Prediction of giant electroactuation for papyruslike carbon nanoscroll structures: First-principles calculations

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We study by first-principles calculations the electromechanical response of carbon nanoscroll structures. We show that although they present a very similar behavior to carbon nanotubes in their axial deformation sensitivity, they exhibit a radial response upon charge injection which is up to one order of magnitude larger. In association with their high stability, this behavior makes them a natural choice for a new class of very efficient nanoactuators.

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With the advent of nanotechnology great effort has been devoted to the study of nanostructures, carbon nanotubes[1] (CNTs) being among the most studied. In spite of more than two decades of intense research, the detailed mechanism of tube formation remains unclear.[2] It has been proposed that CNTs could be a subsequent state of papyruslike carbon structures, generally named carbon nanoscrolls (CNSs) (Fig. 1).[3–9]

CNSs are remarkable structures, sharing some of the rich mechanical and electronic properties exhibited by CNTs and potentially presenting new ones. They have been known since the 1960s from the pioneering work of Bacon[3] who first reported the growth of scroll whiskers. Surprisingly, very few studies[3–16] have been carried out for these systems. This can be explained in part by the intrinsic experimental difficulties in synthesis, purification, isolation, and characterization. However, after the recent advances in the low-temperature synthesis[6–8] of CNSs there is a renewed interest in these materials. Like CNTs, CNSs can be made of a single graphene sheet or by many of them. However, in contrast to CNTs, the scroll diameter can vary easily (expand or contract); thus they are extremely radially flexible. This property can be exploited for a variety of technological applications, such as chemical doping, hydrogen storage, electroactuation (mechanical deformation upon charge injection), etc.

The electromechanical response of CNTs has been investigated by means of first-principles calculations by Verissimo-Alves *et al.*[17] and using an electron-lattice model by Gartstein *et al.*[18] Electron actuation effects are predicted to occur, but of limited magnitude—0.2–0.3 %—since the deformation of sp^2 carbon bond lengths in close tubular structures like CNTs will require a significant amount of energy. An experimental demonstration of a CNT-based actuator has been reported by Baughman *et al.*[19] CNSs, on the other hand, are open structures and the radial expansion needed to accommodate the injected charges should be energetically more favorable. In this case it has simply to overcome the van der Waals interlayer interactions, instead of deforming sp^2 carbon bond lengths, thus producing a more significant electroactuation behavior. Recently, Braga *et al.*[15] have used classical molecular dynamics simulations to suggest that CNSs should exhibit a significant radial expansion upon charge injection. However, it is not possible to have a reliable quantitative estimation using classical methods because quantum effects are not included, and also it is not possible to differentiate between electron and hole injections, which are known to produce different responses for CNTs.[17,18] In order to properly address these issues the use of full quantum methods is necessary. In this paper we report such a study for some selected scroll models.

We have carried out density-functional theory (DFT) calculations in the framework of the local density approximation with the SIESTA code.[20] We have used a double-ζ basis set plus polarization functions and norm-conserving pseudopotentials of the Troullier-Martins type.[21] We have considered two prototype structures in supercell geometry (see Fig. 2): a zigzag and an armchairlike CNS.[15] The Brillouin zone has been sampled with a converged grid of up to $1\times1\times12$ k points. We have relaxed both the cell lattice vectors and the

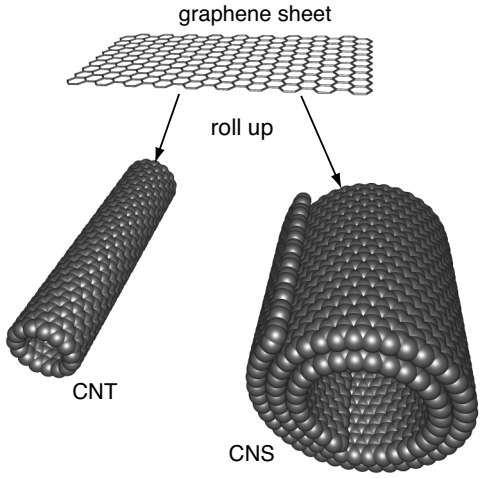

FIG. 1. Carbon nanotubes and scrolls can be topologically considered as cylindrical and papyruslike structures, respectively, obtained from rolled-up graphene layers.

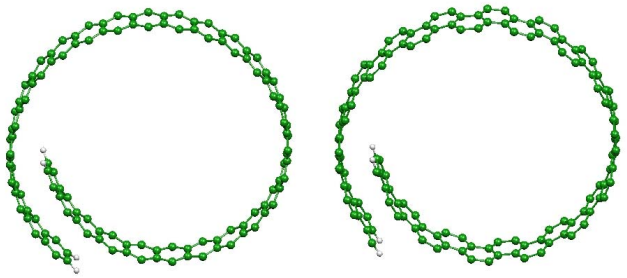

FIG. 2. (Color online) Unit cells used in the calculations of (a) an armchair and (b) a zigzag CNS. We have followed the nomenclature introduced by Braga *et al.* (Ref. 15), in turn derived from previous work on carbon nanoribbons (Refs 27 and 28).

atomic positions, thus accounting for both the axial and radial responses upon charge injection. We have also carried out a set of calculations where the lattice parameter was kept frozen, in order to explore complementary experimental situations, a free-standing actuator (as in Ref. 19) vs a sensor constrained between two electrodes.

In agreement with the molecular dynamics results of Ref. 15, we have chosen starting geometries with an internal radius of ~20 Å. Larger systems, with a higher number of revolutions around the scroll axis—i.e., obtained by wrapping a wider graphite sheet—cannot be efficiently handled within DFT. However, the fundamental mechanisms and driving forces associated with the geometrical expansion or contraction upon charge injection are already qualitatively captured by the systems studied. Nonetheless, we have chosen CNS geometries that already present the critical overlap between sheet layers that assures scroll formation.[15] We have injected a net charge of up to $\pm 0.055|e|$/atom into the systems by adding or removing electrons. In order to accommodate these extra or missing charges the carbon-carbon bond lengths need to adjust their values and this is the origin of the electron-actuation phenomenon.

The electroactuation response relies on the competition between two different effects: an *electronic* actuation, driven by the depletion or population of bonding or antibonding states, and a purely *electrostatic* actuation, which originates from Coulomb repulsion. In the low-injection regime a contraction is expected upon electron removal (hole injection) due to the lack of bond completion, i.e., creation of dangling bonds, which makes the region locally more reactive; the physical principle is the same as in covalent molecules when the bond order, i.e., the difference between bonding and antibonding occupancy, is varied: if the added charge occupies a bonding state, then the bond lengths contract, while if it occupies an antibonding state, the bond lengths increase. Injecting electrons, however, results in a more complex situation. Adding electrons in antibonding states generates an electronic repulsion and some bond lengths will elongate, but this, in turn, could stretch some of the neighboring bonds. In general, for sp^2-carbon-based structures the best compromise is alternating short and long bonds, even at the cost of breaking higher symmetries. This behavior is well known for conducting polymers; for instance, in polymers containing benzenoid rings charge injection transforms them into quinoid

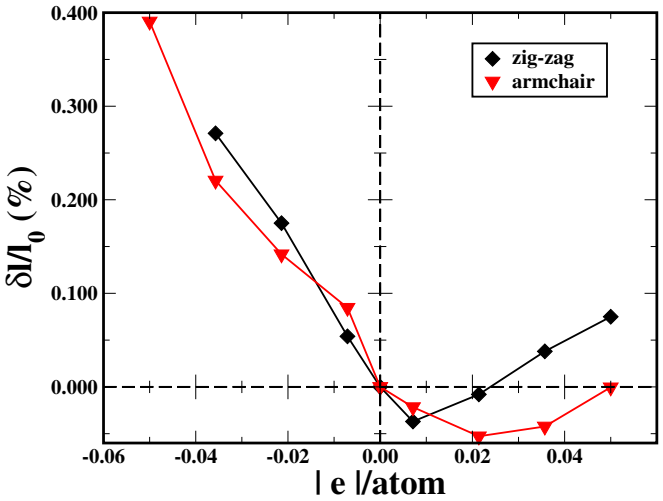

FIG. 3. (Color online) Relative variation of the unit cell lattice parameter l upon charge injection with respect to its equilibrium value in the neutral state l_0.

structures (with a well-pronounced alternation of short and long bonds).[22] In addition, the picture is further complicated by the interplay with Coulomb forces induced by the extra charge injected which will tend to expand the scroll by pushing apart the overlapped layers. Full quantum calculations are then necessary to quantify these effects.

In Fig. 3 we present the results for the relative axial variation of the lattice parameter ($\delta l/l_0$). The dependence on the injected charges follows the general trends exhibit by (5,5) and (12,0) CNTs reported in Ref. 17. CNSs expand to accommodate the extra electrons and slightly contract when holes are injected. In the high-injection regime the Coulombian repulsion dominates and the CNSs expand regardless of the sign of the injected charge. Most importantly, the magnitude of response is very similar to the case of CNTs and can reach values of about 0.2–0.3 %.

On the other hand, for what concerns the radial response (which is shown in Fig. 4), the behavior of CNSs is completely different from that of CNTs. While for CNTs the actuation response is almost equally distributed between the axial and radial parts, we have found the latter to be up to one order of magnitude more intense for CNSs,[23] being approximately 2.5% for the highest injected charge considered.[24] As can be seen, for small values of charge injection armchair and zigzag CNSs behave differently; one contracts while the other expands, and thus the different topologies are still playing an important role. For higher charge values—where the interlayer Coulomb interactions are expected to dominate—both structures converge to almost the same values, recovering an almost linear behavior; again a close parallel with the behavior of doped conducting polymers is observed.[25]

The data reported in Fig. 4 correspond to calculations where the lattice parameter was constrained to its equilibrium value in the neutral state. This arrangement is intended to mimic the situation where the CNS has its extremities clamped, i.e., a suspended scroll. On the other hand, relaxing the lattice better approaches the situation where the CNS is

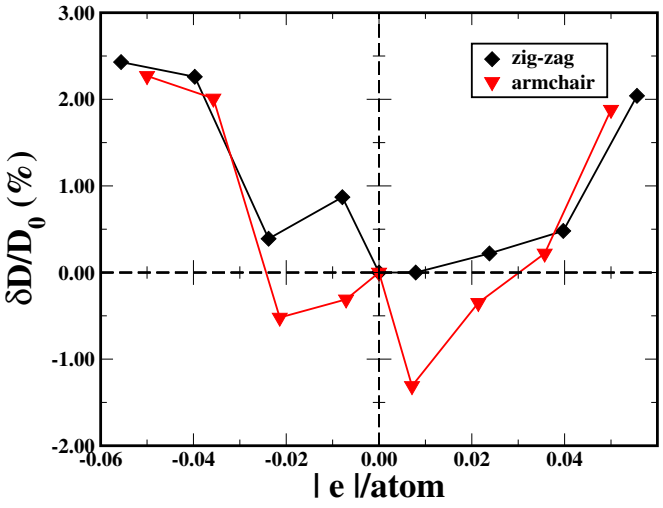

FIG. 4. (Color online) Relative variation of the CNS diameter parameter D upon charge injection with respect to its equilibrium value in the neutral state D_0. The diameter D has been defined as the maximum distance between two carbon atoms with the same axial coordinate.

on a surface and can freely move in the axial direction too. In this case, however, the dependence of the diameter on the injected charge turned out to be much more irregular, especially in the high-charge regime, and it is often accompanied by an elliptization of the structure. The radial response is sometimes even larger, but difficult to reliably associate with the injected charge. In other words, free-standing CNSs on a surface behave axially as CNTs and have an enhanced but noisy radial sensitivity; suspended CNSs, axially constrained, exhibit a giant and ordered radial electromechanical response.

Recent DFT calculations of neutral scrolls have attributed a metallic character to armchair CNSs.[16,26] Our DFT calculations are in very good agreement with the results of Pan *et al.*,[16] as shown in Fig. 5. However, the scroll geometry that we have used differs significantly from theirs (as we had to perform several full relaxations—lattice and atomic

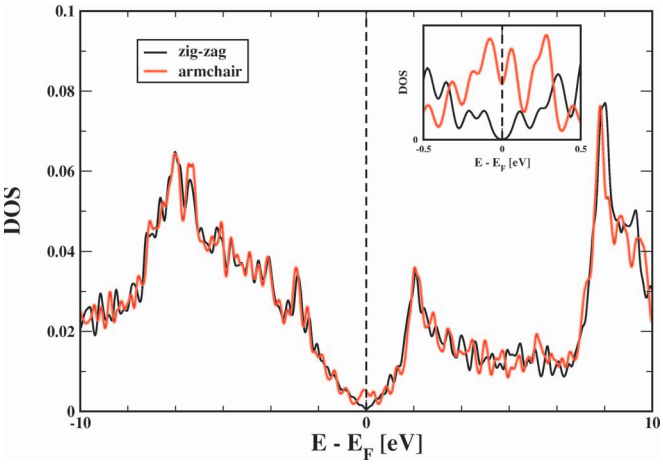

FIG. 5. (Color online) Electronic density of states (DOS) of the armchair [red (gray) line] and the zigzag (black line) CNSs studied. The inset panel shows a magnified view around the Fermi level.

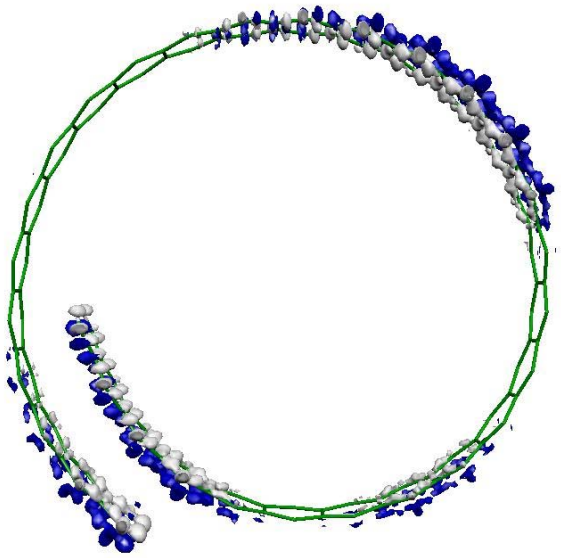

FIG. 6. (Color online) Distribution of the extra charge of $-0.055|e|$/atom in a zigzag CNS.

positions—we had to use smaller structures). Hence, this is a hint that, at least at this scale, the electronic structure is at a first approximation insensitive to the size of the scroll. Zigzag CNSs are predicted to have a small band gap.[26] For both topologies, we have found that the electronic structure of CNSs around the Fermi level is determined by the border states (in agreement with the results reported by Pan *et al.*[16] for armchair CNSs), in analogy with carbon nanoribbons from which they are derived by wrapping.[16,27,28]

In order to gain further insight into the electroactuation process we have studied the localization of the extra charge in the high-injection regime. In Fig. 6 we have plotted the difference between the electronic density of a zigzag CNS with 0.055 extra electrons per atom and the electronic density of the same CNS in the neutral state, i.e., the extra electrons of the charged system. It can be seen that the excess charge accumulates in the central region of the CNS and, with a clear discontinuity, close to the borders. On the other hand, by analyzing the relative elongation of each individual bond, we have found that almost all the bonds elongate in a similar way, despite the excess charge not being homogeneously distributed. The charge accumulated at the CNS boundary carries the large radial electromechanical response, due to efficient interlayer Coulombian repulsion; the excess charge concentrated in the central region, on the other hand, will only be responsible for minor bond elongations, contributing to both the axial and radial responses. However, in the high-injection regime, the bond deformation is uniformly distributed along the CNS. This is no longer true for low injected charge, where the predicted alternation of shortened and elongated bonds is recovered.

Therefore, the electromechanical actuation in the high-charge regime also originates in the charge accumulation in the central region of the CNS. In the studied geometry, pre-

senting a limited layer overlap, this charge has only a minor impact on local bond elongation. In CNSs with a larger layer overlap also the extra charge concentrated in the CNS center could contribute with an efficient interlayer Coulomb repulsion. Hence we do not discard the idea that, in absence of other side effects, e.g., interlayer sliding, the central charge could lead to a larger electromechanical response.

In summary, we have carried out *ab initio* DFT calculations of the electroactuation effect in carbon nanoscrolls. While the axial sensitivity of CNSs has very similar features as in carbon nanotubes, the radial response has a completely distinct behavior, reaching under high-charge injection conditions the giant relative diameter variation of 2.0–2.5 %, which is one order of magnitude higher than the values reported for CNTs. In suspended CNSs it is much easier to correlate the charge injection with the electromechanical response, as the circular symmetry of the scroll is qualitatively maintained for a wide range of injected charge. Freestanding CNSs are more naturally used as axial actuators, even though in such a case their response is similar to the case of CNTs. These results suggest that CNSs provide a simple and flexible path toward the development of efficient electromechanical actuators at the nanoscale. We hope the present study will stimulate further experimental work to test these predictions.

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[1] S. Ijima, Nature (London) **354**, 56 (1991).
[2] W. A. de Heer, P. Poncharal, C. Berger, J. Gezo, Z. M. Song, J. Bettini, and D. Ugarte, Science **307**, 907 (2005).
[3] R. Bacon, J. Appl. Phys. **31**, 283 (1960).
[4] O. Zhou, R. M. Flemming, D. W. Murphy, C. H. Chen, R. C. Haddon, A. P. Ramirez, and S. H. Clanum, Science **263**, 1744 (1994).
[5] W. Ruland, A. K. Schapper, H. Hou, and A. Greiner, Carbon **41**, 423 (2003).
[6] H. Shioyama and T. Akita, Carbon **41**, 179 (2003).
[7] L. M. Viculis, J. J. Mack, and R. B. Kaner, Science **299**, 1361 (2003).
[8] Z. Khang, E. Wang, L. Gao, S. Lian, M. Jiang, C. Hu, and L. Xu, J. Am. Chem. Soc. **125**, 13652 (2003).
[9] J. C. Lauin, S. Subnamoney, R. S. Ruoff, S. Berber, and D. Tománek, Carbon **40**, 1123 (2002).
[10] A. Ameclinckx, D. Bennates, X. B. Zhang, G. van Thendeloo, and J. van Landuyt, Science **267**, 1334 (1995).
[11] V. Z. Mordkovich, M. Baxendale, S. Yoshimura, and R. P. H. Chang, Carbon **34**, 1301 (1996).
[12] Y. Maniwa, R. Fujiwaral, H. Kiral, H. Toul, E. Nishibori, M. Takata, M. Sakata, A. Fujiwara, X. Zhao, S. Iijima, and Y. Ando, Phys. Rev. B **64**, 073105 (2001).
[13] D. Tománek, W. Zhong, and E. Krastev, Phys. Rev. B **48**, 15461 (1993).
[14] D. Tománek, Physica B **323**, 86 (2002).
[15] S. F. Braga, V. R. Coluci, S. B. Legoas, R. Giro, D. S. Galvão, and R. H. Baughman, Nano Lett. **4**, 881 (2004).
[16] H. Pan, Y. Feng, and J. Lin, Phys. Rev. B **72**, 085415 (2005).
[17] M. Verissimo-Alves, B. Koiller, H. Chacham, and R. B. Capaz, Phys. Rev. B **67**, 161401(R) (2003).
[18] Y. N. Gartstein, A. A. Zakhidov, and R. H. Baughman, Phys. Rev. Lett. **89**, 045503 (2002).
[19] R. H. Baughman, C. X. Cui, A. A. Zakhidov, Z. Iqbal, J. N. Barisci, G. M. Spinks, G. G. Wallace, A. Mazzoldi, D. De Rossi, A. G. Rinzler, O. Jaschinski, S. Roth, and M. Kertesz, Science **284**, 1340 (1999).
[20] P. Ordejón, E. Artacho, and J. M. Soler, Phys. Rev. B **53**, R10441 (1996); J. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, J. Phys.: Condens. Matter **14**, 2745 (2002); see also http://www.uam.es/siesta/
[21] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
[22] D. S. Galvão, D. A. dos Santos, B. Laks, C. P. de Melo, and M. J. Caldas, Phys. Rev. Lett. **63**, 786 (1989).
[23] A detailed comparison with equivalent results for CNTs is not possible. In Ref. 18 the authors considered a very small charge injection ($|e|$/atom=0.005). Reference 17 investigates a wider range of electron and hole injection, comparable to ours, but they only report the results concerning the axial response, suggesting, however, that the radial behavior is qualitatively similar.
[24] The interlayer separation cannot be accurately predicted by our calculations, because it is mostly due to van der Waals interaction which is not properly described within DFT. On the other hand, the radial expansion is quantitatively captured, because DFT reliably accounts for the main effects that contribute to it, i.e., Coulomb repulsion and bond-length variation due to depletion or population of bonding or antibonding states.
[25] *Handbook of Conducting Polymers*, edited by T. A. Skotheim (Dekker, New York, 1986).
[26] We know of no data other than ours on the *ab initio* electronic structure of zigzag CNSs available at present. We have performed an extensive tight-binding study of several different geometries, both varying the number of layer revolutions or the wrapping angle [D. Porezag, T. Frauenheim, T. Köhler, G. Seifert, and R. Kaschner, Phys. Rev. B **51**, 12947 (1995); R. Rurali and E. Hernández, Comput. Mater. Sci. **28**, 85 (2003)]. The comparison with DFT results, available in the case of the smaller structures, turned out to be very good, suggesting that the tight-binding results are highly reliable. The conclusions hinted by the density-functional calculations proved to be quite robust and all the geometries considered exhibit a similar electronic structure, with a density of states vanishing at the Fermi level.
[27] M. Fujita, K. Wakabayashi, K. Nakada, and K. Kusakabe, J. Phys. Soc. Jpn. **65**, 1920 (1996).
[28] K. Nakada, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. B **54**, 17954 (1996).