PHYSICAL REVIEW B **83**, 245403 (2011)

Controllable healing of defects and nitrogen doping of graphene by CO and NO molecules

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(Received 2 May 2011; published 17 June 2011)

Controllable defect healing and N-doping in graphene would be very valuable for potential device applications. Here we report first-principles molecular-dynamics simulations that suggest a procedure with fast dynamics and low thermal budget. Vacancies can be healed by sequential exposure to CO and NO molecules. A CO molecule gets adsorbed at a vacancy site and a NO molecule subsequently removes the extra O by forming NO_2. Controllable N-doping can be achieved by sequential vacancy creation (e.g., by an electron beam) and subsequent exposure to NO molecules at room temperature. A combination of CO and NO molecules can potentially provide simultaneous healing and doping at a desirable ratio. The proposed strategy introduces no extra defects and is promising for graphene-based materials in radiation environments.

DOI: 10.1103/PhysRevB.83.245403 PACS number(s): 68.65.Pq, 61.48.Gh, 61.72.J−, 71.15.Nc

I. INTRODUCTION

Graphene exhibits unusual electronic properties that can be exploited for device applications.[1,2] Recent efforts have focused on making high-performance graphene devices by optimizing the fabrication process[3,4] or by band-gap engineering of graphene nanoribbons.[5,6] Point defects, such as atomic vacancies, are not favored thermodynamically due to their high formation energy.[7] However, they have been introduced intentionally by electron or ion irradiation as a way to alter the physical and chemical properties of graphene[8–10] and to achieve desirable effects, such as enhanced chemical activity.[11–13] On the other hand, radiation-induced point defects degrade electrical transport by increasing carrier scattering.[14–16] In radiation environments as in space applications, vacancies can be generated by energetic ions and cause device degradation.

Impurities are yet another way to modify a material's properties in desirable ways. As-prepared graphene is readily p-doped by adsorbates.[17,18] Substitutional boron or nitrogen can also be used as p-type and n-type dopants, respectively,[19] providing a way to tailor the electronic structure of graphene-based materials for the fabrication of electronic devices.[20–25] N-doped graphene can also be exploited to achieve enhanced magnetism[26–28] and high electrocatalytic activity.[29–31] One difficulty that must be overcome is the introduction of a suitable energy gap to achieve semiconducting properties.[23] Another difficulty in doping single- or multisheet graphene by impurities is the potential preference for adsorption or intercalation as opposed to substitutional incorporation.[32–34] Efforts to dope graphene with N using nitrogen plasma[30,31,35] or ammonia plasma,[36] or ammonia gas accompanied with electrical joule heating or thermal annealing,[37] or by adding NH_3 gas during the chemical vapor deposition (CVD) growth,[29,38] or by reduction of graphene oxide,[39] or by arc discharge in a N-containing molecule atmosphere,[40,41] met only partial success. N-doped graphene was obtained, but the process alters the material significantly, e.g., by introducing topological defects[30,36,38,40,42] that may result in considerably lower conductance.[38,42] The dissociated H atoms (from NH_3 gas used as a N source) may also bind to defects behaving as electron scattering centers.[43–45] Another drawback of these processes is their high temperature (800–1100 °C).

In this paper, we report a first-principles molecular-dynamics study, through which we propose a strategy of controllable vacancy healing and N-doping. We show that exposure to CO can heal existing vacancies by direct adsorption, with the extra O atom removed by subsequent exposure to NO molecules that lead to NO_2 formation. Controllable N-doping can be achieved by sequential vacancy creation (e.g., by an electron beam) and subsequent exposure to NO molecules. Finally, by using an adjustable ratio of CO and NO gases after vacancy creation, one can fine-tune doping. This procedure results in n-type graphene without introducing additional impurities and can be performed at room temperature.

II. METHODS

DFT calculations were carried out using the VASP package.[46] The exchange-correlation functional of Perdew, Burke, and Ernzerhof (PBE)[47] in the generalized-gradient approximation was used, and electron-core interactions were treated in the projector augmented wave method.[48,49] The cutoff energy was set to 400 eV and the Brillouin zone was sampled with a 5×5 k point centered at Γ for structure optimization. The graphene layer and the adsorbates were free to relax until the self-consistent forces reached 0.02 eV/Å. First-principles molecular dynamics (MD) was performed with an energy cutoff of 300 eV and a single k point at Γ to sample the Brillouin zone. A time step of 1 fs was used and the temperature was controlled by velocity scaling at each step.

III. RESULTS AND DISCUSSION

The focus of the investigations reported here is a single vacancy because it is a primitive topological defect in carbon-based materials[50–53] and is the dominant defect in graphene after irradiation with Ar^+ ions and annealing.[54] To heal the vacancy, we propose that a carbon-containing molecule without H atoms is preferable since H atoms can be easily

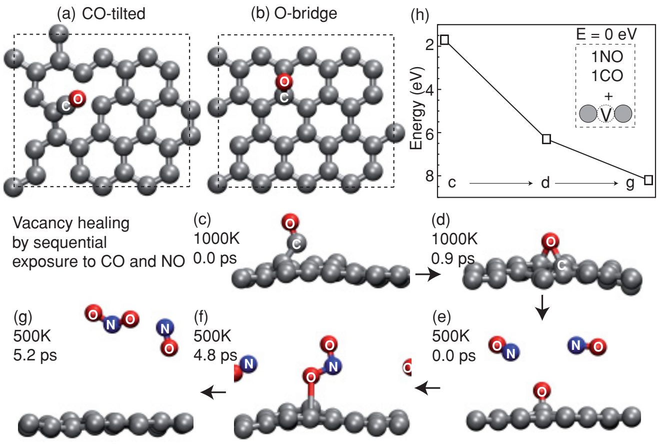

FIG. 1. (Color online) Vacancy healing by a CO molecule. (a) Optimized structure of CO in tilted configuration, (b) the most stable configuration with O sitting above a C-C bond, (c)–(g) snapshots of MD simulation. The initial structure (c) converts to the most stable configuration (d) after 0.9 ps at 1000 K. NO molecules are introduced in (e), and a NO_2 molecule is formed after 4.8 ps at 500 K (f) and desorbs rapidly leaving pristine graphene (g). The energy gain diagram for the process (c)–(g) is shown in (h). The inset in (h) shows the reference energy, which is the sum of the total energy of graphene with vacancies and molecules in gas phase. C, N, and O atoms are colored gray, blue, and red, respectively. The unit cell adopted in the calculation is indicated by a dashed rectangle. The arrows are there to guide the eyes.

trapped at the vacancies and are difficult to remove, as discussed below. CO is the intuitive candidate for the purpose of vacancy healing.

A two-step procedure is performed, the first of which is exposure to CO molecules. CO adsorption on pristine graphene has been studied and has been found to be endothermic.[55] We found that, on graphene with a single vacancy, CO has two very stable configurations (tilted and O-bridge) as shown in Figs. 1(a) and 1(b), with adsorption energies of 1.7 and 6.3 eV, respectively. An adsorbed molecule in the tilted configuration converts into the O-bridge configuration within 1 ps at 1000 K. Once the C atom is incorporated in the graphene layer, the extra O atom is bonded robustly by forming an epoxy group with a binding energy of 2.5 eV, indicating that high temperatures would be necessary to remove it by thermal annealing. The alternative strategy that we propose here is to remove the extra O atom in a chemical way by forming a molecule that binds to graphene weakly. As a radical molecule, NO is reactive and a reaction with the extra O atom can be expected. Thus, NO molecules are introduced in the system [Fig. 1(e) and movie 1 in the supplemental material[56]] to start the second step. As expected, NO binds to the extra O atom by forming a NO_2 molecule. At 500 K, the reaction occurs within 5 ps and an energy gain of 1.9 eV [Fig. 1(h)], which suggests that diffusion of NO would be the rate-determining step. Because of the fast dynamics of NO_2 formation, one can estimate from an Arrhenius equation that, at room temperature, the reaction would occur on a time scale of μs. Since CO, NO, and NO_2 all bind to pristine graphene weakly,[57,58] once all the vacancies are healed, the two-step procedure can be turned off by pumping and low-temperature annealing, e.g., at 150 °C, to reduce the

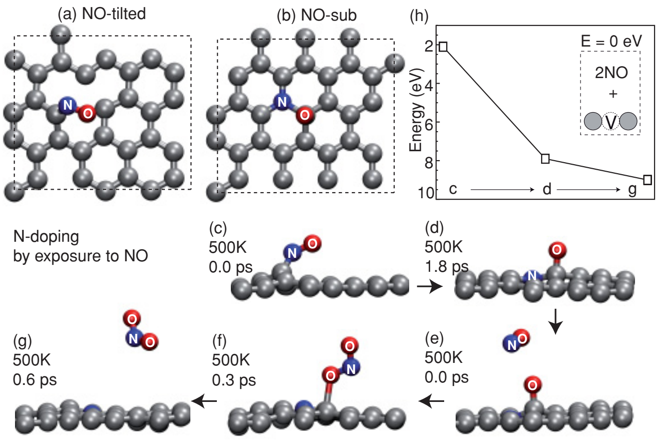

FIG. 2. (Color online) Controllable N-doping by NO molecules. Optimized structure of NO in a tilted configuration (a), and the most stable structure with N embedded in graphene (b). (c)–(g) Snapshots of MD simulation. The initial structure (c) converts into the most stable configuration (d) after 1.8 ps at 500 K. The additional NO molecule in (e) forms a NO_2 molecule with the extra O atom on surface after 0.3 ps (f) and desorbs quickly leaving N-doped graphene (g). The energy gain diagram for the process (c)–(g) is shown in (h). The inset in (h) shows the reference energy.

doping caused by physical adsorption,[18,59] leaving a perfect graphene sheet.

Encouraged by this observation, we further study the controllable N-doping in graphene with a similar procedure. The first step would be the controlled introduction of vacancies in an otherwise pristine, impurity-free, graphene sheet by an electron beam.[9,10] The choice of molecule to achieve doping should be carefully considered since it may induce other defects in the graphene layer. Here, we suggest that NO is a suitable candidate because it is expected to behave in a way similar to that of CO described above. We will consider NH_3 as an alternative later on.

The stable configurations of NO adsorption on graphene with a single vacancy are shown in Figs. 2(a) and 2(b). NO is stable in the tilted configuration [Fig. 2(a)] with an adsorption energy of 2.1 eV. The most stable structure with an adsorption energy of 7.9 eV is the one where N is incorporated in the graphene layer and the O atom sits on top of the C atom by forming a carbonyl group [Fig. 2(b)]. The stronger binding of NO than CO on graphene results from the unpaired electron in NO. The extra O atom binds to the graphene layer with a binding energy of 3.0 eV, indicating the carbonyl group is highly stable, agreeing with a recent theoretical study of the reduction of graphene oxide.[60]

Starting with the tilted configuration [Fig. 2(c)], the N-substituted structure [Fig. 2(d)] can be reached within 2 ps at 500 K. Another NO molecule then binds to the O atom by forming a NO_2 molecule and desorbs rapidly (movie 2 in the supplemental material[56]) as in the case of vacancy healing described earlier in this paper. The formation of NO_2 from NO and O in the carbonyl group is exothermic by gaining an energy of 1.3 eV. The whole process, including N substitution and O removal described in Figs. 2(c)–2(g), takes less than 3 ps at 500 K, suggesting that this strategy can be performed at room temperature. It should be pointed out that this controllable

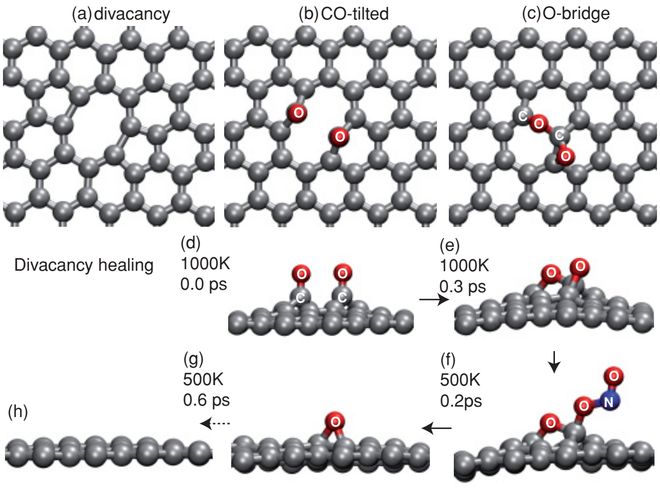

FIG. 3. (Color online) Divacancy healing by CO molecules. Optimized structure of divacancy (a), two CO molecules in the tilted configuration (b), and O sitting on the bridge configuration (c). (d)–(g) Snapshots of MD simulation. The initial structure (d) converts into the more stable configuration (e) after 0.3 ps at 1000 K, with an energy gain of 0.6 eV. Additional NO molecules are introduced. NO binds to one extra O atom by forming a NO_2 molecule after 0.2 ps at 500 K (f) and the NO_2 molecule desorbs quickly leaving one O atom occupying the bridge site (g). As shown in Fig. 1, the left O atom can be removed similarly by a NO molecule, resulting in a perfect graphene sheet (h).

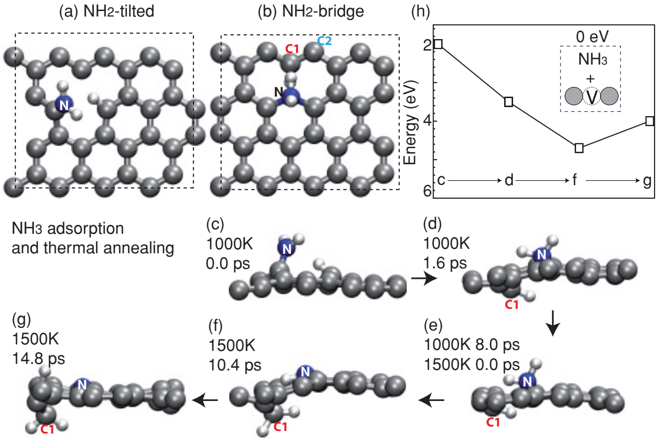

FIG. 4. (Color online) NH_3 adsorption on graphene with a single vacancy. (a) and (b) Tilted and bridge configurations, (c)–(g) snapshots of MD simulation. The initial structure (c) converts to a bridge configuration (d) after 1.6 ps at 1000 K. Further annealing to 8 ps induces no change of the structure (e). After annealing at 1500 K for 10.4 ps, one H moves to a C1 atom (red) by forming a CH_2 group (f), and the last H attached to N transfers to a C2 (cyan) atom after 14.8 ps (g). (h) The energy gain diagram for the process (c)–(g). The inset in (h) shows the reference energy. Visualization of the MD simulation was carried out using the VMD program.[62]

N-doping of graphene with an existing vacancy needs only one step following vacancy creation, namely exposure to NO molecules. NO molecules introduced in the system would be trapped at the vacancies due to the high adsorption energy, and other NO molecules remove the extra O atoms simultaneously. NO acts as a dopant and also a self-cleaner in this approach. Another option would be to introduce vacancies and then anneal in a mixture of CO and NO gases, adjusting the ratio to heal and dope and thus fine-tune the doping level. CO, NO, and NO_2 weakly bind to N-doped graphene[58] thus can be removed easily by low-temperature annealing.

Divacancies also exist in graphene as found by both experiments and theory, and may even dominate.[7,10] We performed similar calculations, as shown in Fig. 3, for the healing process and found that CO molecules adsorb sequentially with an adsorption energy of 1.9 eV per CO, leaving two bridge-O atoms on graphene, and then NO molecules remove them one at a time on a time scale of ps at 500 K. Removal of the first O atom by forming NO_2 is exothermic with an energy gain of 1.8 eV. Once the first O atom is removed, removal of the second one is the same as what has been discussed in Fig. 1. Thus, the healing scenario works for divacancies. The process also works for the doping case. NO molecules adsorb at divacancies sequentially with an adsorption energy of 2.7 eV per NO. Removal of the two O atoms by forming NO_2 is exothermic with energy gains of 2.0 and 1.4 eV, respectively. Inspection of the energy levels showed that both single N and N-pair contribute electrons to the conduction band.

The proposed scenario of vacancy healing and N-doping can be easily checked in experiments by measuring NO_2 generated in the gas phase by mass spectroscopy, etc. Based on the proposed scenario, measured concentrations of NO_2 provide direct information of doping level—the amounts of N incorporated in graphene. The current study also indicates an approach in which graphene oxide is reduced. It has been found that epoxy and hydroxyl groups are the majority of functional groups in graphene oxide with the presence of ketones and phenols.[61] Hydroxyl groups can be removed by thermal annealing without introducing additional defects, but epoxy groups bind more strongly, requiring high-temperature annealing that results in holes in the basal plane of graphene.[60] The present findings suggest that epoxy and carbonyl groups can be removed by exposure to NO molecules with fast dynamics at low temperature. Thus, annealing graphene oxide in NO gas at room temperature may serve as a "soft" way to remove epoxy groups.

Finally, we consider NH_3, which has been used in efforts to dope graphene by N.[29,36–38,40,42] We find that, at a vacancy, NH_3 dissociates to a NH_2 group and a H atom. The stable structures shown in Figs. 4(a) and 4(b) have adsorption energies of 2.0 and 3.5 eV, respectively. The dissociated H atom and NH_2 group are on the same side in Fig. 4(a) and opposite sides in Fig. 4(b). After annealing at 1000 K for 1.6 ps, the tilted configuration changes into the bridge configuration [Fig. 4(d)], which remains stable under further annealing [Fig. 4(e)]. By increasing the temperature to 1500 K, one H atom from the NH_2 group moves to a C1 atom (marked in red) by forming a CH_2 group [Fig. 4(f)] after about 10 ps, leaving a NH group. The last H atom bonded to N transfers to a C2 atom (marked in cyan) after about 15 ps, leaving the N atom incorporated in the graphene plane. However, the bonding of these H atoms is very robust, indicating the dynamics of H desorption is very slow and beyond the reach of our simulation times achieved

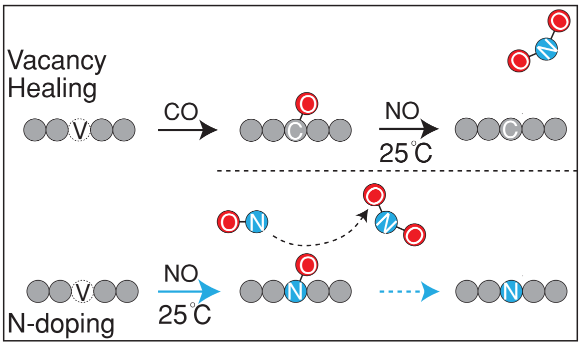

FIG. 5. (Color online) Schematic view of the vacancy healing and N-doping process of graphene with vacancies (V) by CO and NO molecules.

in this study. H atoms bind strongly to graphene vacancies resulting from the presence of unpaired electrons at vacancies. We find that desorbing a H_2 molecule from the hydrogenated vacancies is an endothermic process with an enthalpy change of about 3 eV, and the activation barrier should be even larger. Thus the atomic H generated during annealing in NH_3 gas is not easy to be thermally removed, and the residual H atoms may act as impurities that increase the resistivity due to electron scattering.[43,44]

IV. CONCLUSION

In conclusion, as summarized in Fig. 5, a procedure for controllable vacancy healing and N-doping of graphene has been revealed by the present first-principles molecular dynamics simulations. Vacancies can be healed by sequential exposure to CO and NO molecules in a two-step recipe. Controllable N-doping in graphene can be achieved by sequential vacancy creation (e.g., by an electron beam) and subsequent exposure to NO molecules. Our strategy introduces no extra defects and also suggests a potential way to reduce graphene oxide.

ACKNOWLEDGMENTS

This work was supported by DTRA Grant No. HDTRA1-10-1-0016 and the William A. and Nancy F. McMinn Endowment at Vanderbilt University. The calculations were performed at ORNL's Center for Computational Sciences.

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