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Mechanical properties and electronic structure of edge-doped graphene nanoribbons with F, O, and Cl atoms†

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In this study, we present the structural, electronic, and mechanical properties of edge-doped zigzag graphene nanoribbons (ZGNRs) doped with fluorine, oxygen, and chlorine atoms. To the best of our knowledge, to date, no experimental results concerning the mechanical properties of graphene-derived nanoribbons have been reported in the literature. Simulations indicate that Cl- and F-doped ZGNRs present an equivalent 2-dimensional Young's modulus E^{2D} , which seems to be higher than those of graphene and H-doped ZGNRs. This is a consequence of the electronic structure of the system, particularly originating from strong interactions between the dopant atoms localized at the edges. The interaction between dopant atoms located at the edges is higher for Cl and lower for F and O atoms. This is the origin of the observed trend, in which $E_{Cl}^{2D} > E_F^{2D} > E_O^{2D}$ for all the analyzed ZGNRs.

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1. Introduction

Lamellar carbon materials, such as graphene, have received significant attention due to their promising technological applications ascribed to their particular electronic structure. Among these materials, graphene nanoribbons (GNRs) have been a subject of interest because they offer a model to study correlations due to their reduced dimensionality and potential use in spintronics since they can work as perfect spin filters and their production has made possible important advances.^{1–3} Among the properties of these carbon nanoribbons, note that the in-plane electric field, perpendicular to the periodic axis, induces a half-metal state in zigzag nanoribbons (ZGNRs).^{4,5}

Chemical vapor deposition (CVD) is the route that has been reported for the bulk production of long, thin, and highly crystalline graphene ribbons. The technological possibilities of GNRs were enhanced *via* improvement in their production and advances in the processing of graphene and graphitic materials.⁶

For graphene nanoribbons, the presence of different types of boundary shapes, called edges, modifies the electronic structure of the material. The major effects are observed at the Fermi

level, which cause unusual magnetic and transport features.⁷ The zigzag edges (ZGNR) present electronically localized states at the boundaries, corresponding to the non-bonding states that appear at the Fermi level as a large peak in the density of states. The non-magnetic state presents many states at the Fermi level, which produces a strong instability that can be resolved *via* spin polarization or geometrical distortion. Due to the non-bonding character of the zigzag-localized edge states, geometrical reconstruction is unlikely to happen,⁸ and the spin polarization of the electronic density establishes an antiferromagnetic arrangement with the opening of a gap, yielding a Slater insulator.⁹ The value of the electronic band gap is strongly related to the width of the ZGNR since it can be understood as a consequence of the interaction between edges and quantum confinement. For this reason, wider ribbons with longer distances between opposite edges recover the graphene geometry with a gap equal to zero. The tendency observed corresponds to an exponential decay of the energy gaps when the nanoribbon's width (N) is increased.

In the literature, many representative results concerning the simulation mechanical properties of carbon nanostructures can be found. In particular, classical methods have been widely and successfully applied to polymerized nanotubes,¹⁰ nanotube networks and super carbon nanotubes,¹¹ and Möbius and twisted graphene nanoribbons.¹² The main conclusions from these studies indicate that there is no important variation of the electronic properties of zigzag nanoribbons upon stress-strain effects (*i.e.* energy gaps and local magnetic moments). The Young's modulus, Poisson's ratio, and shear modulus have

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been calculated in a systematic report; in all the cases, GNRs have larger constants than graphene, but they approximate to this material when the GNR's width is increased. This effect was explained in terms of the hardness of the C–C bonds positioned at the edges of the GNRs due to the observed geometrical reconstruction.

Apart from the conventional variations in the electronic properties, such as the ribbon width and the chirality, of the GNRs, doping of these materials with atoms of different electronegativities provides us the opportunity to enhance this richness and explore new potential materials in the pursuit of novel properties.

Among the possible elements to investigate, the lighter halogens, *i.e.* F and Cl[−], are reasonable candidates since the preparation of the doped materials is experimentally achievable through halogenation.^{13,14} Oxygen is also a very important element to be studied as a dopant due to its presence when oxidizing treatments are performed on graphene-derived nanomaterials.

Finally, to the best of our knowledge, to date, experimental results concerning the mechanical properties of graphene-derived nanoribbons have not been reported in the literature. For this reason, we thought that it was important to theoretically contribute to the mechanical properties of the edge-modified GNRs upon their doping with O, F, and Cl and discuss the relationships of the properties with the electronic structure.

2. Methodology

2.1 Structural geometry and electronic structure

The theoretical study of the uniaxial stress on different ZGNRs is based on the first principles – density functional theory.^{15,16} The simulations have been performed using the SIESTA code,^{17–20} which adopts a linear combination of numerical localized atomic-orbital basis sets for the description of valence electrons and norm-conserving non-local pseudopotentials for the atomic core. The pseudopotentials have been constructed using the Trouiller and Martins scheme,²¹ which describes the interaction between the valence electrons and atomic core. We selected a split-valence double- ζ basis set with polarization orbitals for all the carbon atoms. The extension of the orbitals was determined *via* the cut-off radii of 4.994 a.u. and 6.254 a.u. for the s and p channels, respectively, as obtained from an energy shift of 50 meV due to the potential-induced localization. The total energy was calculated within the Perdew–Burke–Ernzerhof (PBE) parametrization of the generalized gradient approximation GGA xc-potential.^{22,23} The real-space grid used to represent the charge density and wave functions was equivalent to an energy cut-off of 230 Ry. The atomic positions were fully relaxed in all the cases using a conjugate-gradient algorithm until all forces were smaller than 10 meV Å^{−1}. A Monkhorst Pack grid²⁴ of 300 × 2 × 2 was defined in terms of the selected supercells, allowing a total of 600 *k*-points in the full Brillouin Zone. All these parameters allow the convergence of the total energy. It is important to mention that all the cases were initialized with an antiferromagnetic arrangement

according to the expected spin-density solutions for these small-width GNRs.

The ZGNRs selected for simulation correspond to *N*-dimers, taking values from *N* = 4 to 10. All the designed supercells were orthogonal, with the GNR placed in the *ab* plane and oriented with the periodic direction along the *a*-axis. To avoid interference between symmetry images, vacuum regions of 15 Å were added along the *b* and *c* directions. In the case of the smallest unit cell, the *a*-axis value for every cell is approximately $a_0 = 2.495$ Å, with a total number of atoms of $2N + 2$. For the purpose of increasing the number of degrees of freedom in each case, the cells were expanded in four units along the *a*-axis ($a = 4a_0$); this allowed us to increase the total number of atoms inside the supercells by fourfold according to $8N + 8$. The total number of atoms in each case corresponds to 40, 48, 56, 64, 72, 80, and 88.

Finally, with the purpose of evaluating the effect of the selected xc-functional, we proceeded with further DFT calculations utilizing the hybrid HSE06 functional.²⁵ For this purpose, we utilized the VASP code^{26–29} using the PAW-PBE³⁰ pseudo-potentials with the same electronic configuration as for the SIESTA setup.

2.2 Mechanical properties

The Young's modulus *E* is a measure of the stiffness of a solid specimen and defines the mechanical properties of a material. As it has been previously presented for the case of graphene,³¹ it is of more sense to define the in-plane stiffness (E^{2D}) instead of the classical 3D Young's modulus (E^{3D}) because of the reduced dimensionality of this material. For this reason, in graphite, the elastic properties can be considered to be independent of the interlayer distance between graphene, $c_0 = 3.35$ Å, and the Young's modulus can be described as follows: $E^{2D} = \frac{1}{A_0} \left(\frac{\partial^2 E_S}{\partial \epsilon_x^2} \right)_{E_0} = E^{3D} c_0$, where E_S , ϵ_x , and A_0 correspond to the total energy, linear strain, and equilibrium reference area of the 2D material, respectively. The in-plane stiffness of graphite, calculated to achieve the *N* limit, is obtained considering an axial load on graphene. The value obtained in this case was $E^{3D} = 1.02(3)$ TPa³² and allowed us to obtain $E^{2D} = 3.41(9)$ TPa Å. This value is almost identical to that experimentally obtained for graphene, *i.e.* $E^{2D} = 3.42(30)$ TPa Å,³³ using nano-indentation with an atomic force microscope, and it is in agreement with those reported by Kuddin *et al.* ($E^{3D} = 1.02$ TPa Å)³⁴ and Van Lier *et al.* ($E^{3D} = 1.11$ TPa Å)³⁵ using the *ab initio* methods. The stress–strain curves were obtained by applying different stresses on the GNR; this allowed full atomic relaxation together with full unit cell parameter optimization until the desired stress tensor was reached. Since we were considering uniaxial strain only, the Voigt tensor had only one non-zero component: $[\sigma_{xx}, \sigma_{yy}, \sigma_{zz}, \sigma_{xy}, \sigma_{xz}, \sigma_{yz}] \Rightarrow [\sigma_{xx}, 0, 0, 0, 0, 0]$. The selected stress components of the Voigt tensor allowed us to determine the strains in the range of $\epsilon_x = \pm 0.020$ for the whole series, which assured a linear stress regime.^{36,37} It corresponds to a quadratic dependence of the total energy on the strain. *Via* this procedure, we obtained all the mechanical properties and, additionally, the equilibrium unit cell parameters for the whole set of systems.

3. Results and discussion

3.1 Energetics

To address the thermodynamics of the systems, we calculated the formation and cohesion energy. In the first case, we applied the following expression:

$$E_{\text{form}} = E_{\text{X-ZGNR}} - n_{\text{X}}\mu_{\text{X}} - n_{\text{C}}\mu_{\text{C}} \quad (1)$$

where $E_{\text{X-ZGNR}}$ is the total energy of the X-doped ZGNR, n_{X} (X = F, O, and Cl) is the total number of atoms in the supercell, and μ_{X} (X = F, O, and Cl) is the corresponding chemical potential. In the case of carbon, the chemical potential was determined by the graphene system, and for the rest of the atoms, the diatomic species were utilized (F_2 , O_2 , and Cl_2) in the gas phase. All the values are presented in Table 1.

As can be observed, when diatomic molecules are used as reactants, the formation energy is only unfavorable for Cl_2 . This is due to the stability of the Cl_2 molecule and pristine graphene as compared to that of the corresponding edge-doped nanoribbon. However, it is well known that there exist many possibilities of chemical sources for preparing these kinds of materials with F, Cl, and O atoms. When we used these atoms as reactants, the chemical potential μ_{X} (X = F, O, and Cl) corresponded to the total energy of the isolated F, O, and Cl atoms, and the energy expression corresponded to the cohesion energy (E_{coh}). On analyzing these values, it can be observed that they all correspond to favorable processes. It is not our objective to discuss or propose possible chemical routes for the preparation of the X-ZGNR, but these values are relevant for us for comparison purposes. In conclusion, what is observed in every case is that the formation and cohesion energies per atom become more favorable at larger widths (high N values). Herein, again, the effect of edge interactions is stronger for smaller widths, but the effect becomes diluted for larger widths.

3.2 Structural geometry

To characterize the structural geometry of the substituted ZGNRs, we represent the width of a GNR through the shortest C–C width (d_1) and the longest C–C width (d_2) for the different N cases (see Fig. 1). These are the lengths that have been used to calculate the Young's modulus, named E_1^{2D} and E_2^{2D} while utilizing the d_1 and d_2 distances, respectively. There is no reason to think that one of them is more correct than the other; this is why we have always presented both. As abovementioned in last part of

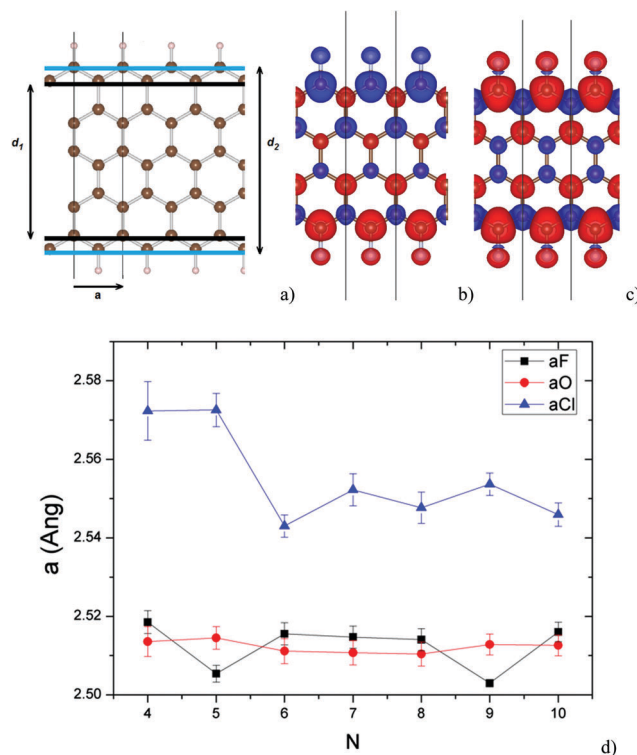


Fig. 1 (a) Schematic of the ZGNR supercell for $N = 4$, showing characteristic distances: a , d_1 , and d_2 . The spin density for the AFM and FM arrangement is presented in (b) and (c), respectively, where blue indicates positive and red negative spin densities at the isosurface of $0.004 \text{ e } \text{\AA}^{-3}$. (d) Evolution of the characteristic distance a (Å) with N for F, O, and Cl.

the methodology, the unit cell a -axis parameter was obtained from the energy–strain curve taking the value that minimized the total energy. Thus, the complete list of the structural parameters for the X-ZGNRs are given by the length a , and its evolution with N is shown in Fig. 1.

The characteristic bond lengths for the three substituted nanoribbons for the extreme N cases, $N = 4$ and $N = 10$, are presented in Table 2. The shortest C–X distance (X = O, F, and Cl) was observed in the case of F-doping, which was expected due to the small size and high electron affinity of fluorine. Although there were no major differences, variations occurred at lower N values since in these cases, there was a proximity effect between edges and a reduction in the number of degrees of freedom. This introduced important changes in the corresponding electronic

Table 1 Formation energies and cohesion energies expressed as eV per atom

N	Formation energy (eV per atom)			Cohesion energy (eV per atom)		
	Cl	F	O	Cl	F	O
4	0.11	−0.31	−0.18	−6.34	−6.76	−7.04
5	0.09	−0.25	−0.15	−6.58	−6.93	−7.16
6	0.09	−0.22	−0.13	−6.74	−7.06	−7.26
7	0.07	−0.19	−0.11	−6.88	−7.15	−7.32
8	0.06	−0.17	−0.10	−6.99	−7.23	−7.38
9	0.07	−0.15	−0.09	−7.06	−7.28	−7.42
10	0.05	−0.14	−0.08	−7.13	−7.33	−7.45

Table 2 The bond distances C–X, C–C at edges of the GNRs, and C–C in the bulk region of the GNRs are presented in Å for X = Cl, F, and O

$N = 4$ (Å)		Cl	F	O
C–X		1.77	1.35	1.46
C–C _{edge}		1.41	1.41	1.34
C–C _{bulk}		1.45	1.45	1.41
$N = 10$ (Å)		Cl	F	O
C–X		1.76	1.36	1.46
C–C _{edge}		1.42	1.42	1.34
C–C _{bulk}		1.44	1.44	1.41

structure of the systems, affecting edge and bulk atoms; this fact has been reconsidered hereinafter. When going to higher N values, the interaction between edges becomes dilute, and thus, the C–C distances become closer to those expected for graphene^{31,38} although the structural distortions at the edges are still present.

Fig. 1 shows the evolution of the a -axis value for all the doping cases. In the case of $X = F$ and O , almost constant variation was observed. This is probably due to the chemical nature of the involved atoms, where F_2 and O_2 molecules present the equilibrium distances of 1.41 Å and 1.21 Å,³⁹ respectively, which are low as compared to the $X \cdots X$ distances between periodical images for $X = O$ and F (a -axis values). This fact would imply that the hybridization between the edge doping atoms could be reduced, and thus, the $X \cdots X$ distance (a -axis) remained almost constant and originated from the carbon backbone. In the case of Cl doping, the situation is different maybe due to the similarity between the obtained a -axis values with the corresponding bond equilibrium distance in the Cl_2 molecule, which is 1.99 Å³⁹ and can contribute to a potential $X \cdots X$ interaction. Herein, again, the edge proximity effect, together with the change in the electronic structure, could be the reason for the explanation of this trend. It has been further analyzed hereinafter.

3.3 Mechanical properties

The calculations presented in this manuscript were validated in a previous study of hydrogen-terminated ZGNR. The mechanical properties were analyzed in terms of the earlier presented 2D normalized Young's modulus E^{2D} . Fig. 2 shows the variation of the E^{2D} with the ZGNR's width N . The results show that E_1^{2D} and E_2^{2D} decrease, whereas N increases. This tendency was observed earlier as well, particularly for hydrogen-terminated ZGNRs³¹ where edge hardening was observed, even showing a Young's modulus higher than that of graphene. This effect disappears when going to larger widths because of the dilution of the edge hardening as a result of the presence of bulk C–C bonds; this explains why E^{2D} decreases. The F and Cl edge doping presents stiffer values than graphene independent of the way of

calculating the E^{2D} . The O -substituted ZGNR is the one that lies apart from this general behavior, even observed for non-substituted ZGNR.³¹ The unusual shortening of the C–C edge length leads to this exception, apart from the differences in its electronic structure, which has been discussed hereinafter. In particular, it can be inferred that the Cl -substituted nanoribbons are stiffer. The Cl -substituted case is stiffer than the non-substituted case,³¹ especially for narrow ZGNRs, possessing similar stiffness when the nanoribbon broadens. Finally, it is important to mention that as compared to that of the H -ZGNR, the equivalent Young's modulus for $X = Cl$ is an inconclusive measure of stiffness due to the ambiguity of the E^{2D} definition, see Fig. 2. However, it is possible to conclude that both $X = Cl$ and H are the stiffest ZGNRs.

3.4 Electronic structure

The band structure for the three substituted cases for the extreme widths, $N = 4$ and 10, are presented in Fig. 3. Since the spin contribution to the band structure is the same for up- and down-states, only that for the first case is reported for the sake of clarity in all the figures.

In the case of $X = F$, the band structure presents the same features of H -ZGNR, where antiferromagnetic (AFM) and semiconductor behavior is observed. In this situation, it is possible to merge the AFM semiconducting behavior and ferromagnetic (FM) metallic behavior, but as obtained previously for $X = H$, the AFM spin solution is the ground state.^{31,40} In particular, for $X = F$ and $N = 4$, the energy difference between both solutions is $\Delta E_{AFM-FM} = E_{AFM} - E_{FM} = 8.5$ meV per supercell. This difference rapidly reduces with the increasing ZGNR width, becoming $\Delta E_{AFM-FM} = E_{AFM} - E_{FM} = 1.9$ meV per supercell in the case of $N = 10$.

In the case of $X = Cl$, the situation slightly changes. While the number of bands remains equal between F and Cl , since both present the same number of valence electrons, apart from being located very close in the periodic table of elements, the semiconductor behavior and the spin-density is lost for $X = Cl$.

For $X = Cl$, a metallic behavior was observed, with localized states at the Fermi level (FL), and contributing with an

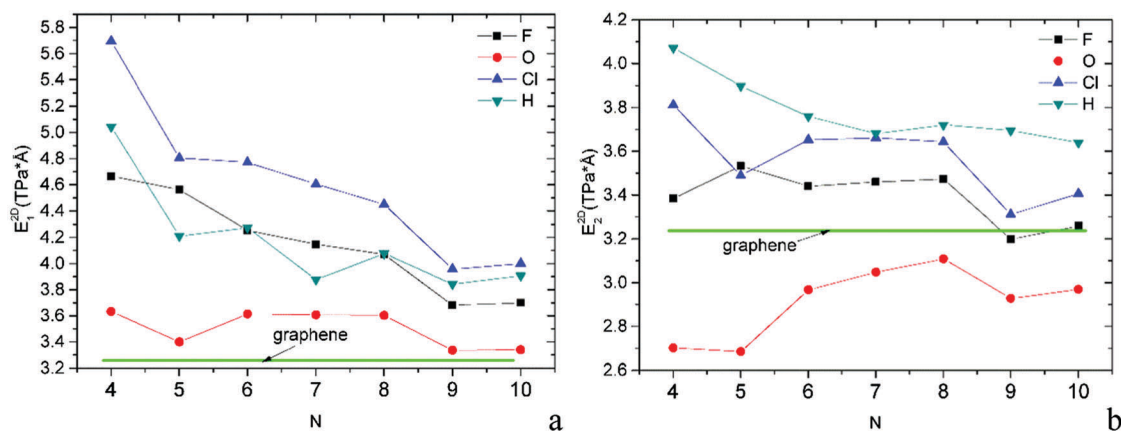


Fig. 2 Evolution of E^{2D} with X -ZGNR with N , for $X = F$, O , Cl , and H . For the sake of clarity, we have presented the two E^{2D} calculated with the characteristic lengths d_1 (a) and d_2 (b). For comparison purposes, the graphene values are represented by the green line.

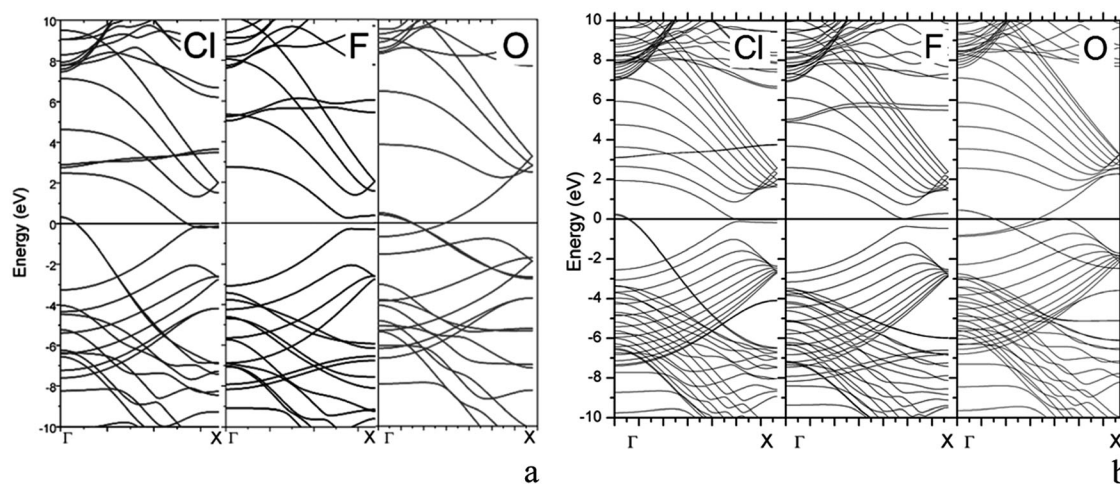


Fig. 3 Band structure of X-ZGNRs for $N = 4$ (a) and $N = 10$ (b).

additional double degenerated band, being crossed by the Fermi level close to the Γ -point. This situation for Cl remains for every width, in which there exists more contribution from the bulk state, but the physics at the Fermi level is governed by the same kind of edge states.

The situation for $X = O$ is really different, with two bands double degenerated each, being crossed by the Fermi level, constituting again a metallic behavior without the development of magnetic ordering. Once again, the nature of the chemical doping at the edges controls the electronic structures and thus its derived structural and mechanical properties. To obtain deeper insights into this discussion, we proceeded to determine the single-electron pseudo-wave functions for the most relevant bands at the high symmetry points of the Brillouin zone, X - and Γ -point, see Fig. 4.

In the case of $X = F$, the bands that contribute to the gap opening upon magnetic ordering correspond to π -states located at different edges. In the other cases, there exist mixed contributions from σ - and π -states coming from the C atoms from the bulk and edge positions.

When considering $X = O$, the situation changes, as stated earlier. First, the lower number of valence electrons of O as compared to those of F makes the band filling different between them. The original band gap opening is lost, and the highest occupied band in $X = F$ becomes depopulated for $X = O$, being crossed by the Fermi level. Additionally, one antibonding band appears and is crossed at the Fermi level too, being almost filled and crossed by the FL. These double degenerated bands present an important contribution from the edge states, particularly from the O orbitals with the p_x symmetry. Due to the proximity of the edge doping atoms, there exists an important hybridization between states localized at the edges, see Fig. 4. However, these $O \cdots O$ interactions are not structurally relaxed due to the presence of the carbon backbone of the GNR that fixes the $O \cdots O$ distances, establishing, for this particular case, a comparatively inferior stability. This observation is extracted from the band running that can be energetically stabilized if the band dispersion is reduced by an increase in the $O \cdots O$ distance, not allowed

again due to the carbon backbone of the ribbon. This could be the origin of relative softening of the mechanical properties of $X = O$ when compared with those of F.

Next, we discussed the situation of $X = Cl$. It can be interpreted as an intermediate situation between $X = F$ and $X = O$. First, because F and Cl present the same number of valence electrons, the band filling should be similar, and in fact, this is the case. The major differences between Cl- and F-ZGNR lie in the loss of magnetic ordering for Cl-ZGNR that again conducts to a metallic solution with localized states at the FL. Similar to $X = O$, $X = Cl$ presents an antibonding band, crossed by the FL close the Γ -point. This is a double degenerated band being mainly contributed from the edge states, again from the $Cl \cdots Cl$ interactions, particularly from orbitals with p_x symmetry. In relation to the size of Cl, which is bigger than that of the F and O atoms, the interaction is more pronounced, as observed in the band dispersion that runs from $E = 0$ to -7 eV. This band is less dispersed for $X = O$, running from $E = 0$ to -3 eV; and totally filled for $X = F$, running from $E = -3.5$ to -6 eV.

On the one hand, this close $Cl \cdots Cl$ distance generated from the carbon backbone of the ZGNR contributes to interesting edge-localized bands that harden the Cl-ZGNRs as compared to those of $X = F$ and O. On the other hand, this $Cl \cdots Cl$ distance makes the Cl-ZGNRs relatively unstable from the formation energy point of view; this explains the abovementioned trend for E_{form} and E_{coh} .

Finally, it is important to mention that we preliminarily evaluated the effects of using a hybrid functional such as HSE06²⁵ to evaluate the eventual changes in the electronic structure of the systems and thus its consequences in the mechanical properties. In particular, we selected a ZGNR with $N = 4$, the thinnest case, since in this case, the confinement effects are stronger and the changes should be more pronounced. In the first case $X = F$, the PBE xc-functional conducts to an AFM and insulator solution with $E_{gap} = 0.3$ eV, whereas with HSE06, the energy gap increases to $E_{gap} = 1.4$ eV, retaining the AFM spin arrangement. In the case of $X = Cl$, PBE establishes a nonmagnetic metallic solution, which is also the case for HSE06 in which there are no

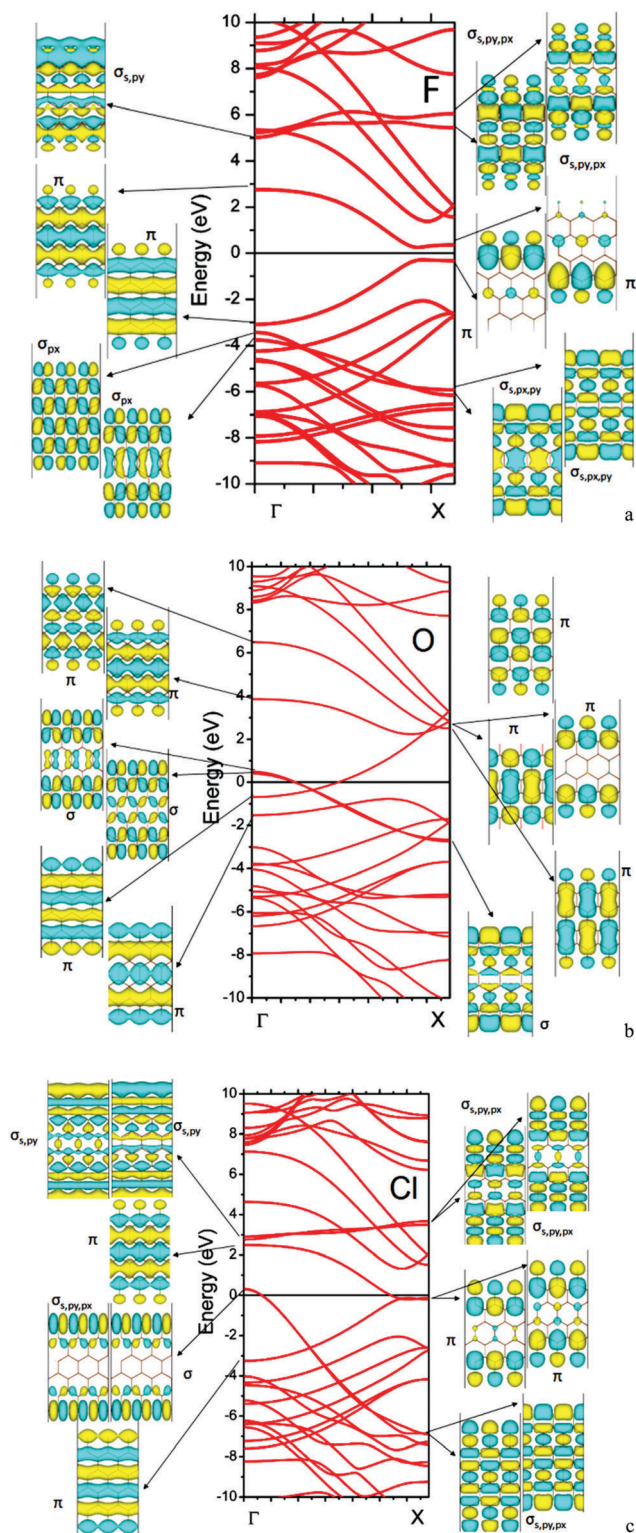


Fig. 4 Band structure and single electron pseudo-wave functions at high symmetry points for the most relevant bands close to the Fermi level for: (a) F, (b) O, and (c) Cl.

important changes. Finally, for $X = O$, the original nonmagnetic and metallic solution obtained with the PBE xc-functional changes to an AFM insulator solution with a band gap opening

of 0.33 eV, see the ESI.† This is the only case in which there exists an important change from a metallic to an insulator solution. In any case, this gap opening is clearly low as compared to that for $X = F$ and rapidly reduces for higher N values. For all these reasons, we consider that our original PBE results are still valid for our main conclusions in reference to the mechanical properties of the studied systems.

4. Conclusions

In this study, we presented a comprehensive analysis of the structural, electronic, and mechanical properties of a X-ZGNR modified at the edge positions with $X = F, O$, and Cl atoms. The simulations indicate that Cl - and F -doped ZGNRs present equivalent 2-dimensional Young's modulus E^{2D} values, larger than those of graphene and H -doped ZGNRs. This is a consequence of the electronic structure of the system, particularly originating from strong interactions between the dopant atoms localized at the edges. The interaction between dopant atoms at the edges is higher for Cl and lower for F and O and can be understood in terms of their electronic structures. This behavior explains the observed trend in the mechanical properties, establishing that $E_{Cl}^{2D} > E_F^{2D} > E_O^{2D}$ for the whole set of ZGNRs with different widths.

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