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Successful doping of an electronic material entails the existence of stable dopant configurations that cause a shift in the Fermi level without altering significantly the electronic states of the host system. The selection of chemical groups that satisfy these conditions when adsorbed on graphene is still an open challenge. Here we show with first-principles calculations that ammonium groups meet the criteria of stable physisorption and efficient doping of graphene. We also describe processes of deactivation of ammonium dopants through their dissociation over graphene impurities or nanoribbon edges. Finally, we show that carbon nanotubes can be used to spatially confine the dopants and avert their edge-related de-activation.

PACS numbers:

I. INTRODUCTION

Graphene nanoribbons (GNR), stripes of carbon nanosheets with finite width, are being intensely pursued as building blocks in future electronic devices.[1–5] One of the main challenges, in this respect, is the controlled generation of charge carriers within GNRs. In traditional electronic materials, this challenge is answered by introducing dopant impurities at substitutional sites through implantation. A similar strategy is pursued in carbon-based nano-materials like carbon nanotubes or graphene. However, given the fact that substitutional doping may also give rise to unwanted defects or impurities,[6–10] efforts have focused on alternative methods of doping. Perhaps the most appealing recent approach is doping graphene using adsorbed chemical species, instead of substitutional impurities.[3,5,11]

Theoretical calculations[5,11] have suggested that NO_2, N_2O_4, and NO molecules can act as graphene donors. Experiments,[3] on the other hand, have shown that reactions with ammonia lead to effective doping of GNRs with electrons. However, all these dopant candidates have small energies of physisorption on graphene, typically in the order of 0.1 eV or less.[5,11] For this reason, it is doubtful that they can serve as efficient stable dopants of the graphene basal plane. It is assumed, for example, that NH_3 molecules[3] react with GNR edges and some reaction products, as yet unidentified, act then as dopants. If this scenario is true, it will likely pose the new challenge of finding and preparing those edge morphologies that favor the formation of dopant configurations. Clearly, a simpler solution would be to identify other chemical groups that physisorb more strongly on graphene and shift its Fermi energy inside the valence or conduction bands.

In this article we show that ammonium groups (NH_4) are ideal candidates for the molecular doping of graphene. They have large physisorption energies (more than 1 eV) and they transform graphene to an n-type material. We also show that NH_4 species dissociate readily at GNR edges by giving away one or two H atoms. The deactivation of dopants at GNR edges can be suppressed if carbon nanotubes (CNT) are used to block the migration of NH_4 groups and trap them within areas of the graphene basal plane. In this way, the two indispensable conditions of successful molecular doping, injection of carriers and dopant stability, are satisfied.

II. METHOD

The results were obtained with the density-functional theory code VASP[12] using ultra-soft pseudopotentials[13] for the valence electrons. We used a local-density approximation (LDA) exchange and correlation (xc) functional[14] and an energy cutoff of 300 eV for the plane-wave basis. For selected configurations we also used a generalized gradient approximation (GGA) xc-functional.[15] It is known that GGA results normally underestimate binding on sp^2 carbon, especially for physisorbed configurations.[16–18] Reaction barriers were obtained with the nudged elastic band method,[19] which in previous studies[20,21] provided activation energies in good agreement with experimental data.

The supercells for calculations on a graphene layer contained 160 carbon atoms in a simulation box with in-plane dimensions of 19.65 Å and 21.27 Å. Total energy calculations for this case used the Monkhorst-Pack[24] scheme for sampling of the reciprocal space and a $3\times3\times1$ k-mesh. Calculations of electronic densities of states (DOS) employed the tetrahedron method[25] and $9\times9\times2$ grids for k-point sampling. The supercells used in the case of zig-zag GNRs contained 128 carbon atoms and had in-plane dimensions of 19.65 Å and 25.08 Å. The edges of the nano-ribbons were passivated with hydrogen atoms. The actual width of the GNRs was about 17.73

Å. The simulations for the hybrid CNT-graphene system used supercells with in-plane dimensions of 42.53 Å and 14.73 Å, with the latter being the size along the CNT axis. The supercells contained 384 C atoms, 240 of those on the graphene layer and the rest in an arm-chair (6,6) CNT. Total-energy calculations for the zig-zag GNR and CNT-graphene systems used the Γ point for sampling of reciprocal space. The thickness of empty spaces between periodic images in the third out-plane direction was at least 10 Å.

III. RESULTS AND DISCUSSION

In the following we describe the details of adsorption and the associated electronic effects of ammonia-related groups on pristine and defective graphene. First, we present results for physisorbed NH_3 and NH_4 species on a defect-free graphene layer. We then focus on possible de-activation processes for the ammonium dopants either on the graphene basal plane or at GNR edges. We conclude with results on blocking the NH_4 migration by using CNTs on graphene.

A. NH_3-related species on a pristine graphene layer

The interaction between physisorbed NH_3 molecules and a pristine graphene layer is weak. According to our calculations, various molecular configurations are possible, but the binding energy for all of the them is less than 0.12 eV. The nitrogen atom of the physisorbed molecule is located 3.1 Å above the graphene layer. The results are in agreement with those already reported in previous studies[11] on the binding energies of physisorpted NH_3 molecules on graphene. Also in agreement with those studies,[11] we found that physisorbed ammonia molecules do not have a tangible effect on the electronic density of states of graphene close to the Fermi level. Because of these results we can infer that ammonia molecules are not good candidates for effective molecular doping of graphene.

Hydrogen is an ubiquitous impurity in electronic devices,[22,23,26] playing both beneficial and detrimental roles depending on growth and operating conditions. Reactions between physisorbed NH_3 molecules and hydrogen adatoms generate chemical species that have stronger interactions with the graphene layer. Specifically, an isolated H impurity on graphene can be captured by an NH_3 molecule in an exothermic reaction that releases 1.00 eV of energy. The NH_4 group remains close to the graphene layer with its N atom in a distance of 2.7 Å from the carbon sheet. Two of the NH_4 hydrogen atoms point towards the graphene sheet, while the other two H species are on the other side of the ammonium group. The binding energy against separation of the NH_4 impurity from the layer is 1.55 eV. This value is large enough to suggest that NH_4 desorption off graphene requires annealing at high temperatures.

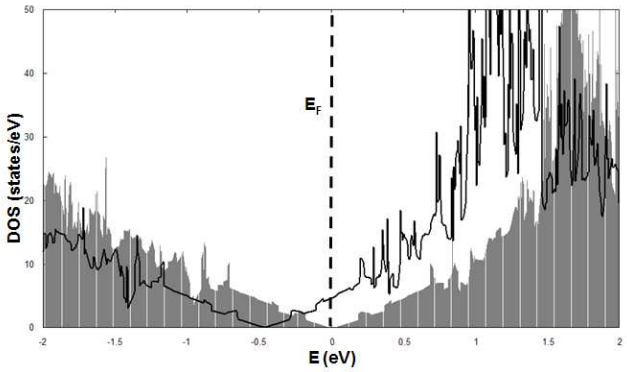

FIG. 1: Electronic density of states (DOS) for graphene with no impurities (shaded area) and with a physisorbed NH_4 group (black solid line). E_F is the Fermi level.

The stabilization of ammonium on graphene has a pronounced effect on the electronic properties of the system. The data depicted in Fig. 1 demonstrate that reactions with NH_4 is an effective means of molecular doping of graphene. The attachment of one ammonium group per 160 carbon atoms gives rise to a shift of the DOS so that the Fermi level of the NH_4-laden system lies within the conduction band. In other words, NH_4 physisorbed impurities act as donors for the basal plane of graphene. Two NH_4 groups may react to form a hydrogen molecule and two NH_3 species. This de-activation reaction, however, is not likely because NH_4 groups repel each other. In particular, bringing two initially remote ammonium impurities to a distance of 10.53 Å and 4.38 Å raises the energy by 0.30 eV and 0.61 eV, respectively. On the other hand, an NH_4 donor can be de-activated through a reaction with another H impurity of graphene. The process creates H_2 and NH_3 molecules and releases 1.42 eV of energy.

The results described above reveal a complex dynamics for ammonia-related species on graphene. One possible scenario to achieve n-type doping with ammonium cations is to anneal in an NH_3 ambient a graphene sample with a small number of atomic H impurities. In this way, a number of NH_4 donors can be formed by the direct reaction of the H adatoms with the ammonia molecules. If the temperature is subsequently raised, then the weakly physisorbed NH_3 molecules will desorb off graphene, leaving behind strongly physisorbed ammonium dopants.

B. De-activation of NH_4 dopants on graphene

Though ammonium donors are stable against dissociation when they are over a pristine graphene layer, they may dissociate when they arrive close to graphene defects or impurities. One example relates to the breakup of the NH_4 group in the vicinity of a substitutional N impurity.

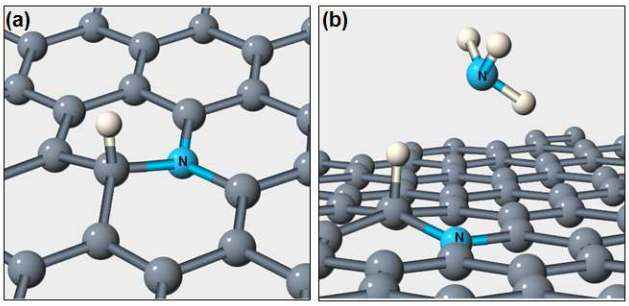

FIG. 2: (Color online) (a) N-H complex: H atom trapped at a substitutional N dopant site of graphene. (b) a NH_3 molecule physisorbed over a N-H complex. [C: gray, N: light gray (cyan), H: white spheres]

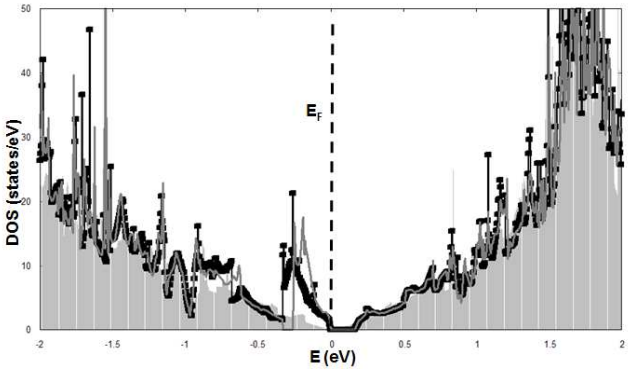

FIG. 3: Electronic density of states (DOS) for graphene with no impurities (shaded area), with one N-H complex of the type shown in Fig. 2(a) (black line with squares), and with the complex of Fig. 2(b) (gray line). E_F is the Fermi level.

As shown in Fig. 2(b), the ammonium cation deposits one of its H atoms to a C site next to the N impurity, forming thus an N-H complex on graphene. The energy gain of this process is about 0.10 eV. The N atom of the NH_3 molecule is attracted by the H atom of the N-H complex and the interaction results in a sizeable binding energy of 0.27 eV. A finite value of 0.12 eV is obtained also using GGA calculations. Annealing in elevated temperatures may force the NH_3 molecule to desorb. The N-H complex, on the other hand, is more resilient because it has a significant binding energy of 0.55 eV against release of its H atom to a remote graphene position.

The formation of the N-H complex modifies the DOS of graphene as shown in the related data of Fig. 3. While pristine graphene has a vanishing band gap at the Fermi level (E_F), one N-H complex per 160 graphene sites creates a peak right below E_F and induces a small gap of 0.18 eV. This effect constitutes a significant deviation from the ideal doping profile of an isolated substitutional N impurity. The DOS associated with the N-H complex differ significantly also from the DOS profile on an isolated H impurity on graphene. H-related DOS data show that the impurity generates a band gap of 0.5 eV and a narrow, strong peak in the middle of the gap. On the other hand, the effect of the stable N-H-NH_3 complex of Fig. 2(b) on the DOS of graphene resembles that of the N-H defect. The corresponding DOS data of Fig. 3 show that physisorption of the NH_3 molecule narrows slightly the N-H related DOS peak and opens an additional small gap between this peak and the rest of the valence band.

C. De-activation of NH_4 dopants at graphene edges

The dissociation of NH_4 species at N substitutional sites is an adverse effect with respect to graphene doping. However, the importance of this dissociation scenario is limited only to those graphene samples that have significant numbers of N substitutional impurities. In contrast, the de-activation pathway we will discuss in the following poses a more prevalent risk to the NH_4-induced doping scheme because it relates to reactions at the ever present edges of a graphene layer. In particular, we have found that an NH_4 dopant dissociates readily when it arrives at the zig-zag edge of a graphene nano-ribbon. At first, an NH_4 group that is brought above an edge C atom of a GNR transforms spontaneously (in a barrier-less process) to an NH_3 molecule by releasing one of its H atoms to an edge ethylene (CH2) group. A second breakup reaction may then ensue. Following a multi-step dissociation process, the ammonia molecule may release a H atom to a neighboring edge C atom, while the NH_2 amine moiety gets attached to another C edge site. The configuration is shown in Fig. 4(b). Its energy is 0.1 eV lower than that of the NH_3 structure of Fig. 4(a). The breakup of the NH_3 molecule has a barrier of 0.6 eV.

The system is stabilized further when the H atom hops away from the NH_2 group to another C edge atom. Specifically, the configuration depicted in Fig. 4(c) is more stable than the geometry of Fig. 4(a) by 0.65 eV. The corresponding GGA energy difference is 0.08 eV. Another 0.2 eV is gained when the released H atom migrates to more remote sites. The results on the energies of the above structures are summarized in Table 4. Other possible structures include C-NH_2 groups as protrusions at the edge and a released H_2 molecule, or a C-NH_3 edge group and a released H atom on a neighboring edge C atom. These types of geometries have, in fact, been employed in previous studies[27–29] on N-related doping of graphene nano-ribbons. Compared to the most stable structure of the type of Fig. 4(c), however, the C-NH_2 and C-NH_3 edge configurations lie higher in energy by more than 1 eV.

D. NH_4 trapping by carbon nanotubes on graphene

As mentioned above, the dissociation of NH_4 species at GNR edges poses the challenge of how to retain a non-negligible number of ammonium dopants over graphene.

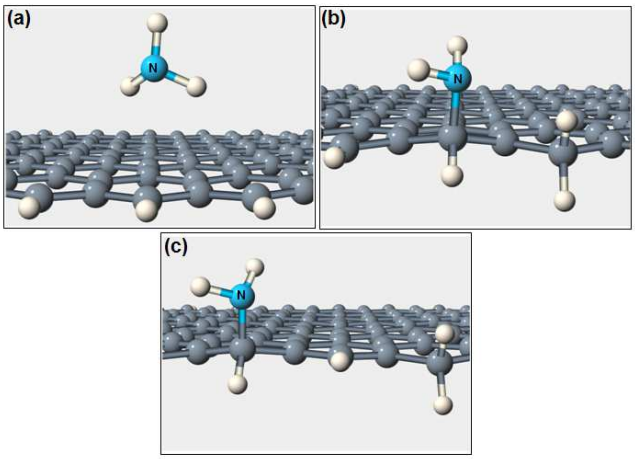

FIG. 4: (Color online) Adsorption of a NH_3 molecule at the edge of zig-zag graphene nano-ribbon: (a) physisorbed NH_3, (b) and (c) chemisorbed NH_2 group and a H atom following the dissociation of the NH_2 molecule. [C: gray, N: light gray (cyan), H: white spheres)

TABLE I: Relative stability of NH_3-related configurations at the edge of a zig-zag graphene nanoribbon. The energy of the most stable structure is set to zero.

Figure	Description	E (eV)
Fig. 4(a)	Physisorbed NH_3	0.85
Fig. 4(b)	Proximal NH_2 and CH_2 units	0.75
Fig. 4(c)	Remote NH_2 and CH_2 units	0.20
	Isolated NH_2 and CH_2 units	0.00

We have found that there is a very small spread of energies, less than 0.1 eV, for neighboring NH_4 configurations over graphene. This tiny energy difference suggests that the diffusion barrier is also very small and that the NH_4 dopants migrate rapidly over graphene. Therefore, the ammonium-based doping scheme can be successful only under conditions that block the movement of the physisorbed species towards the GNR edge. In the following we show that this role can be played by carbon nanotubes that are deposited on graphene.

Figure 5 depicts a number of configurations for

TABLE II: Relative stability of the NH_4-related configurations shown in Fig. 5. The second column describes the relative position of the NH_4-related species with respect to the carbon nanotube (CNT) and the graphene layer (GL). The energy of the most stable structure is set to zero.

Figure	Description	E (eV)
Fig. 5(a)	wedged between CNT and GL	0.00
Fig. 5(b)	on the GL, away from the CNT	0.50
Fig. 5(c)	on top of the CNT	0.90
Fig. 5(d)	H adatom-NH_3 complex on the CNT	0.90

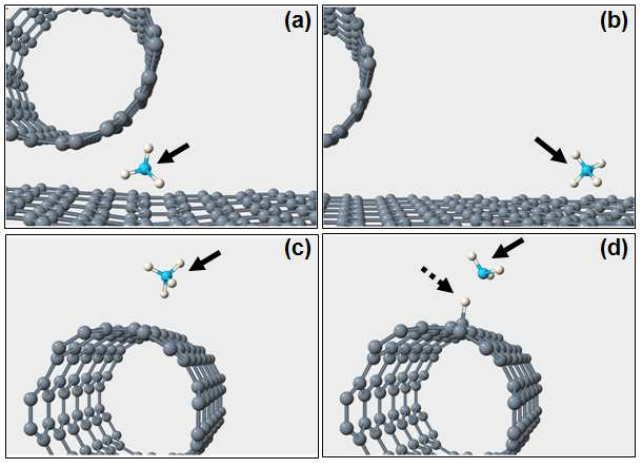

FIG. 5: (Color online) Configurations for NH_4 related species in a hybrid graphene-carbon nanotube (CNT) system: (a) NH_4 wedged between graphene and a (6,6) CNT, (b) NH_4 over graphene, (c) NH_4 physisorbed only on the CNT, and (d) complex between a H adatom (shown with a dotted arrow) on the CNT and an NH_3 molecule (shown with a solid arrow). The arrows in (a)-(c) point to the NH_4 group. [C: gray, N: light gray (cyan), H: white spheres]

ammonium-related species in a system that comprises graphene and a (6,6) CNT. In the most stable geometry of Fig. 5(a) the NH_4 cation is wedged between the CNT and the graphene layer. The energy of the configuration of Fig. 5(b), wherein the NH_4 is physisorbed on graphene, but away from the CNT, is 0.5 eV higher. When the NH_4 is lifted away from graphene, but remains close to the CNT, the energy increases by 0.9 eV. An energy increase of about 0.9 eV accompanies also the dissociation of ammonium over the CNT and formation of a complex between a chemisorbed H atom and a physisorbed NH_3 molecule. The last two structures are shown in Figs. 5(c)-(d). The results on the relative stability of the above structures are summarized in Table II

These results show that it is energetically favorable for a NH_4 group to stay on one side of the CNT, and not climb over the nanotube either as physisorbed, or as chemisorbed species. This fact effectively means that CNTs can be used as walls to trap the NH_4 (or, possibly, other molecules of choice) within certain areas over graphene. There is an energetic preference for the NH_4 cation to physisorb close to the CNT, but the relatively small energy difference of 0.5 eV, combined with the fact that NH_4 groups repel each other, suggest that a significant number of ammonium dopants can be stabilized on the graphene basal plane. In addition, future studies can explore variants that could decrease the effect of dopant wedging between the graphene sheet and a CNT fence, averting thus the scenario of inhomogeneous distribution of dopants. For example, NH_4 wedging could be partly frustrated in the case of CNTs that have been functionalized with electropositive chemical units.

IV. SUMMARY

Using first-principles calculations we have identified ammonium groups as graphene donors. Unlike other small molecular species, the NH_4 radicals have a large binding energy of 1.3 eV when they are physisorbed on graphene. Carbon nanotubes can trap these dopants over certain areas of a graphene layer, suppressing their de-activation through dissociation reactions at graphene nano-ribbon edges.

V. ACKNOWLEDGEMENTS

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