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Tunable band gap and magnetic ordering by adsorption of molecules on graphene

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We have studied the electronic and magnetic properties of graphene and their modification due to the adsorption of water and other gas molecules. Water and gas molecules adsorbed on nanoscale graphene were found to play the role of defects which facilitate the tunability of the bandgap and allow us to control the magnetic ordering of localized states at the edges. The adsorbed molecules push the wave functions corresponding to α-spin (up) and β-spin (down) states of graphene to the opposite (zigzag) edges. This breaks the sublattice and molecular point group symmetry that results in opening of a large bandgap. The efficiency of the wave-function displacement depends strongly on the type of molecules adsorbed.

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Monolayer graphene[1] with its high-electron mobility, unique magnetic phenomena,[2] and unusual relativisticlike properties[3] has generated an upsurge of activities in materials science. Materials exhibiting magnetic properties are in great demand for applications in nanoscale electronics and spintronics. Most magnetic materials are metals, where ferromagnetism (which results from an imbalance between the spin-up and spin-down unpaired electrons) is often destroyed by thermal fluctuations. In carbon systems the magnetic properties are stable even at room temperatures. The nonmetallicity of carbon systems makes them biocompatible and therefore are ideal for a wide range of applications not only in nanoelectronics and spintronics,[4–6] but also in medicine and biology. In most carbon systems the origin of magnetism is unclear, but in graphene it is expected to be the result of spin-ordered states localized at the edges.[7–13]

The absence of a bandgap is however a major hindrance for graphene's application in nanoelectronics. Various mechanisms for opening a gap have been developed that involve breaking of certain symmetries in graphene by defects,[11] an applied bias,[4,5] and interaction with other materials.[14] Noting that the conductivity of the carbon systems[15,16] is extremely sensitive to adsorption of gas molecules due to the charge exchange between them, we assume that a more controllable way to induce interactions that break a symmetry of graphene would be gas adsorption. The charge exchange between the adsorbed molecules and graphite was found to be rather low,[17] and donor or acceptor behavior is exhibited depending on the type of molecules adsorbed. However, since gas adsorption changes the electronic properties of graphene due to the charge exchange between them, we suspect that adsorption should affect the localization of electronic states along the edges and can facilitate opening of a gap.

Here we study the influence of adsorption of water on the electronic and magnetic properties of graphene by molecular mechanical methods using the spin-polarized density-functional theory with semilocal gradient corrected functional (UB3LYP/6–31G)[18] in the Jaguar 6.5 program.[19] The van der Waals interactions, which impact the interaction between graphene and adsorpant, are not considered in density-functional theory (DFT), that lead to underestimation of the adsorption energy.[17] However, the DFT is reliable for investigation of the influence of the adsorption on the electronic properties of the graphene. We chose the nanoscale graphene structures as shown in Fig. 1. The number of rings along the armchair edges was varied as $m=0\ldots k$ or $m=1\ldots(k-1)$ to take into account different geometries of the graphene *seams* (indicated in Fig. 1), where k was always odd. The number of carbon rings along the zigzag edges N was varied from three to seven.

For a nanoscale graphene the highest possible symmetry is $D2h$, i.e., the planar symmetry with an inversion center, where all four seams are characterized by the same boundary conditions and exhibit the lowest energy in the system due to the confinement effect. The optimization process makes these seams structurally identical with the same density distribution. Therefore, the seams have the same spin order and play the role of the center for spin ordering along the edges [see Fig. 2(a)]. The resulting spin polarization exhibits a ferromagnetic ordering between the seams and between the zigzag edges, but a mixed ordering along the zigzag edges. Most molecular orbitals including the highest occupied and the lowest unoccupied [highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)] exhibit zero spin density, because they have the same density distribution for the α- and β-spin states, but with opposite sign. For the HOMO and LUMO each spin state is equally

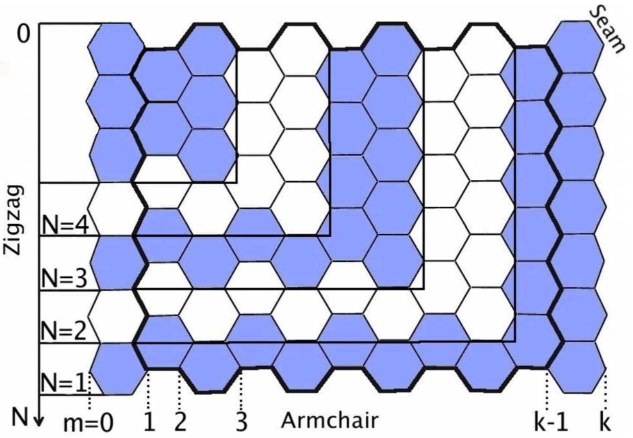

FIG. 1. (Color online). Nanoscale graphene structures, where N is the number of rings along the zigzag edges and m is that along the armchair edges.

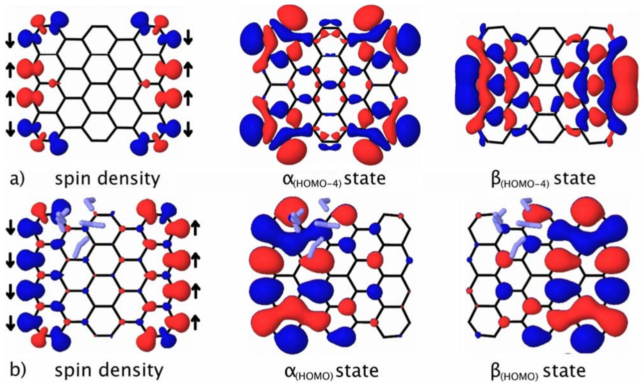

FIG. 2. (Color online). Spin polarizations in nanoscale graphene of size $N=4$ and $m=0\ldots k$: The spin density and electron density for the α-spin (up) and β-spin (down) states are plotted for isovalues of ± 0.01 e/Å^3. For the spin density, different colors indicate the α- and β-spin states, while for the electron density distribution (α- and β-states) the different colors correspond to different signs of the molecular orbital lobes. (a) The electron density distribution in pure graphene for α-spin ($E_{\text{HOMO-4}}=-7.119$ eV) and β-spin ($E_{\text{HOMO-4}}=-7.295$ eV) states for the fourth orbital below the highest occupied molecular orbital (HOMO-4). In pure graphene, a nonzero spin density is obtained only for an even number of carbon rings along the zigzag edge ($N=4,6,\ldots$). (b) The electron-density distribution of the α-spin state ($E_{\text{HOMO}}=-5.386$ eV) and the β-spin state ($E_{\text{HOMO}}=-5.270$ eV) for the HOMO for graphene with adsorbed water. The water cluster plays the role of a defect pushing the α- and β-spin wave functions to the opposite edges.

delocalized over the two zigzag edges. The molecular orbitals contributing to a nonzero spin density are located far from the HOMO-LUMO gap and they are not localized along zigzag edges. The spin density and spin polarization for graphene of size $N=4$ are presented in Fig. 2(a). For nanoscale graphene optimized without any symmetry, with the planar symmetry $C1$ or with the $C2v$ symmetry, the seams are not constrained to be identical. That makes the zigzag edges exhibit the lowest energy and as a result, a ferromagnetic ordering of the spins along the zigzag edges with a bandgap of ~1.6 eV for $C2v$ and $C1$ symmetry, instead of ~0.5 eV for $D2h$ symmetry. In these cases, the HOMO and LUMO are characterized by the α- and β-spin states localized on the opposite zigzag edges. Although the state of graphene with $D2h$ symmetry is comparable in energy to the states of $C2v$ and $C1$ symmetries, the difference between them is already less than 0.02 eV for the $N\geq 6$ and $m\geq 7$. This indicates high metastability of the ground state of $C2v$ symmetry. Therefore, $D2h$ is chosen here in order to study the influence of adsorption of gas and water molecules on both spin ordering and the bandgap.

The $D2h$ symmetric graphene structures with an even number of rings along the zigzag edges $N=4,6$ and the number of rings at the armchair edges that are varied as $m=0\ldots k$, are found to be the only case with a nonzero spin density [Fig. 2(a)]. For these structures and sizes, the atomic wave functions from the opposite seams cancel each other at the center of the edge, where they are out of phase. In that case, the α- and β-spin states are spatially separated which leads to nonzero spin density for certain orbitals. The α state is localized on the seams, while the β state at the center of the zigzag edges [see Fig. 2(a)]. We found this effect for several molecular orbitals that are far from the HOMO-LUMO gap, while other orbitals including the HOMO and LUMO have zero spin density. These states are nondegenerate, that diminish with increasing structure size. For example, the energy difference between the α- and β-spin states for HOMO is 0.0764 eV if $N=4$ and 0.00625 eV if $N=6$. This can explain the experimental observation of the single local-density peak in the valence or the conduction band for large graphene structures.[20,21] For an odd number of carbon rings along the zigzag edges $N=3,5,7$ and $m=0\ldots k$, the spin density at the edges is close to zero because the α- and β-degenerate states exhibit almost the same electron-density distribution over all molecular orbitals. In a structure where the armchair edge is varied as $m=1\ldots(k-1)$, we found the opposite behavior of the spin degeneracy: degenerate α- and β-spin states are observed for the even ring number on the zigzag edges, while for odd N the states are nondegenerate.

Our most striking results are for the case of adsorbed water molecules on nanoscale graphene. The interaction between water and graphene is weak because the attractive forces between the water molecules within a cluster are stronger than the attractive force of the graphene surface. Therefore, several water molecules will tend to form a water cluster that was studied for graphene structure of sizes $m=0\ldots k$ and $N=3,4,5,6$. A single water molecule on the graphene surface is localized at the center of a carbon ring, ~3.0 Å above the graphene surface. The optimized position of the water molecule on the graphene surface corresponds to its dipole moment being perpendicular to the graphene surface and directed inward, which provides an effective charge donation from the oxygen to the graphene through the unshared pair of p electrons of the oxygen. When we increase the number of water molecules, this water molecule becomes a "cluster link" to the graphene, i.e., the extra water molecules are connected to the cluster link by the hydrogen bonds. Therefore, the charge donation to graphene occurs mostly through oxygen in the cluster link, while charge acceptance by the cluster is through the hydrogen atoms. For the graphene structure with $N\leq 4$, where the confinement effect is strong, the interaction between the armchair edge and the water cluster leads to unrolling of the water cluster in such a way that one termination side is attached to the armchair edge and the other—the cluster link—to the center of a carbon hexagon. The attachment to the armchair edge is a result of its low energy in comparison to the zigzag edge.[22] The reconstruction of the zigzag edge can lead to lowering of its energy that would change the direction of cluster unrollment. For $N\geq 4$ the water cluster is formed at the center of graphene.

Water can be treated as a defect on the otherwise defect-free graphene surface. Figure 2(b) shows that this defect repels the wave functions of the molecular orbitals corresponding to α- and β-spin states toward opposite zigzag edges of the nanoscale graphene. This leads to spin ordering of the localized electrons on the edges such that the α-spin state is localized on one sublattice while the β-spin state on the other sublattice. The nonzero spin density and repulsion of the

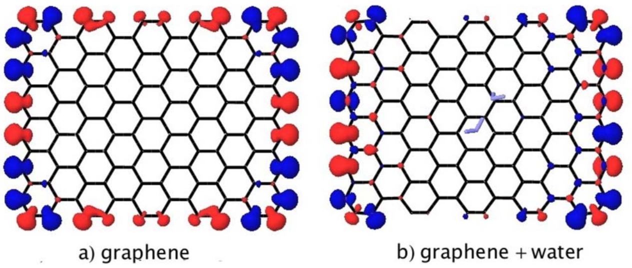
a) graphene b) graphene + water

FIG. 3. (Color online). Spin polarizations in nanoscale graphene of size $N=6$ and $m=0\ldots k$. The spin densities are plotted for isovalues of ± 0.01 e/Å^3: (a) in pure graphene; (b) for graphene with adsorbed water.

wave functions by water were observed for all types of graphene structures independent in size. Just as for pure graphene, the size is found to be crucial only to preserve the nondegeneracy of the α- and β-spin states. The defects affect the wave-function distribution only for the nearest carbon rings. This means that, depending on the graphene size and the size of the water cluster, the wave functions can be repelled locally, or over the whole structure. For a graphene size of $N=6$, the water molecules build a cluster close to the graphene center. Then the α- and β-spin wave functions are pushed toward the edges only for the localized states along the line of the water location (Fig. 3).

The repulsion of the α- and β-spin wave functions to opposite zigzag edges discussed above, breaks the molecular and sublattice symmetries and opens a gap. The magnitude of the gap directly depends on the interaction of the graphene surface with water, particularly on the charge exchange and the association energy. For a single water molecule, if the dipole moment of the water molecule is directed inward (toward the graphene surface), the gap increases by up to $\sim$2.0 eV, but if the dipole moment is directed outward then the charge donation from oxygen to graphene does not occur and the gap opens by only up to 0.8 eV. For the inward directed dipole, the gap slightly decreases with increasing distance between the water molecule and the graphene surface. For the water cluster, the cluster link usually is a donor and its interaction with the graphene surface defines the association of the water cluster to graphene and the efficiency of opening a gap. The orientation of the cluster link to the graphene surface is changed due to the intrinsic interaction within the water cluster. Therefore, the association energy of the water cluster on graphene and hence the graphene gap oscillates depending on the orientation of the cluster link to the graphene surface and correlation between attractive forces inside the water cluster and attractive forces of the graphene surface. For a cluster containing three water molecules, the association energy has a global minimum and the same minimum is observed for the graphene gap [Fig. 4(a)]. With an increase in the graphene size, the gap decreases ($\sim$1.2 eV for $N \geq 6$) due to the vanishing of the confinement effect and the gap oscillation diminishes [the dashed lines in Fig. 4(a)]. The energy gap of 1.2 eV is in perfect agreement with earlier investigation of the bandgap of nanoribbons with ferromagnetic ordering along the zigzag edges by the B3LYP method.[5] We predict that using a water detergent would be a way to reduce the attractive forces inside the water cluster and thereby increase the water-graphene interactions. This would allow one to tune the energy gap in graphene and improve the repulsion of the wave functions toward the opposite zigzag edges.

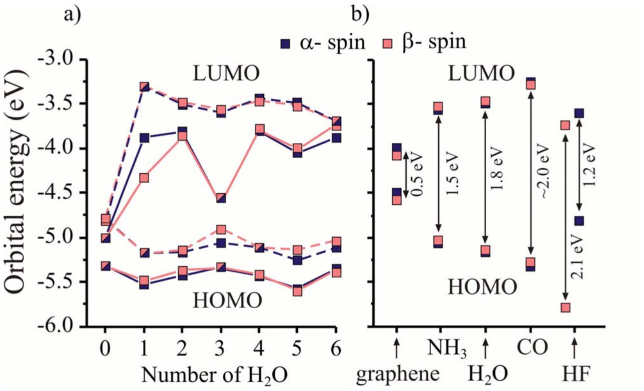

FIG. 4. (Color online). The effect of adsorption on the gap in nanoscale graphene. (a) The HOMO and LUMO energies for graphene of size $N=3$ (solid line) and $N=5$ (dashed line) versus the number of adsorbed water molecules. (b) Influence of adsorption of different adsorbed molecules on the bandgap of the nanoscale graphene of size $N=4$.

Opening of the gap is a result of breaking the sublattice and molecular symmetries of graphene, but the gap size can vary depending on the interaction between the adsorpant and the graphene surface. Therefore, we also investigated the possibility to tune the energy gap by changing the type of adsorbed molecules. The HOMO-LUMO gap for nanoscale graphene with adsorbed NH_3, H_2O, HF, or CO molecules are presented in Fig. 4(b). Since the gap opens due to the symmetry breaking, the interaction of nanoscale graphene with any molecule leads to a gap opening of up to $\sim$1.5–2.0 eV. The ability of the adsorbed molecules to push the wave functions of α- and β-spin states to edges is found to differ between the type of molecules chosen and the HF and CO were least effective. Moreover, the HF adsorption leads to spin-selective semiconductor behavior of the graphene.

In summary, the adsorbed molecules on graphene are found to act as defect centers which alters the magnetism through the repulsion of the wave functions corresponding to α- and β-spin states to the opposite zigzag edges. This results in a bandgap opening and stabilization of the state with parallel spin ordering along the zigzag edges and antiparallel one between the opposite edges. The reversible breaking of the graphene symmetry and opening of a gap due to adsorption, as observed in experiments,[14,23] would open a way to control the electronic properties of graphene. In particular, transition from metallic to semiconductor state by molecular adsorption is a promising route to develop fast on-off switching devices,[23] supersensitive gas sensors[15,16] and field-effect transistor (FET),[24] where adsorption can help ambipolar-to-unipolar conversion. For FET application, the graphene can operate similar to carbon nanotubes. The gap opening in graphene induced by adsorption can provide ambipolar-unipolar conversion of FET, as a result of occurrence of a significant Schottky barrier at metal/graphene contact, leading to modification of the conducting channel operation. The spin-polarized state of graphene stabilized by adsorption provides an opportunity to manipulate spin current by an in-plane electric field applied across the zigzag edges.[4] The applied field increases the bandgap for one-spin state, while suppressing the other, thereby generating half metallicity in graphene. This effect can be used for developing spin-related electronic devices[4,6,25] such as a spin valve[6] or digital memory devices.[25]

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