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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_2O 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 electronegative 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.

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I. INTRODUCTION

The edges of graphene, in particular, the zigzag edges, play an important role in defining the electronic properties of graphene.[1] 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 points, and the size of the gap between them is defined by the contribution of the confinement effect and shape of the edges.[2,3] Any changes in the edge geometry, such as termination, reconstruction or distortion, would modify the electronic properties of graphene.[4] Termination of the edges most often is realized through the edge hydrogenation, which alters the sp^2 network at the zigzag edges.[3] For the pure graphene edges, there is a mixture of the sp and sp^2 hybridizations while for hydrogenated graphene the sp^2 and sp^3 hybridizations dominate providing an increase in the size of the gap. In addition to hydrogenation, structural changes in the zigzag edges such as reconstruction and aromaticity also influence the electronic properties of graphene.[5] Moreover, the geometry of pure zigzag edges is 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.[6] 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,[5] $k<2\pi/3$, and their dispersion for $k>2\pi/3$ (the zigzag edges imposes the flat degenerate conduction and valence bands within the interval,[1] $2\pi/3\leq|k|\leq\pi$). Coexistence of the zigzag and reczag edges in graphene samples has been confirmed experimentally.[7]

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,[8] chemical-vapor-deposition method,[9] and chemical sonication,[10] the control of the nanoribbon size and quality of the edges are poor. Most recent achievement in fabrication of graphene nanoribbons is by unzipping the carbon nanotubes.[11,12] Unzipping of multiwalled or single-walled carbon nanotubes by plasma etching provides smooth edges and a small range of the nanoribbon width[11] (10–20 nm). The second unzipping method—the solution-based oxidative process allows one to perform the longitudinal cut of the nanotubes and to obtain the nanoscale structures characterized by the predominantly straight linear edges.[12] 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 in samples in the N_2H_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.[12]

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 (DFT) with semilocal gradient corrected functional [UB3LYP/6–31G (Ref. 13)] in the JAGUAR 6.5 program[14] 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[15] 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 wave functions. In particular, because all border carbon atoms across a single zigzag edge belong to the same sublattice, the wave functions at the zigzag edge vanish on a single sublattice, while at the armchair edges on both sublattices. The generated localized states at the zigzag edges are responsible for formation of the conduction and valence bands near the Dirac points. Depending on the spin ordering of the localized states

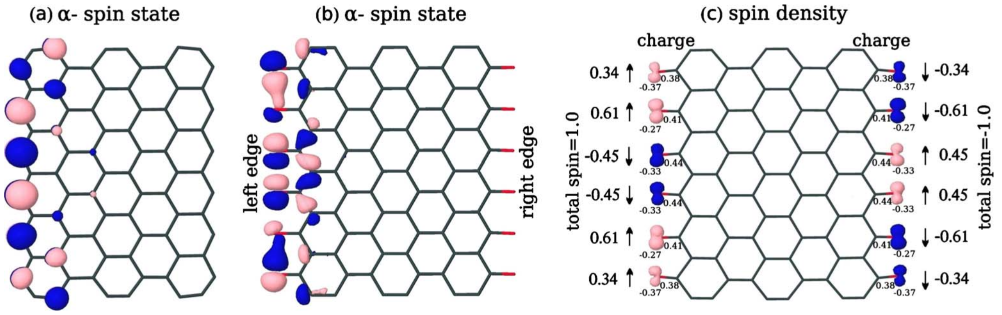

FIG. 1. (Color online) Electron- and spin-density distributions in a pure graphene flake and graphene with oxidized zigzag edges. The electron and spin densities are plotted for isovalues of $\pm 0.03\ \mathrm{e/\AA^3}$. (a) The electron density distribution in the pristine graphene for a state of C_{2v} 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.

between the zigzag edges, graphene of finite size can be gapless or has a gap. If spins of the localized electrons are antiferromagnetically ordered between the opposite zigzag edges for which the border carbon atoms belong to different sublattices, the sublattice symmetry is preserved. In the 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 the C_{2v} symmetry when the mirror plane of symmetry is perpendicular to the zigzag edges[16,17]), the α-spin state is localized on one zigzag edge, while the β-spin state on the opposite zigzag edge. We present 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. 16).

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 wave functions. We choose the structure of graphene presented in Fig. 1(a) as a model compound for which oxidation of the zigzag edges is performed. The structure of graphene with oxidized zigzag edges [see Fig. 1(b) for details of the graphene size] has been optimized with the DFT method (UB3LYP/6–31G). The obtained electron density is mostly localized on the sides of the polar C-O bonds, as shown in Fig. 1(b). For the structure in Fig. 1(b), the electron density for the HOMO and LUMO are delocalized over the entire 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, depending on the size of the structure the localized states can be shifted closer to the band gap that is related to the ordering of the subbands with modification of the shape of the edges as elaborated elsewhere.[18] Therefore, if we increase the width of the model compound of nanoscale graphene [see Fig. 1(b)] by adding two rows of the carbon hexagons along the single zigzag edge, the localized states in the valence band are shifted to HOMO-5 and HOMO-6 orbitals, while if we decrease the width by two rows the localized states are becoming HOMO and LUMO.

The spin density for graphene with oxidized edges is mostly localized on the oxygen atoms, as shown for nanoscale graphene in the C_1 symmetry state in Fig. 1(c). Ordering of spins of the localized electrons along the zigzag edges and between the opposite edges is defined by the applied symmetry. For the D_{2h} symmetry, the spin ordering is ferromagnetic along the edges and between the edges, while for the C_{2v} symmetry (when the symmetry plane is perpendicular to the zigzag edges) and for the C_1 symmetry, there are mixed spin ordering along the zigzag edges and antiferromagnetic ordering between the zigzag edges. 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 nonzero, particularly the total spin equals $+1.0$ 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 $\Delta_{D_{2h}}=0.18$ eV, $\Delta_{C_{2v}}=1.0$ eV, and $\Delta_{C_1}=1.33$ 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[19] (NBO) 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 electronegative oxygen atoms within the polar C-O bonds are more chemically active than on the nonpolar 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 in 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_2O 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.[20–26] However, according to the theoretical predictions, interaction between the surface of graphene and most of the molecules adsorbed on graphene should be weak[15] 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.[16,27–29] Therefore, doping observed in experiments[20–26] is most probably the result of lattice defect in graphene.[30] In this respect we would like to emphasize two important advantages of oxidation of the zigzag edges of graphene: potentials to achieve controllable doping (because oxidation will enhance interaction of the edges with the surrounding environment) and stabilization of the edge geometry. For the pristine graphene the adsorbed molecules are kept on the surface due to the van der Waals interactions[16] while the oxidized zigzag edges attract polar molecules from the environment more strongly than the graphene surface due to polarity of the C-O bonds. Therefore, the adsorbed polar molecules would move toward the oxidized edges and when possible will make hydrogen bonds with oxygen belonging to the C-O bonds at the zigzag edges. 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.[20,21]

The H_2O or NH_3 molecules are chosen for our investigation because of their polarity and the presence of more than two hydrogen atoms in their structures. Adsorption of H_2O or NH_3 molecules on graphene with oxidized edges has been performed for primary optimized geometry of oxidized graphene. We started from adsorption of single molecule whose position is optimized with the DFT method (UB3LYP/6–31G). To decrease the cost of the optimization procedure, the positions of the carbon atoms belonging to the graphene lattice, which is tested here and in a previous work,[16] to be rigid in interaction with adsorbates, were kept fixed during the optimization procedure. On the other hand, the position of the oxygen atoms within the C-O bonds and the adsorbed molecules were found to be uncertain due to the significant interaction between them and therefore, were relaxed during the optimization procedure. Because the charge transfer between the adsorbate molecule and graphene can grow with increasing number of adsorbed molecules (N), we gradually increase the number of molecules first along one zigzag edge and after that along the other edge. The building up procedure was performed stepwise by adding one extra molecule of adsorbate at each step for which the optimization procedure has been performed.

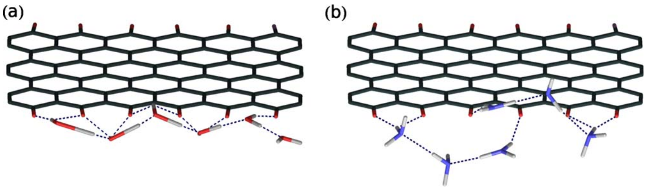

FIG. 2. (Color online) Structure of nanoscale graphene with oxidized edges where the adsorbed molecules ($N=6$) are attached to the zigzag edge by hydrogen bonds. Several adsorbed molecules form a cluster due to the hydrogen bonding with zigzag edge of the oxidized graphene and between each other. (a) Adsorbate is the H_2O molecule. (b) Adsorbate is the NH_3 molecule.

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 electronegative 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 Figs. 2(a) and 2(b) for the H_2O and NH_3 molecules, respectively. We have estimated the binding energy required to dissociate graphene from the adsorbed molecules (E_b). The binding energy of the cluster formed by the adsorbed molecules grows almost linearly with increasing number of the molecules (N) but have a slight tendency for saturation because some of adsorbed molecules are not bound to graphene but only to each other. Thus, $E_{b(12H_2O)}=-12.6$ eV and $E_{b(12NH_3)}=-12.2$ eV, while the lengths of the hydrogen bonds vary from 1.9 to 2.2 Å for the adsorbed water molecules and from 2.1 to 2.4 Å for the adsorbed NH_3 molecules. Therefore, the average value of the binding energies for single H_2O and NH_3 molecules is $E_b \sim -1.0$ eV. Within the water cluster the hydrogen bonds are shorter and vary in the range of 1.0–1.6 Å but within the cluster composed of NH_3 molecules the length of the hydrogen bonds is in the range of 1.7–2.0 Å. Moreover, in the case of interaction of the polar molecules when the length of the hydrogen bonds is shorter than the sum of the van der Waals radius of the participating atoms (>2.8 Å for the $\text{H}\cdots\text{O}$ and $\text{H}\cdots\text{N}$ hydrogen bonds), the contribution from the van der Waals forces should increase the binding energy and shorten the hydrogen bonds.

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, this breaks the sublattice symmetry. The size of the band gap after adsorption is similar to the value of that for pristine graphene in the C_1 symmetry state ($\Delta_{C_1}=1.33$ eV). However, if the HOMO or LUMO are localized on the ad-

TABLE I. Influence of adsorption of H_2O or NH_3 molecules on spin and charge distributions in graphene with oxidized edges, where N_{H_2O} and N_{NH_3} indicate the number of the adsorbed molecules. 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_O 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 the left and right zigzag edges as shown in Fig. 1(b).

H_2O

N_{H_2O}	Q_{H_2O}, $\bar{e}$		S_{H_2O}		S_O		Q_{tr}, $\bar{e}$
	Left	Right	Left	Right	Left	Right	
1	0.028		0.00		0.00	0.00	0.006
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

NH_3

N_{NH_3}	Q_{NH_3}, $\bar{e}$		S_{NH_3}		S_O		Q_{tr}, $\bar{e}$
	Left	Right	Left	Right	Left	Right	
1	0.247		−0.26		−0.74	1.00	−0.018
2	0.906		1.00		−0.01	−1.03	0.035
3	0.922		1.00		0.01	−1.00	0.057
4	0.925		1.00		0.01	−1.00	0.052
5	0.933		1.00		−2.00	1.00	0.043
6	0.926		1.00		0.01	−1.01	0.048
7	0.925	0.271	−1.00	0.28	−0.01	0.72	0.054
8	0.921	0.903	−1.00	1.00	0.01	−0.01	0.127
9	0.921	0.922	−1.00	1.00	−0.01	0.01	0.109
10	0.924	0.921	1.00	−1.00	−0.01	0.01	0.100
11	0.924	0.928	−1.00	−1.00	1.99	−0.02	0.094
12	0.924	0.924	−1.00	1.00	−0.01	0.01	0.097

sorbed 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. II).

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 electronegative oxygen from the C-O bonds and the electropositive hydrogen atoms belonging to the adsorbed molecules. Therefore, the interaction of the adsorbates and graphene triggers a charge redistribution between them. Accumulation of the natural charge on the adsorbed molecules determined within the NBO analysis is presented for H_2O (Q_{H_2O}) and NH_3 (Q_{NH_3}) molecules in Table I. As we mentioned above, first the number of adsorbed molecules (see N_{H_2O} and N_{NH_3} in the Table I) has been increased gradually along the "Left" zigzag edge of graphene. After six molecules were adsorbed along this edge and no free C-O bonds left for further adsorption at the "left" zigzag edge, the similar procedure has been performed at the "right" zigzag edge.

We estimated the charge exchange between graphene and the adsorbates within the NBO procedure as $Q_{tr}=Q_{DA}-Q_{AD}$, where Q_{DA} is the charge transfer from graphene to the adsorbates and Q_{AD} is the charge transfer from the adsorbates to graphene. The Q_{DA} and Q_{AD} parts are calculated as the

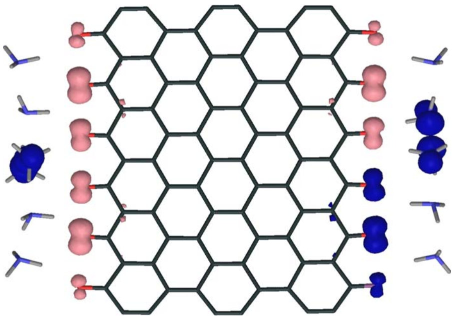

FIG. 3. (Color online) The spin distribution in graphene with eleven adsorbed NH_3 molecules plotted for isovalues of ± 0.01 e/Å^3. The left edge has a total spin 2.0 while for the right edge the total spin is zero. The adsorbed molecules maintain spin of −1.0 from each side of graphene, however the balance of the total spin between two sides of graphene with the adsorbates is maintained, i.e., −1.0 for one side and 1.0 for other side.

sum of the $\Omega_i \rightarrow \Omega_j^*$ charge transfers between the donor orbital Ω_i and the acceptor orbital Ω_j^* defined within the NBO procedure as:

$$Q_{DA} = \sum_{i,j} Q_{i,j} = \sum_{i,j} q_i F_{i,j}^2/(\epsilon_i - \epsilon_j)^2, \qquad (1)$$

where q_i is the donor orbital occupancy, ϵ_i, ϵ_j are the orbital energies, and $F_{i,j}$ is the off-diagonal element. The charge occupancy transfer is considered for stabilizing orbital interactions, i.e., when the second-order interaction energy $\Delta E_{i,j} = -2F_{i,j}^2/(\epsilon_i - \epsilon_j)$ has a positive sign. The results for the charge exchange (Q_{tr}) between graphene and the adsorbates (H_2O 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 nonzero 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 spins +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 nonzero total spin and are spin-polarized while the rest of the molecules are unpolarized. The accumulation of the positive natural charge on the adsorbed molecules (Q_{H_2O} and Q_{NH_3}) occurs mostly due to the contribution from the spin-polarized molecules which carry the positive natural charge ($\sim 0.5\bar{e}$ for each of the spin-polarized molecule) while its accumulation on the nonpolarized adsorbed molecules is not significant ($\sim 0.05\bar{e}$). 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.[31]

The charge transfer from pristine graphene to water is not expected to be efficient and was reported to be in the range,[27] $-0.02/0.01\bar{e}$ 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 Ref. 16). 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 I). For adsorption of H_2O molecules, the charge donation from graphene to adsorbates increases gradually. However for a single H_2O molecule adsorbed at the zigzag edge, the charge exchange is insignificant because of the location of the molecule relative to the edges. A single H_2O molecule interacts with graphene by both of its hydrogen atoms which are directed to two nearest oxygen atoms at the zigzag edge. The resulting distance between the H_2O molecule and the edges is large (the distance between O-H and O-C is ~2.2 Å) and the H_2O molecule lies parallel to the graphene plane. Therefore, the overlapping of orbitals is weak. For two or more adsorbed molecules, one hydrogen of the H_2O molecule makes a hydrogen bond with the other H_2O 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···O-C is ~1.2 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 NH_3 adsorbates, a similar behavior is obtained for up to three NH_3 molecules. The most efficient charge exchange occurs when two or three molecules are placed along the zigzag edge while a further increase in their number suppresses the charge transfer. The effect is related to clustering of the NH_3 molecules along the zigzag edge. Two or three 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···O-C is ~2.0 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···O-C is ~2.5 Å). Thus, in the cluster containing more than three 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

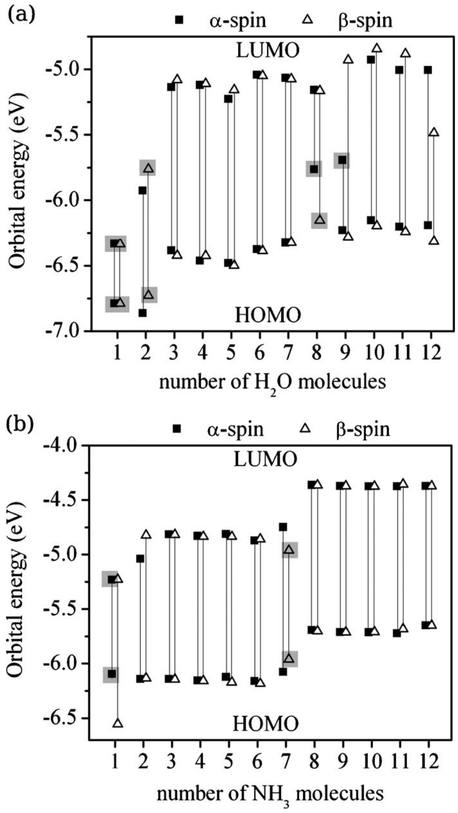

FIG. 4. Effect of adsorption on the orbital energies of the HOMO and LUMO. The results are presented for both the α- and β-spin states: (a) adsorbate is the H_2O molecule and (b) adsorbate is the NH_3 molecule. The shaded areas are used to mark orbitals which are localized on the adsorbates.

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 I). 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 H_2O or NH_3 molecules tend 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 adsorbates and its efficiency is defined by the intermolecular distance and by the location of the adsorbed molecules relative to the plane of graphene. In the case of H_2O 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 NH_3 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.

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