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Polymeric nitrogen in a graphene matrix: An *ab initio* study

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A hybrid material where polymeric nitrogen chains are sandwiched between graphene sheets in the form of a three-dimensional crystal, is predicted by means of *ab initio* simulations. It is demonstrated that chainlike polymeric nitrogen phase becomes stable at ambient pressure when intercalated in a multilayer graphene matrix. The physical origin of this stabilization is identified by studying the electronic properties of the system. This approach of stabilizing polymeric nitrogen by means of external three-dimensional matrix constitutes a path toward synthesizing different types of nitrogen-based high-energy materials.

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I. INTRODUCTION

The search for efficient and environmentally friendly high-energy materials is among the most important tasks of science and technology. A potential use of nonmolecular forms of nitrogen as a propellant or explosive is extremely promising in this regard.[1] The idea of creating nitrogen-based high-energy-density materials is based on a uniquely large energy difference between single and triple N-N bonds. The energy density of single-bonded polymeric nitrogen was estimated to be at least three times higher than that of the most powerful energetic materials known today.[2,3] Moreover, as a result of reaction, these systems decompose into molecular nitrogen which is environmentally safe. Several stable forms of polymeric nitrogen have been proposed by extensive theoretical studies[4,5] and one of them, the so-called cubic gauche (CG) form, has already been experimentally demonstrated at high pressure and temperature.[1] Several other metastable forms of polymeric nitrogen have also been proposed recently,[6–8] they tend to consist of continuous nitrogen polymeric chains or chainlike clusters, packed together to form three-dimensional crystals. Some of these structures were shown to be thermodynamically competitive with the CG phase but none to be stable at ambient pressure and temperature.

Recently, several authors of this paper proposed a conceptually different way of stabilizing polymeric nitrogen.[9] It was theoretically demonstrated that nitrogen chain can be effectively stabilized when encapsulated in carbon nanotubes (CNT) of proper diameter.[9] This so-called "confined" polymeric nitrogen was shown to be stable at ambient pressure and temperature by total-energy calculations. The mechanism of stability was found to be due to a piece of elegant physics, namely, a charge transfer from the nanotube to a hybridized orbital that is created by conduction states of the nanotube and the nitrogen chain.[9] This charge-transfer mechanism is however found to be sensitive to the radius and chirality of the nanotube. For example, calculations showed that for (3,3) and (9,9) carbon nanotubes, the stabilization mechanism disappears and nitrogen chain breaks into N_2 molecules.

In this study, we theoretically propose a bulk hybrid compound where polymeric nitrogen chains are sandwiched between multiple graphene layers. We show by total-energy calculations that being intercalated in this multilayer graphene matrix, polymeric nitrogen phase becomes stable at ambient pressure conditions. We demonstrate that the stability is also caused by charge transfer from the graphene matrix to the nitrogen chain which also stabilizes the entire three-dimensional structure. Since graphite structure does not involve geometric parameters, such as radius and chirality in carbon nanotubes, the polymeric nitrogen intercalated graphite crystal should be a promising candidate for bulklike nitrogen-based high-energy material.

II. METHODOLOGY

Our calculations were performed within density-functional theory (DFT) approach,[10] and generalized gradient approximation (GGA) (Ref. 11) was used to describe exchange-correlation interactions. We used an accurate PWSCF electronic structure code[12] which employs norm-conserving pseudopotentials[13] and expands electronic eigenstates on a set of plane waves. A 75 Ry plane-wave energy cutoff was used in all calculations. A unit cell contained one graphene sheet and one armchair-type nitrogen chain. The nitrogen chain is placed on top of the graphene and oriented along the zigzag carbon bonds of the graphene. We applied a commensurability condition in the nitrogen chain direction, taking two unit cells of nitrogen chain (eight atoms) and three unit cells of graphene in the same direction. This resulted in a small lattice mismatch of 0.04 Å per N atom and allowed to keep the system size at computationally affordable level. Figure 1 shows the unit cell of the hybrid material (which we refer to as N_8@graphene), doubled in the nitrogen chain direction, as well as in direction perpendicular to the graphene layers. For geometry relaxations, Brillouin zone was sampled in 8 and 4 k points along the chain and intersheet directions, respectively, which showed a good total-energy convergence. The k sampling was significantly increased for calculation of electronic properties, such as the density of electronic states. The structure was completely relaxed both with respect to atomic positions and to the unit-cell size and geometry.

To test pseudopotentials and the basis set cutoff we first performed structural relaxation of two forms of bulk nitro-

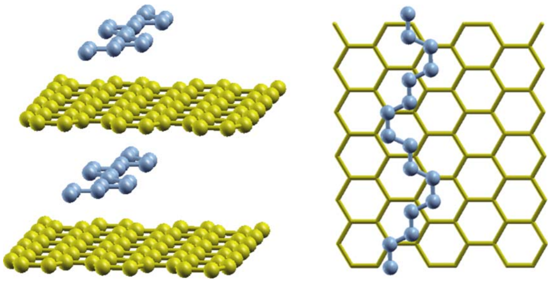

FIG. 1. (Color online) Left: the unit cell of the N_8@graphene crystal structure, doubled in the stacking direction, as well as in the direction of the nitrogen chain periodicity. Right: the same system viewed from the stacking direction, showing the configuration of the planar nitrogen chain. The graphene sheet is represented schematically for sake of clarity.

gen: CG structure and an unstable simple-cubic (SC) phase. The obtained lattice parameter for the CG phase (3.78 Å) agrees well with the experimental value (3.75 Å);[14] as well as with previous theoretical results (3.79 Å).[14] The lattice parameter for the SC structure (1.79 Å) is also consistent with the one obtained by Mailhiot *et al.*[4] (1.84 Å). As one of the test calculations, we also performed relaxation of the "empty" graphene matrix, containing one graphene layer per unit cell. The obtained interlayer distance of 4.54 Å agrees with previously reported GGA results (4.5 Å) (Ref. 15) and overestimates the experimental interlayer distance in graphite (3.35 Å). This is a well-known feature of generalized gradient approximation, which fails to correctly describe the van der Waals interactions between the graphene layers. However, our choice of GGA was dictated by its higher ability (as compared to local-density approximation) to correctly describe atomic and electronic structures of complex hybrid compounds with inhomogeneous electronic-density distributions. In particular, using of GGA became standard in calculations of nitrogen structures in linear, planar, and bulk phases, as well as in hybrid systems.[8,9,16]

III. RESULTS AND DISCUSSION

A. Atomic structure

The N_8@graphene structure was relaxed starting from different geometric configurations of the nitrogen chain. Both armchair and zigzag nitrogen chains were used as starting configurations in parallel and perpendicular orientations relative to the graphene sheet. For each of four starting configurations, nitrogen atoms were additionally shifted by 0.3 Å in random directions to break a possible symmetry of initial configuration. As a result of structural relaxation, the perpendicular orientation of the nitrogen chain was always transformed into a parallel one. Figure 1 shows the final lowest total-energy configuration obtained as a result of geometry optimization. The relaxed distance between the N chain and the graphene sheet is 3.6 Å, which is smaller than the distance between the graphene sheet and the N_2 molecule, relaxed on top of it (4 Å). The following important conclusion can be made from the geometry analysis of the relaxed structure: the nitrogen chain sandwiched between the graphene sheets has a perfectly planar structure as a stable lowest total-energy configuration. This is obviously not the case for free-standing nitrogen chains which show strong off-plane deformations due to electrostatic repulsion of the "lone-pair" electrons localized on neighboring nitrogen atoms. The same planar configuration of the nitrogen chain was observed in the previously studied N_8@CNT(5,5) structure[9] which suggests that a similar stabilization mechanism takes place in both CNT and graphite cases.

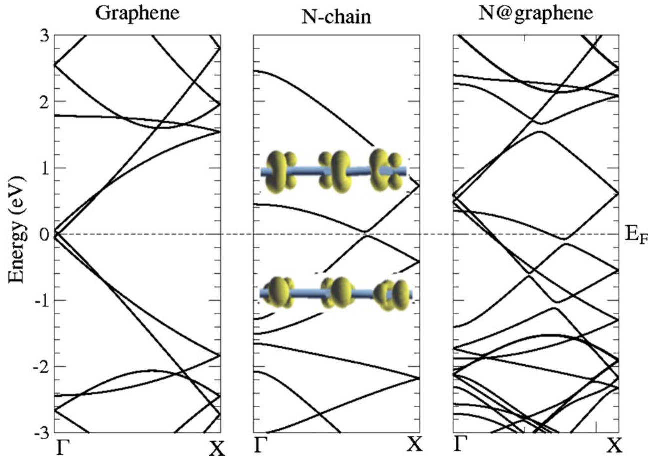

FIG. 2. (Color online) Band structure of isolated graphene sheet (left), isolated nitrogen chain (center), and the N_8@graphene system, plotted along the periodicity direction of the nitrogen chain. The zero of energy corresponds to the Fermi level for each system. The central panel shows the squared wave functions for valence-band maximum and conduction-band minimum of standalone nitrogen chain.

B. Electronic structure

To understand the physical mechanism leading to the stability of the N_8@graphene, we turn to the electronic structure of this hybrid compound. Figure 2 shows the band structure of N_8@graphene, plotted along the momentum direction oriented along the nitrogen chain. Band structures of the isolated nitrogen chain and of the graphene sheet are shown for sake of comparison. Here the atomic coordinates of both isolated structures were taken from the relaxed N_8@graphene geometry to highlight the effects of chain-graphene interaction. We observe in Fig. 2 that in the energy range from −1 to +1 eV the band structure of the N_8@graphene is formed by a superposition of electronic bands of the graphene sheet and the nitrogen chain, and no hybridization takes place between the states of two systems in this energy interval. At the same time, due to the difference in electronegativities between carbon and nitrogen, the electronic bands of the two systems are rigidly shifted relative to each other by 0.6 eV, leading to a charge transfer from the graphene sheet to the nitrogen chain.

The charge-transfer effect can be clearly seen on the electronic density of states (DOS) projected onto the atomic orbitals (Fig. 3). To calculate this projection we use the SIESTA program package[17] which is a self-consistent DFT pseudopotential code, employing atomiclike numerical orbitals as a

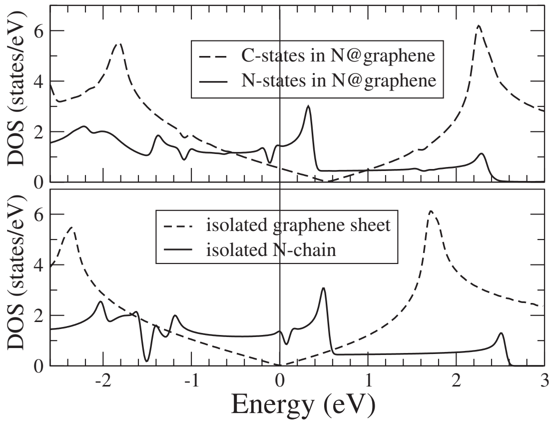

FIG. 3. Electronic DOS for the N_8@graphene system, as well as for the isolated graphene sheet and nitrogen chain. DOS, projected on the orbitals of graphene and nitrogen chain is shown for the N_8@graphene structure. A 0.05 eV broadening is used.

basis set. Comparing DOS projected on the graphene sheet and on the nitrogen chain with the one of the isolated graphene and standalone nitrogen chain, we observe that charge transfer brings the Dirac point of the graphene sheet to 0.5 eV above the Fermi level of the system. Integrating the graphene-projected DOS from the Fermi level up to the Dirac point gives 0.4 missing electrons which the graphene sheet is donating to the nitrogen chain. Interestingly, the same amount of charge transfer was found in previously studied N_8@CNT(5,5) structure.[9] To visualize the redistribution of electronic charge in the system, we plot in Fig. 4 the difference between the real-space charge distribution in N_8@graphene system and the superposition of real-space charges for isolated graphene sheet and isolated nitrogen chain. The accumulation of negative charge on the nitrogen chain and the positive one on the graphene sheet creates an effective electric field, which stabilizes nitrogen chain in its planar form and counter forces possible off-plane deformations. Moreover, the accumulation of negative charge between positively charged graphene layers (Fig. 4) creates an effective electrostatic attraction between them which stabilizes the entire hybrid structure.

To get a more detailed understanding of the stabilization mechanism, let us have a look at the electronic structure of the standalone nitrogen chain, "extracted" from the graphene matrix (Fig. 2). The chain shows an insulating behavior, with a small band gap of 60 meV. The top valence and lowest conduction bands are formed by π-character states. Their anticrossing behavior with the formation of the gap at the Fermi level is a well-known effect of Peierls distortion (chain dimerization). Indeed, the observed bond alternation for the nitrogen chain is ~4% (1.27, 1.32 Å) and the same effect was previously observed for zigzag nitrogen chains.[18] To visualize the valence and conduction states of the nitrogen chain, we calculated the squared wave function of these states, integrated in the energy window of 0.1 eV below the valence-band maximum and above the conduction-band minimum. The results are plotted in (Fig. 2). We clearly see that both states are of π type. Also, it can be noticed that the orbitals of the valence states are oriented within the plane of the N chain while those of the conduction states are oriented perpendicular to this plane. When the chain is placed in the graphene matrix, these conduction states become partially populated by the charge transfer from the graphene sheets. Their orientation toward the graphene sheets creates a set of directed electrostatic bonds, which, in our opinion, stabilizes the polymeric nitrogen chain by counterforcing any off-plane deformations.

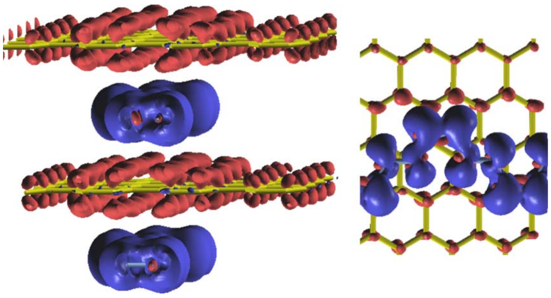

FIG. 4. (Color online) Electronic density redistribution upon intercalation of the N chain into the graphene matrix. Accumulations of positive and negative charges are shown with red and blue color, respectively.

Together with a "rigid-band-model" type of charge transfer, Figs. 2 and 3 also demonstrate a weak hybridization between certain electronic states of the N chain and the graphene sheet. This effect happens at 1.1 eV below and 1.6 eV above the Fermi level, and is due to the interaction between the π bands of the N chain and the graphene sheet. This weak coupling leads to band repulsion with the formation of gaps of the order of 0.2 eV and modifies the DOS of the nitrogen chain at the energies below -1 eV.

C. Total energy

To complete our study, we now discuss the total-energy characteristics of the proposed N_8@graphene structure, including its cohesive energy, as well as total-energy differences with other nitrogen phases. As in any calculations of binding energy for complex structures, the interpretation of the obtained value strongly depends on the choice of reference systems. These systems should be carefully defined based on our choice of "building blocks" of the complex structure, between which the interaction needs to be estimated. In the case of N_8@graphene system it is the interaction between nitrogen chain and the graphene matrix, which needs to be estimated, and the problem becomes even more complicated, as far as one of these building blocks—standalone nitrogen chain—is itself an unstable system. To overcome this problem we decided to take as reference systems a standalone, completely relaxed graphene sheet, and nitrogen chain, which atomic coordinates equal to those in relaxed N_8@graphene system. Using of the N-chain configuration, "extracted" from N_8@graphene structure allows us to estimate the interaction between nitrogen chain and graphene matrix, caused only by changes in their electronic structure, namely, by the discussed above charge transfer.

Using the described above reference systems, we found that nitrogen chain gains 45 meV per N atom when it is introduced in graphene matrix. At first glance this interaction is on the order of van der Waals interaction between neighboring carbon layers in graphite ($\sim$43 meV,[15]). However, one should keep in mind that our calculations were performed with GGA *XC* functional, which almost neglects van der Waals interactions. For sake of comparison we calculated the binding energy between two bare graphene sheets, relaxing the interlayer distance to the minimum of the total energy. Indeed, the obtained binding-energy value ($\sim$2 meV) is considerably smaller, and agrees well with the results of previous study, where the same value was obtained using GGA functional.[15] We also calculated the binding energy for the system where polymeric nitrogen was replaced by the N_2 phase, taking the graphene sheet and N_2 molecules as reference systems. The obtained binding energy of $\sim$5 meV was significantly smaller than 45 meV, observed in the case of polymerized N chain. These test calculations demonstrate that the interaction between nitrogen chain and graphene matrix is more of electrostatic nature, and is due to the charge transfer, caused by modifications in their electronic structure. We should also note that the correct description of van der Waals interactions should bring graphene sheets even closer to each other, thus increasing the charge transfer between two subsystems, which, in turn, should further increase the stability of the whole system.

To have an idea about possible ways of experimental synthesis of the proposed structure, we calculated the energy difference between N_8@graphene system and the molecular phase of nitrogen, confined between graphene sheets. The results show that these two phases are separated by a significant energy gap of 2.2 eV per N_2 molecule. The most natural way to reduce the energy separation between these two phases can be, in our opinion, the application of external pressure in the direction perpendicular to graphene sheets. We believe that applying pressure in stacking direction, combined with employing certain catalysis elements, which allow to extend the bondlength of N_2 molecule,[19] could be the most probable way of experimental synthesis of N_8@graphene structure. Of course, one should be aware of additional reaction barrier, which separates the metastable N_8@graphene phase from the lower-energy N_2 gas phase. The estimation of this barrier would be of large importance because it will give us the interval of temperature stability of the N_8@graphene system. This shows the necessity of a separate profound study of formation barriers and thermal stability of N_8@graphene structure, in a similar way as it has already been performed for N_8@CNT(5,5) system.[20]

D. Comparison with N@CNT(5,5) system

It is interesting to discuss the analogy of the presently proposed structure with previously studied N@CNT(5,5) system[9] where nitrogen chain is encapsulated in carbon nanotube. In both systems the polymeric nitrogen is stabilized via interaction with the graphene sheet: in the N@CNT(5,5) case this sheet is rolled around the nitrogen chain in the form of a nanotube while in the graphene case the nitrogen chain is sandwiched in a multilayer graphene matrix. This similarity explains exactly the same amount of charge ($0.4e$) transferred to the nitrogen chain in both systems. We do observe two important differences between the CNT and graphite polymeric nitrogen structure. First, the charge transfer in graphite-polymer nitrogen hybrid structure occurs without the formation of hybridized orbital between the nitrogen chain and the host carbon matrix. For this reason, the stabilization mechanism should be less sensitive to the geometry and size of the system. Second, the proposed graphite system has a layered bulk structure where the distance between the graphene layers can change thus allowing to maximize their interaction with the nitrogen chain. This is clearly not the case when a nanotube with a fixed diameter is used as a host material. A further advantage of a bulk layered form is that by changing the type of stacking we can build a structure where one nitrogen chain is sandwiched between two effectively independent graphene surfaces. This may increase the amount of charge transfer and therefore increase the stability of the confined polymeric nitrogen. Finally, a possibility to effectively squeeze the N_8@graphene structure in the stacking direction, which is obviously not the case for N_8@CNT(5,5) system, opens more perspectives for experimental synthesis of this high-energy material.

IV. CONCLUSION

In conclusion, we theoretically propose a hybrid compound where polymeric nitrogen chains are intercalated in multilayer graphene matrix. First-principles calculations of structural and electronic properties of this system have shown that the hybrid structure is stable at ambient pressure. We found that polymeric nitrogen chains are stabilized in the planar form by charge transfer from the host graphene matrix. We have identified several advantages of using multilayer graphene matrix to stabilize polymeric nitrogen in a form of a three-dimensional bulk crystal, as compared to the one-dimensional nanotube-based system. This result offers a path toward experimental synthesis of bulk nitrogen-based high-energy materials and invites further studies of hybrid systems containing polymeric nitrogen.

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[1] M. I. Eremets, A. G. Gavriliuk, I. A. Trojan, D. A. Dzivenko, and R. Boehler, Nature Mater. **3**, 558 (2004).

[2] K. Christe, Propellants, Explos., Pyrotech. **32**, 194 (2007).

[3] J. Uddin, V. Barone, and G. Scuseria, Mol. Phys. **104**, 745 (2006).

[4] C. Mailhiot, L. H. Yang, and A. K. McMahan, Phys. Rev. B **46**, 14419 (1992).

[5] M. M. G. Alemany and J. L. Martins, Phys. Rev. B **68**, 024110 (2003).

[6] F. Zahariev, S. V. Dudiy, J. Hooper, F. Zhang, and T. K. Woo, Phys. Rev. Lett. **97**, 155503 (2006).

[7] F. Zahariev, A. Hu, J. Hooper, F. Zhang, and T. Woo, Phys. Rev. B **72**, 214108 (2005).

[8] W. D. Mattson, D. Sanchez-Portal, S. Chiesa, and R. M. Martin, Phys. Rev. Lett. **93**, 125501 (2004).

[9] H. Abou-Rachid, A. Hu, V. Timoshevskii, Y. Song, and L. S. Lussier, Phys. Rev. Lett. **100**, 196401 (2008).

[10] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[11] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[12] S. Baroni, A. Dal Corso, S. de Gironcoli, and P. Giannozzi, http://www.pwscf.org

[13] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991); L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[14] X. Q. Chen, C. L. Fu, and R. Podloucky, Phys. Rev. B **77**, 064103 (2008).

[15] Y. Ma, Phys. Rev. B **76**, 075419 (2007).

[16] J. Kotakoski and K. Albe, Phys. Rev. B **77**, 144109 (2008).

[17] P. Ordejón, E. Artacho, and J. M. Soler, Phys. Rev. B **53**, R10441 (1996); J. M. Soler E. Artacho, J. D Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, J. Phys.: Condens. Matter **14**, 2745 (2002).

[18] A. Pohl, H. Meider, and M. Spingborg, J. Mol. Struct.: THEOCHEM **305**, 165 (1994).

[19] Wei Ji (private communication).

[20] Wei Ji, V. Timoshevskii, H. Abou-Rachid, L.-S. Lussier, and H. Guo, Appl. Phys. Lett. **95**, 021904 (2009).