Doping graphene by adsorption of polar molecules at the oxidized zigzag edges

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We have theoretically investigated the electronic and magnetic properties of graphene whose zigzag edges are oxidized. The alteration of these properties by adsorption of H$_2$O and NH$_3$ molecules has been considered. It was found that the adsorbed molecules form a cluster along the oxidized zigzag edges of graphene due to interaction with the electro-negative oxygen. Graphene tends to donate a charge to the adsorbates through the oxygen atoms and the efficiency of donation depends on the intermolecular distance and on the location of the adsorbed molecules relative to the plane of graphene. It was found that by appropriate selection of the adsorbates, a controllable and gradual growth of $p$-doping in graphene with a variety of adsorbed molecules can be achieved.

PACS numbers: 73.22.-f,73.20.Hb,73.21.La,75.25.+z

I. INTRODUCTION

The edges of graphene, in particular the zigzag edges, play the most important role in defining the electronic properties of graphene. Geometry of the zigzag edges localizes the electrons with maximum of the electron density at the border carbon atoms. The localized states form the flat conduction and valence bands near the Dirac point and the size of the gap between them is defined by the contribution of the confinement effect and shape of the edges. Any changes in the edge geometry, such as termination, reconstruction or distortion, would modify the electronic properties of graphene. Termination of the edges most often is realized through the edge hydrogenation, which alters the $sp^2$ network at the zigzag edges. For the pure graphene edges, there is a mixture of the $sp$ and $sp^2$ hybridization, while for hydrogenated graphene the $sp^2$ and $sp^3$ hybridization dominates providing an increase in the size of the gap. Additionally to hydrogenation, structural changes in the zigzag edges, such as reconstruction and aromaticity, also have effect on the electronic properties of graphene. Moreover, the geometry of pure zigzag edges are found to be metastable. It was shown that the planar reconstruction of the zigzag edge to reczag type is possible because it lowers the edge energy. The electronic structure of graphene with reczag edges differs significantly from that with zigzag edges, namely by the appearance of the degeneracy of conduction and valence bands for the momentum range $k < 2\pi/3$, and their dispersion for $k > 2\pi/3$ (the zigzag edges impose the flat degenerate conduction and valence bands within the intervals $2\pi/3 \leq |k| \leq \pi$). Coexistence of the zigzag and reczag edges in graphene samples has been confirmed experimentally.

In fabrication of graphene-based devices the control of the shape and quality of the edges is clearly an important issue. With the standard approaches developed to create graphene nanoribbons, such as lithographic patterning, chemical vapor deposition method and chemical sonication, the control of the nanoribbon size and quality of the edges is poor. Most recent achievement in fabrication of graphene nanoribbons is by unzipping the carbon nanotubes. Unzipping of multiwalled or singlewalled carbon nanotubes by plasma etching provides smooth edges and a small range of the nanoribbon width (10-20 nm). The second unzipping method - the solution-based oxidative process allows to perform the longitudinal cut of the nanotubes and to obtain the nanoscale structures characterized by the predominantly straight linear edges. However, because of the applied solution-based oxidative method, the zigzag edges of graphene are oxidized and so the surface of graphene can be partially oxidized. Annealing or chemical reduction of samples in the N$_2$H$_4$ environment reduces the number of oxygen-containing functionals at the surface and edges of graphene and, indeed, a significant increase in conductivity of graphene has been obtained.

From our point of view, an important improvement of oxidation of the zigzag edges of graphene is the prevention of reconstruction of the zigzag edges. However, an extensive investigation of the electronic properties of graphene with oxidized zigzag edges is not yet available in the literature. Therefore, the present study is devoted to this particular issue and the possibility of doping nanoscale graphene through adsorption of water and gas molecules. The spin-polarized density functional theory with semilocal gradient corrected functional (UB3LYP/6-31G$	ext{d}$) in the Jaguar 6.5 program has been applied in our work. The impact of the van der Waals interactions is not included within the DFT that leads to underestimation of the adsorption energy, but it should not undermine the reliability of DFT for investigation of the influence of adsorption on the electronic properties of graphene.

II. UNIQUE PROPERTIES OF GRAPHENE WITH OXIDIZED ZIGZAG EDGES

For graphene of finite size with pristine edges, the effect of localization of the electron density at the zigzag edges is a result of specific boundary conditions for the wavefunctions. In particular, because all border carbon atoms across a single zigzag edge belong to the same sublattice, the wavefunctions at the zigzag edge vanish.
The electron and spin densities are plotted for isovalues of ±0.03 e/Å². (a) The electron density distribution in the pristine graphene for a state of C_{2v} symmetry (α-spin for HOMO). (b) The electron density distribution in graphene with oxidized zigzag edges for a state of C_{1} symmetry (α-spin for HOMO-9). (c) The spin density distribution in graphene with oxidized zigzag edges for a state of C_{1} symmetry. Localization of spins on the oxygen atoms obtained within the NBO analysis and the natural charge for the oxygen and carbon atoms within the C-O bonds are also indicated.

Oxidation of the zigzag edges makes a difference in the electron density distribution of the localized states because of alteration of the boundary conditions for the wavefunctions. The electron density is mostly localized on the sides of the polar C-O bonds, as it is presented in Fig. 1 (b). For the structure shown in Fig. 1 (b), the electron density for the HOMO and LUMO are delocalized over the whole graphene structure, while the localized states are shifted deeper into the bands from the gap edges, i.e. to the HOMO-9 and HOMO-10 in the valence band and to the LUMO+1 and LUMO+2 in the conduction band. However, an increase in the size of the structure leads to backward shifting of these states closer to the band gap. Therefore, when we increased the width of nanoscale graphene by adding two rows of the carbon hexagons along the single zigzag edge, the localized states in the valence band has already been shifted to HOMO-5 and HOMO-6 orbitals.

The spin density for graphene with oxidized edges is mostly localized on the oxygen atoms, as it is presented for nanoscale graphene in the C_{1} symmetry state in Fig. 1 (b). The total energy of the system decreases with lowering of the symmetry of graphene and the C_{1} symmetry state is characterized by the lower energy. For the state of the C_{1} symmetry, the total spin at each zigzag edge is -1.0 for one edge and +1.0 for another edge. Because the spin density is mostly localized on the oxygen atoms within the C-O bonds, it is negligible for all carbon atoms in graphene. Symmetry also has influence on the size of the band gap. For the size of graphene presented in Fig. 1 (b), the gaps are Δ_{D_{2h}}=0.18 eV, Δ_{C_{2v}}=1.0 eV and Δ_{C_{1}}=1.33 eV. We consider that graphene obtained by nanotube unzipping would have highly tensile structure for which the high symmetry state would be unreachable, and therefore, we have used the C_{1} symmetry for all our calculations.

We have performed the natural bond analysis (NBO) for which the border carbon atoms belong to different sublattices, the sublattice symmetry is preserved. In the case of an absence of the confinement effect, graphene with preserved sublattice symmetry is expected to be gapless. The ferromagnetic ordering between the zigzag edges leads to breaking of the sublattice symmetry and opening of a gap. In the case of broken sublattice symmetry (for nanoscale graphene the sublattice symmetry is broken already for C_{2v} symmetry when the mirror plane of symmetry is perpendicular to the zigzag edges), the α-spin state is localized on one zigzag edge, while the β-spin state is on the opposite zigzag edge. We presented an example of the distribution of the electron density of the localized α-spin state for the highest occupied molecular orbital (HOMO) in Fig. 1 (a). A similar distribution but with localization of the electron density on the opposite zigzag edge is observed for the lowest unoccupied molecular orbital (LUMO). The maximum of the electron density of these states is located on the border carbon atoms and, as a result, the spin density is localized there as well (see Fig. 2 in Ref. [15]).
for nanoscale graphene with the oxidized edges and defined the natural charges for the carbon and oxygen atoms within the C-O bonds, whose magnitudes are indicated in Fig. 1 (c). The C-O is the polar bond for which the decentralization of the electron clouds between the carbon and oxygen atoms leaves the oxygen atoms negatively charged, while the carbon atoms are positively charged. As a result, the electro-negative oxygen atoms within the polar C-O bonds are more chemically active than on the non-polar surface of graphene. It was found that for the C-O bonds the natural charge distribution (see Fig. 1 (c)) and the length of the bonds deviate along the zigzag edges (from 1.26 to 1.31 Å). However, despite the dispersion of the bond length the variation of the dipole moment among the C-O bonds is consistent with the deviation of the natural charge distribution, i.e. for the bonds characterized by a larger charge difference between the oxygen and carbon atoms, the dipole moment is slightly larger as well. Therefore, interaction of the oxygen atoms with the adsorbed molecules would also slightly deviate along the edges.

III. ADSORPTION OF H$_2$O AND NH$_3$ MOLECULES

The most popular and widely investigated method of doping graphene is by adsorption of the gas molecules which is claimed to be controllable by the nature and concentration of the adsorbates. However, according to the theoretical predictions, interaction between the surface of graphene and most of the molecules adsorbed on graphene should be low and doping of ideal pristine graphene ($sp^2$ network) should not be efficient. Moreover, because of weak interaction of the adsorbates with the ideal graphene surface, the type of doping and its efficiency is defined by the orientation of the adsorbed molecules on the surface. Therefore, doping observed in experiments is most probably the result of lattice defect in graphene. In this respect we would like to emphasize two important advantages of oxidation of the zigzag edges of graphene: potentials to achieve a controllable doping (because oxidation will enhance interaction of the edges with the surrounding environment) and stabilization of the edge geometry. The oxidized zigzag edges attract polar molecules from the environment more strongly than the graphene surface due to polarity of the C-O bonds. The charge exchange between the C-O bonds and the adsorbates would contribute to the alteration of the electronic balance in graphene leading to its doping. Therefore, adsorption would influence the graphene conductivity and offers an unique opportunity for its application in graphene-based gas sensors.

The H$_2$O or NH$_3$ molecules have been chosen for our investigation because of their polarity and the presence of more than two hydrogen atoms in their structure. Adsorption of H$_2$O or NH$_3$ molecules on graphene with oxidized edges has been performed for primary optimized geometry of graphene. After adsorption an additional optimization procedure has been applied. During this optimization the positions of the carbon atoms belonging to graphene are kept fixed, while the oxygen atoms within the C-O bonds and the adsorbed molecules were relaxed. The oxygen atoms within the C-O bonds make hydrogen bonds with the adsorbed molecules due to strong polarity of the C-O bonds. If adsorbed molecules have in their structure several hydrogen atoms and the electro-negative atoms possess the lone pair (oxygen, nitrogen), they have the ability to bind to each other through the hydrogen bonds, thereby forming a cluster. However, the hydrogen bonding with graphene leads to aligning of the cluster structure along the zigzag edge, as presented in Fig. 2 (a) and Fig. 2 (b) for the H$_2$O and NH$_3$ molecules, respectively. We have estimated the binding energy required to dissociate graphene from the adsorbed molecules. It was found that the binding energy grows almost linearly with increasing number of the adsorbed molecules, but have a slight tendency for saturation when the number of molecules is larger than eight.

The highest symmetry applicable for graphene with adsorbates is the $C_1$ symmetry because the charge exchange with the adsorbates generates an imbalance in the electron distribution between the two sublattices in graphene and, therefore, breaking the sublattice symmetry. The size of the bandgap after adsorption is similar to the value of that for pristine graphene in the $C_1$ symmetry state ($\Delta E_{C1} = 1.33$ eV). However, if the HOMO or LUMO are localized on the adsorbed molecules, the size of the band gap is altered. Interaction of graphene with the adsorbed molecules induces a change in ordering of the orbitals, particularly the states localized on the zigzag edges now belong to HOMO (HOMO-1) and LUMO (LUMO+1) orbitals while without adsorbates the localized states are shifted deeper into the conduction and valence bands (see discussion in Sec. III).

Formation of hydrogen bonds between the adsorbed molecules and the oxygen atoms belonging to the C-O bonds of graphene leads to decentralization of the electron clouds between the electron-negative oxygen from the C-O bonds and the electron-positive hydrogens belonging to the adsorbed molecules. Therefore, the interac-
TABLE I: Influence of adsorption of H$_2$O or NH$_3$ molecules on spin and charge distributions in graphene with oxidized edges. All data are obtained within the NBO analysis. $Q_{H_2O}$ and $Q_{NH_3}$ are the charge accumulated on the adsorbed molecules, $S_{H_2O}$ and $S_{NH_3}$ are the total spin on the cluster formed by the adsorbed molecules, $S_D$ is the sum of spin located on the oxygen atoms belonging to the polar C-O bonds of graphene, $Q_{tr}$ is the total charge transfer from graphene to the adsorbates. "Left" and "Right" refer to to the left and right zigzag edges as shown in Fig. 1(b).

|                  | $H_2O$       |                  | $NH_3$       |                  |
|------------------|--------------|------------------|--------------|------------------|
|                  | $Q_{H_2O}$, e | $S_{H_2O}$, e    | $S_{NH_3}$, e | $Q_{tr}$, e      |
| $Q_{H_2O}$, e    | Left | Right | Left | Right | Left | Right | Left | Right |
| 1                | 0.028 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 2                | 0.317 | -0.46 | -0.47 | 1.01 | 0.028 |
| 3                | 0.841 | 0.48 | -1.59 | 1.01 | 0.084 |
| 4                | 0.856 | -1.02 | 2.01 | -1.01 | 0.068 |
| 5                | 0.869 | 1.02 | -2.01 | 1.00 | 0.096 |
| 6                | 0.889 | 1.00 | 0.01 | -1.00 | 0.073 |
| 7                | 0.882 | -0.006 | 1.00 | -0.01 | 0.01 | -1.00 | 0.096 |
| 8                | 0.890 | 0.053 | 1.00 | -0.07 | 0.01 | -0.93 | 0.098 |
| 9                | 0.881 | 0.348 | -1.00 | 0.40 | 0.04 | 0.24 | 0.132 |
| 10               | 0.888 | 0.854 | 1.01 | 0.99 | -1.97 | 0.01 | 0.161 |
| 11               | 0.888 | 0.864 | 1.01 | 1.01 | 0.01 | -1.97 | 0.183 |
| 12               | 0.889 | 0.853 | 1.00 | 1.01 | 0.01 | -1.95 | 0.191 |

$\Delta E_{ij} = -2F_{i,j}^2/(\epsilon_i - \epsilon_j)$ has a positive sign. The calculated results for the charge exchange $(Q_{tr})$ between graphene and the adsorbates (H$_2$O or NH$_3$ molecules) are also presented in Table I. The total spin of the states localized on the oxygen atoms within the C-O bonds $(S_O)$ and on the adsorbed molecules $(S_{H_2O}$ or $S_{NH_3})$ are also indicated in this table separately for left and right zigzag edges of graphene (see notations for the edges in Fig. 1(b)).

According to our studies, both graphene and the cluster formed by the adsorbed molecules are spin-polarized in most cases. For spin-polarized graphene, each zigzag edge is characterized by the non-zero total spin whose sign is different for the opposite edges. The sign and the total spin associated with the adsorbed molecules varies with the number of molecules. However, the balance of the spin density between the left and right sides of the whole system which includes graphene with adsorbed molecules, is preserved (except for the case when a single water molecule is adsorbed). Thus, taking into account the spin localized on the zigzag edge and the adsorbed molecules (see the magnitude of $S_{NH_3} + S_O$ and $S_{H_2O} + S_O$ in Table I) the total spin +1.0 for one side of the system and -1.0 for other side are retained. The spin distribution for the oxidized graphene with eleven NH$_3$ molecules bound to the edges by the hydrogen bonds is presented in Fig. 3. Only one or two molecules within the cluster have the non-zero total spin and are spin-polarized, while the rest of the molecules are unpolarized. For adsorbed molecules characterized by zero spin density the magnitude of the natural charge is almost zero ($\sim 0.05\,\bar{e}$), but for a case of non-zero spin density the charge is non-zero ($\sim 0.5\,\bar{e}$ for each of the spin-polarized molecule). The dependence of spin-polarization and resulting nonzero magnetic moment on the number and
location of the adsorbed molecules can be useful for developing spin-valve devices\textsuperscript{29}.

The charge transfer from pristine graphene to water is not expected to be efficient and was reported to be in the range \(-0.02 \div 0.01\) \(\bar{e}\) depending on the position and orientation of water, while according to our calculations performed for the single water molecule within the NBO analysis, it is \(\sim 0.001\) \(\bar{e}\) (for details of interaction of water with pristine graphene see\textsuperscript{13}). The charge exchange between graphene with oxidized edges and the adsorbates is quite efficient and increases with the number of adsorbed molecules (see \(Q_{tr}\) in Table 1). For adsorption of \(\text{H}_2\text{O}\) molecules, the charge donation from graphene to adsorbates increases gradually. However, for a single \(\text{H}_2\text{O}\) molecule adsorbed at the zigzag edge, the charge exchange is insignificant because of the location of the molecule relative to the edges. A single \(\text{H}_2\text{O}\) molecule interacts with graphene by both of its hydrogens which are directed to two nearest oxygen atoms at the zigzag edge. The resulting distance between the \(\text{H}_2\text{O}\) molecule and the edges is large (the distance between O-H and O-C is \(\sim 2.2\) \(\text{Å}\)) and the \(\text{H}_2\text{O}\) molecule lies parallel to the graphene plane. Therefore, the overlapping of orbitals is weak. For two or more adsorbed molecules, one hydrogen of the \(\text{H}_2\text{O}\) molecule makes a hydrogen bond with the other \(\text{H}_2\text{O}\) molecule, while the second hydrogen bonds to the oxygen atom within the C-O bond of graphene. The cluster that formed is placed close to the zigzag edge (the hydrogen bond of O-H \(\cdots\) O-C is \(\sim 1.2\) \(\text{Å}\)) and water molecules are located not exactly in the plane of graphene but slightly below and above, hence providing an effective overlapping of orbitals between the interacting species (see Fig. 2(a)).

For the \(\text{NH}_3\) adsorbates, a similar behavior is obtained for up to three \(\text{NH}_3\) molecules. The most efficient charge exchange occurs when two or three molecules are placed along the zigzag edge, while a further increase of their number suppresses the charge transfer. The effect is related to clustering of the \(\text{NH}_3\) molecules along the zigzag edge. Two or three \(\text{NH}_3\) molecules adsorbed along the zigzag edge are located slightly below and above the graphene plane somewhat similar to the water molecules in Fig. 2(a) (the hydrogen bond of N-H \(\cdots\) O-C is \(\sim 2.0\) \(\text{Å}\)) generating an efficient charge exchange with graphene due to strong overlapping of their orbitals. However, adsorbates move apart from the plane of graphene when more than three molecules are added (as presented in Fig. 2(b)) and the length of hydrogen bonds for some molecules increases (the hydrogen bond of N-H \(\cdots\) O-C is \(\sim 2.5\) \(\text{Å}\)). Thus, in the cluster containing more than three \(\text{NH}_3\) molecules, they are located significantly out of the plane of graphene that lead to diminishing efficiency of the charge exchange of each adsorbed molecule with graphene.

The charge exchange between graphene and the adsorbed molecules shifts the conduction and valence bands of graphene in the energy scale. In Fig. 4, we have plotted the orbital energies of HOMO and LUMO as a function of the number of adsorbed molecules. The HOMO-LUMO gap is almost unchanged except for the cases when the orbitals are localized on the adsorbed molecules as indicated in Fig. 4 by the shaded areas. The orbital energies are shifted when the number of molecules increases indicating the \(p\)-doping of graphene. Degradation of the bands is clearly consistent with the alteration of the charge transfer from graphene to the adsorbates (see \(Q_{tr}\) in Table 1). Thus, for the adsorption of water, the shift of the orbital energy gradually increases when the number of adsorbed molecules grows, thereby providing an opportunity to control the doping of graphene through adsorption of the polar molecules.

IV. CONCLUSION

We have investigated the alteration of the electronic properties and spin distribution induced by adsorption of the polar molecules in nanoscale graphene with oxidized zigzag edges. The polar molecules interact with oxygen...
atoms belonging to the polar C–O bonds at the edges of graphene. When the adsorbed molecule contains hydrogen atoms they interact with the C–O bonds of graphene through generation of the hydrogen bonds (H···O–C). Several adsorbed H₂O or NH₃ molecules tends to create a cluster due to the strong intermolecular interaction between them, but the interaction with graphene aligns the cluster structure along the zigzag edge. Graphene with oxidized edges tends to donate a charge to the adsorbed molecules along the zigzag edge. Graphene with oxidized edges tends to donate a charge to the adsorbed molecules relative to the plane of graphene. In the case of H₂O adsorption, the charge transfer efficiency and the corresponding shift of the HOMO and LUMO bands as a result of p-doping of graphene increase gradually with the number of molecules. For the NH₃ molecules the maximum efficiency of doping occurs when the number of adsorbed molecules along the zigzag edge is limited by two or three as a result of their closer location to the plane of graphene than when more molecules are adsorbed. Therefore, we can conclude that when the graphene surface or the edges are oxidized, the adsorption of the polar molecules is the most viable option for p-doping of graphene.

V. ACKNOWLEDGMENTS

The work was supported by the Canada Research Chairs Program and the NSERC Discovery Grant.