR to be accommodated within the SWNT can be proposed on the basis of the experimental study [1]. The first mechanism is distortion of the SWNT cross-section into an elliptic shape and bending of the GNR (Fig. 1a) to fit into this cross-section. We show that the balance between the elastic and van der Waals forces between the GNR and nanotube wall leads to a non-trivial dependence of structure of the GNR@SWNT system on the nanotube diameter. The GNR bending is observed for nanotubes with the ratio of the nanotube diameter D_0 to the GNR width w in the ranges $D_0 / w < 1.4$ and $D_0 / w > 1.6$ (Fig. 2). In the SWNTs with $1.4 < D_0 / w < 1.6$, the GNR is found to retain its flat structure. It is also revealed that the nanotubes are deformed upon encapsulation of the GNR, in agreement with the experimental observations [1]. Strong deformation of the nanotube wall is observed for narrow nanotubes with $D_0 / w < 1.5$.

The second mechanism that allows the GNR to be accommodated within the SWNT is transformation of the GNR to a helical conformation (Fig. 1b). We calculate the dependence of energy of the S-ZGNR on the helix angle assuming that atoms of the GNR inside the carbon nanotube lie on the cylindrical surface (Fig. 3a). The calculated dependence has two energy minima. It is seen from Fig. 3a that these minima arise from the van der Waals attraction of sulfur atoms at neighbouring edges of adjacent turns of the GNR.

The hybrid DFT calculations of band structure of the S-ZGNR consisting of 4 zigzag rows show that this GNR is metallic (Fig. 3b). The deformation of the S-ZGNR inside (9,9) – (14,14) carbon nanotubes is found to be insufficient to open the band gap. Therefore, we propose that S-ZGNRs are potentially interesting for the use as nanowires protected by the nanotube wall or inductance nanocoils.

References

[1] A. Chuvilin, E. Bichoutskaia, M. C. Gimenez-Lopez, T. W. Chamberlain, G. A. Rance, N. Kuganathan, J. Biskupek, U. Kaiser, A. N. Khlobystov, Nature Materials,**10** (2011) 687.

Figures

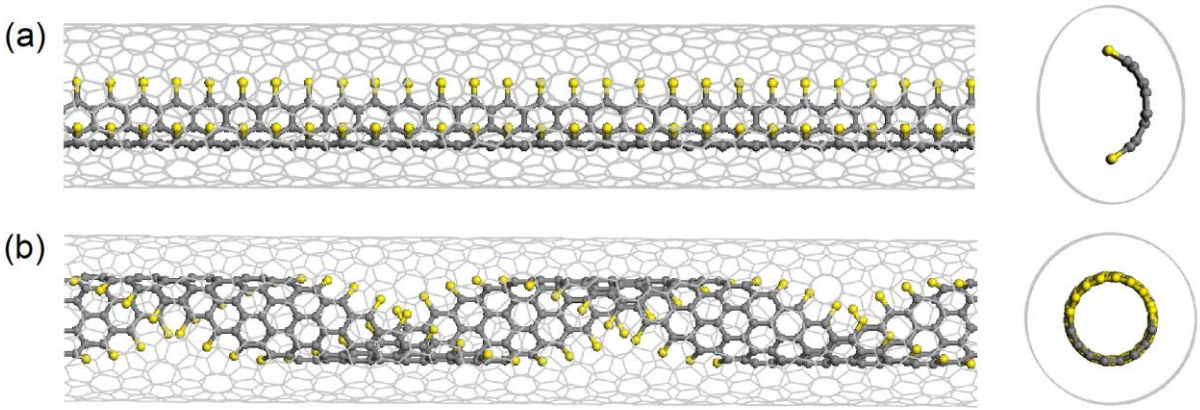

Fig. 1. Schematic representation of two mechanisms of accommodation of a S-ZGNR in a SWNT: (a) distortion of the SWNT cross-section into an elliptic shape and bending of the GNR, and (b) transformation of the GNR to a helical conformation. (Left) side views, (right) on-end views. Sulfur and carbon atoms are coloured in yellow and gray, respectively.

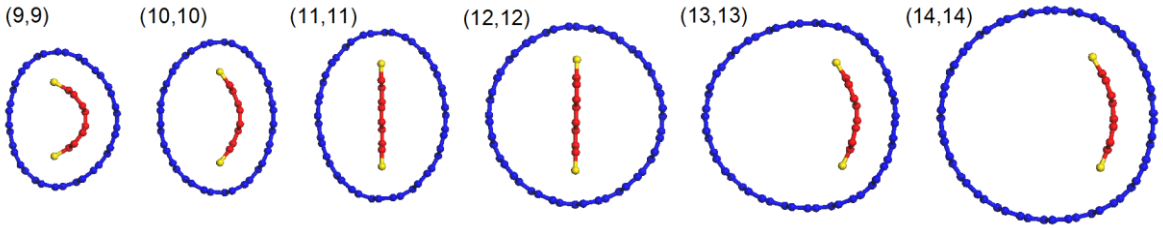

Fig. 2. Optimized structures of the S-ZGNR in armchair SWNTs (end-on views). Sulfur atoms are coloured in yellow. Carbon atoms of the GNR and SWNTs are coloured in red and blue, respectively.

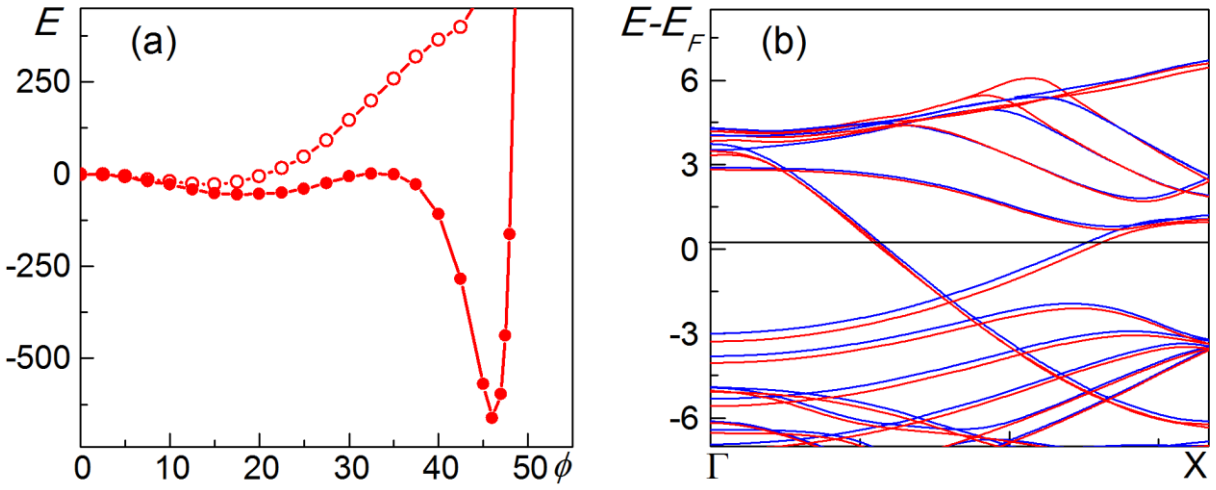

Fig. 3. (a) Energy E (in meV) of the S-ZGNR 74 Å x10.5 Å (240 C atoms and 66 S atoms) with the atoms lying on the cylindrical surface of radius 3.3 Å as a function of the helix angle ϕ (in degrees) calculated (●) with and (○) without the dispersion correction. The case $\phi = 0^{o}$ corresponds to the GNR aligned along the nanotube axis. (b) Calculated band structures of the S-ZGNR consisting of 4 zigzag rows in the cases when the GNR is isolated (solid lines) and encapsulated in the (10,10) SWNT (dashed lines). The energy is given in eV.