PCCP

Accepted Manuscript

ROYAL SOCIETY
OF **CHEMISTRY**

www.rsc.org/pccp

PCCP RSCPublishing

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Hybrid Platforms of Graphane/Graphene 2D Structures: Prototypes for Atomically Precise Nanoelectronics

F. de B. Mota,*[a] R. Rivelino,*[a] P. V. C. Medeiros,[b] A. J. S. Mascarenhas[cd] and C. M. C. de Castilho*[ad]

First-principles calculations demonstrate that line/ribbon defects, resulting from a controlled dehydrogenation in graphane, lead to the formation of low-dimensional electron-rich tracks in a monolayer. The present simulations point out that hybrid graphane/graphene nanostructures exhibit important elements, greatly required for the fabrication of efficient electronic circuits at the atomic level.

Discovery and synthesis of graphene-like two-dimensional (2D) materials have opened a new era for the technology based on atomically thin devices.[1-4] In this direction, Novoselov et al.[5] have isolated free-standing atomic crystals from a variety of strongly layered materials, which exhibit high crystal quality and extended continuity. Among these 2D crystals, graphene is certainly the most prominent because of its exceptional properties.[6] Indeed, its hexagonal packing into a honeycomb structure has served as an inspiration for studying similar structures, such as silicene (2D hexagonal silicon), germanene (2D hexagonal germanium),[7-9] and other promising 2D hexagonal structures.[10-13] However, a difficulty in employing some of these monolayers as components in electronics is the absence of an energy gap in their band structures.[14] Among several solutions to this problem proposed in the literature,[15-20] Britnell et al.[20] have recently reported a scheme based on quantum tunneling, from a graphene heterostructure. In this way, they combine graphene with boron nitride or molybdenum disulfide to establish an efficient vertical transport barrier in the resultant electronic component. This provides a new route for the realization of high-speed graphene-based analog electronics.

An alternative solution for building a monolithic integrated circuit at nanoscale would be working directly on a semiconducting monolayer with high crystal quality. Such a structure can be achieved, for example, by performing a total adatom adsorption on graphene.[19,21-23] Most adsorbed atoms interact weakly with pristine graphene holding on to its surface.[24,25] In this direction, a promising candidate towards a high performance hybrid platform in electronics is the hydrogenated graphene – or graphane as it is known.[19] Additionally, Bianco et al.[26] have reported on the production and characterization of germanane, a one-atom-thick sheet of hydrogenated puckered germanium structure similar to graphene (germanene),[23] but with great potential for a wide range of optoelectronic applications. Interestingly, Wang et al.[27] have proposed a plasma deposition process for preparing monolayer graphene using graphane-like films as well as an intermediate phase.

In contrast to pristine graphene, its fully hydrogenated form is an insulating material characterized by a wide direct gap at the Γ point.[23,28] Notwithstanding, a tunable gap in quasi-freestanding monolayer graphene can be induced by hydrogenation.[29-31] Furthermore, hydrogenation of graphene has been found to be a reversible process,[19,32] which is a great advantage for the application of graphane/graphene hybrid structures[33] in nanoelectronics. In this sense, we can think about the fabrication of a totally integrated hybrid nanostructure, exhibiting high on/off switching ratios, without degrading the electronic quality of graphene. The combination of pure and hydrogenated graphene, distinguished by different band gap energies, is promising for the fabrication of periodic quantum arrays that favours a resonant charge transfer.[34] Moreover, the dependence of the band gap on the hydrogen concentration, as well as on the arrangement of adsorbed hydrogen atoms on the graphene surface, has recently been investigated.[35] More recently, defects resulting from the removal of hydrogen atoms in graphane (creating vacancies and nanoroads) were proposed,[36] and their geometric structure and electronic properties have been studied. However, integrating these materials to create atomically resolved circuits is still an enormous challenge. Fortunately, the atomically precise manipulation of graphene derivatives has been possible thanks to the development of nanolithography techniques.[37]

In connection with recent nanotechnological developments,[19,27,32-34,38] we propose the introduction of several types of zigzag line defects in graphane[28,38] aiming at obtaining a viable platform for nanoelectronics. Such vacancy defects may result from a systematic and ordered removal of the adsorbed hydrogen atoms on both sides of a graphane monolayer. We examine the possibility of using these extended defects as conducting channels in graphane, which could be exploited in prototypical integrated circuits at nanoscale. In this context, various questions can be raised and answered from ab initio calculations. For example, (i) what is the effective way to create permanent conducting routes in a two-dimensional insulating monolayer? (ii) Is the energetics associated to this process facilitated at ordinary conditions? (iii) Is it possible to map conducting tracks in the band structure of a 2D crystal? (iv) Can vacancies created on a graphane monolayer result in an electronic behavior similar to that of quantum dots or conducting polymers? (v) How far from each other may be separated two dehydrogenated carbon lines in a graphane template to avoid electronic superposition? The aim of this Communication is also to shed, at least, some light on these questions.

Our simulations were performed within the framework of Kohn-Sham density functional theory, adopting the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation,[39] which yields appropriate lattice parameters of perfect, infinite periodic graphene or graphane sheets. Theoretical calculations for different conformers of graphane presented in Reference,[38] including different density-functional models, have indicated that PBE is an acceptable approximation. This functional is also preferred in the study carried out by Singh et al.[33] In our calculations, we employ PBE combined with finite-range numerical pseudoatomic orbitals to mimic a double-zeta polarized basis set. The energy shift for determining the confining radii of the pseudoatomic orbitals was set in 0.10 eV. The structures were fully relaxed until residual forces became less than 0.01 eV/Å. The real-space mesh cutoff was set to at least 300 Ry. The Monkhorst-Pack[40] special k-points scheme was employed for sampling the Brillouin zone (BZ) with a mesh of 13×31×1. The SIESTA code[41,42] was employed in all these simulations.

The graphane/graphene hybrid systems studied here are displayed in Figure 1 (a)-(f). Considering the primitive unit cell of graphane (red rectangle in Figure 1(a)), 4×1 superlattices (enclosed by black rectangles) were considered as the periodic unit in the calculations. These supercells were chosen in order to properly simulate the extended defective structures using unit cells of the same size. Thus, they allow a more concise and systematic analysis of our results within a perspective of building prototypes for atomically precise nanoelectronics. For example, the dimensions of the 4×1 supercell of our graphane piece are 17.76 Å by 2.56 Å (optimized values). All defective structures were also completely optimized at the same level of theory. This ensures that nonphysical interactions are avoided when multiple point defects are taken into account in the calculations.

[**Figure 1**]

Fig. 1. Illustration of the superlattices considered as prototypes for atomically precise nanolithography in a graphene monolayer. (a) Pristine graphane; (b) zigzag carbon line resulting from the removal of hydrogen atoms on both sides of graphane; (c) acene-like carbon ribbon consisting of two neighbor dehydrogenated lines on both sides of graphane; (d) two fully dehydrogenated zigzag lines separated by a single hydrogenated line; (e) two fully dehydrogenated zigzag lines separated by two hydrogenated lines; and (f) acene-like ribbon with both-side removal of hydrogen atoms on the adjacent carbon atoms. Black rectangles indicate 4×1 supercells employed in the simulations, whereas the red rectangle encloses the 1×1 reference unit cell of graphane.

Starting from the supercells displayed in Figure 1, we have obtained the relaxed structures of the usual configuration of graphane[19,28] and the corresponding defective graphane-based systems, i.e., the graphane/graphene hybrid platforms. The geometry of the relaxed structures can be better visualized in Figure 2. As it is well known, carbon atoms in graphane are in an sp^3 configuration, as displayed in Figure 2(a), originating an insulating direct band gap material.[28,38] On the contrary, as indicated in Figure 2 (b)-(e), systems (b), (c), (d), and (e) exhibit dehydrogenated carbon lines/ribbons with delocalized electron densities, since these bare carbon atoms recover their sp^2 hybridization along the line defects, as in graphene, leading to π-type tracks on the graphane monolayer. Among these systems, the defect proposed in (f) exhibits the most strongly distorted structure and breaks the delocalized π-pattern observed in systems (b)-(e), giving rise to more localized electron states along the dehydrogenated ribbon (see Figure 2(f)). As we shall see in the following, system (f) features a band gap opening of 1.65 eV, while systems (b)-(e) exhibit conducting characteristics. These findings indicate that the systems proposed here exhibit important elements that are greatly required for the fabrication of efficient electronic circuits at the atomic level.[1-4]

[**Figure 2**]

Fig. 2. Relaxed structures of pristine graphane (a) and defective graphane/graphene systems upon removal of hydrogen lines on both sides of graphane (b)-(e). Calculated Kohn-Sham electron densities (in red) around the Fermi level are displayed for each of these systems.

We have calculated the formation energy, per removed hydrogen molecules, of these defects with respect to a perfect graphane sheet, which can be defined as

$$E_f^{def} = \left(E_{tot}^{def} - E_{tot}^{0} + n\mu_H\right)/n$$

where E_{tot}^{def} is the total energy of the defective sheet, E_{tot}^{0} is the total energy of a perfect graphane sheet, $\mu_H = \frac{1}{2}E_{H_2}$ is the chemical potential of hydrogen, and n is the number of released hydrogen molecules. The same calculation was also performed to consider the formation of non-bonded hydrogen pairs upon the formation of these defects. Our results are reported in Table 1. We notice that the values of the formation energy of these defects, when releasing molecular hydrogen, lie in the range of photon energies below the visible light (1.2–1.4 eV), which may be important for generating such defects via, for example, low laser ablation techniques. In addition, these results are in line with the formation of nanoroads in graphane.[36] More importantly, our results reveal that the formation energy of these defects may be sufficiently low at ordinary conditions, which would favor a controlled fabrication of dehydrogenated lines and ribbons in a graphane monolayer.

Table 1. Calculated formation energy per hydrogen molecule ($E_f^{def}[H_2]$) and per hydrogen atom pairs ($E_f^{def}[H]$) with respect to pristine graphane for the systems (b)-(f) displayed in Figure 2. The values are given in eV.

System	$E_f^{def}[H_2]$	$E_f^{def}[H]$
(a)	0	0
(b)	1.36	2.85
(c)	1.20	2.77
(d)	1.36	2.85
(e)	1.36	2.85
(f)	1.31	2.82

The results reported in Table 1 indicate that the removal of H_2 is more likely to occur than isolated atomic species. Moreover, the formation energy of one zigzag line, such as in system (b), is similar to the formation energy of two zigzag lines separated by hydrogenated lines, such as in systems (d) and (e). This finding gives an indication about how weak can be the interaction between two separated line defects in comparison with two adjacent lines, as proposed in system (c). Theoretically, removing hydrogen islands from both sides of a graphane matrix leaves a potential well typical of confined electrons, which may also be useful in creating arrays of dots for many applications in nanoelectronics.[33,36] In this sense, we investigate in more detail the electronic structure of the extended defects generated in a graphane monolayer. For this purpose, we have considered a special set of directions in the superlattice BZ, i.e., the Γ-X-M-Γ directions (see Figure 3 for clarity), in order to analyze the electronic properties of these linear defects in a sheet.

[**Figure 3**]

Fig. 3. Illustration of the special directions (left) in the sperlattice Brillouin zone (BZ) used to investigate the systems (a)-(f) and calculated energy spectrum (right) of a dehydrogenated zigzag carbon line (b) in the BZ. The π and π* bands touch each other in the edge of the BZ.

In Figure 4, we display the calculated band structure in the Γ-X-M-Γ directions and corresponding density of states (DOS) of our proposed systems (a)-(f). As expected from Kohn-Sham DFT calculations, our band gap of graphane at the Γ point is 3.5 eV (see Figure 3(a)), which is in line with previous theoretical results.[28] Most importantly, our results show that the band structure of graphane is strongly affected by even small concentrations of dehydrogenated sites. For example, in the case of system (b), a single dehydrogenated zigzag carbon line in graphane, two conducting states are created in the Fermi level of the system ($E_F = -3.53$ eV). These states correspond to an extended charge density along the zigzag line, as displayed in Fig. 2(b). Along the Γ-X direction, the π and π* bands touch each other at the edge of the superlattice BZ, leading to a zero band gap system (see Figure 3), which corresponds to a kind of zigzag quantum wire along the graphane layer. We notice, however, the removal of hydrogen atoms from only one side of the zigzag carbon line, differently from what occurs in system (b), opens a band gap of about 1.74 eV in the whole system. For this reason, the fully dehydrogenated zigzag line appears to be a more appropriate candidate for a one-dimensional conducting channel in a graphane/graphene hybrid template.

[Figure 4]

Fig. 4. Calculated band structure along the Γ-X-M-Γ directions in the BZ and corresponding density of states (DOS) of (a) pristine graphane and (b)-(f) graphane/graphene hybrid monolayers.

Now, considering the cases of two zigzag lines, i.e., systems (c), (d), and (e), we notice a common pattern in their band structures, despite the differences in distances between the parallel line defects. For example, in system (c), containing two adjacent dehydrogenated lines and forming an acene-like ribbon defect (i.e., sequentially juxtaposed hexagons), there are two π bands crossing the Fermi level ($E_F = -3.61$ eV); being one of them semi-occupied, and additionally, two π bands approaching to the Fermi level from the conduction and valence bands in the X-M direction. In this case, because of the relatively strong defect interaction, the charge density is more localized at the bare carbon atoms, which are further apart from each other, as displayed in Figure 2(c). This is interesting because system (c) could overcome a real problem in organic synthesis and organic field-effect transistors areas, since high order acenes (n > 5) are very reactive and need to be isolated using a proper polymeric matrix.[43] Here, we predict the possibility of create this kind of structure by selective dehydrogenation of graphane, allowing to design precise nanoelectronic prototypes.

In contrast to the acene-type defect, when the dehydrogenated carbon lines are separated by one completely hydrogenated carbon line, such as in system (d), the additional π bands lie in the Fermi level ($E_F = -3.60$ eV). A similar result is found for system (e), in which the line defects are separated by two completely hydrogenated carbon lines. As displayed in Figure 4, the π bands of systems (d) and (e) are almost degenerated in the Fermi level (X-M direction) and form delocalized electronic states at the Γ point. This result clearly indicates the possibility of introducing conduction channels along the zigzag carbon lines.

In the case of system (f), an acene-like defect with additional removal of hydrogen atoms from the adjacent carbon atoms, we observe that an energy gap of 1.65 eV is opened in its band structure. As discussed above, this system forms a strongly distorted structure, in comparison to systems (b)-(e), originating a periodic set of localized double bonds, which disrupts the delocalized π-pattern along the ribbon, giving rise to a wider semiconducting ribbon. However, system (f) exhibits a band gap smaller than the band gap of a perfect graphane sheet (calculated as 3.5 eV in the present work), which further reinforces the possibility of tuning an energy gap by creating proper dehydrogenated defects in graphene. Indeed, Singh et al.[33] have demonstrated that the energy gap of dehydrogenated islands in graphene decreases with the linear dimension. Interestingly, the electronics of these defects in graphane can be affected by the width and geometry of the vacancy, and may exhibit a typical confinement of Dirac fermions.[33,42]

Conclusions

In summary, we have assessed the possibility of creating line and ribbon defects in a graphane sheet, originating stable hybrid graphane/graphene platforms, which may be employed as prototypes for atomically precise nanoelectronics. As demonstrated by first-principles DFT calculations, the creation of both-side dehydrogenated zigzag lines in graphane leads to the formation of structures potentially containing conducting channels. We emphasize that such systems may be interesting candidates for monolithic integrated circuit at nanoscale. Our results also demonstrate that these conducting defects consist mainly of degenerated π-bands in the Fermi level, forming delocalized states at the Γ point. Moreover, these results have pointed out the possibility of tuning an energy gap by creating appropriate dehydrogenated defects in graphane. As a prospective study, we point out that such vacancies may be still filled by alkaline metals (lithium, for example, is an interesting candidate to do that[24,45]), which could enhance the conducting properties of the channels via a possible low-dimensional metallization mechanism. Finally, recent progress in nanotechnology[27,37] indicates that it is realistic to consider nanolithography with atomic precision to produce the structures proposed in this study.

Acknowledgements

This work has been partially supported by Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Fundação de Amparo à Pesquisa do Estado da Bahia

(FAPESB). P.V.C.M. acknowledges the Swedish Research Council (VR) for funding.

Notes and references

[a] Instituto de Física, Universidade Federal da Bahia, 40170-115 Salvador, Bahia, Brazil.
[b] Department of Physics, Chemistry and Biology, IFM, Linköping University, 58183 Linköping, Sweden.
[c] Instituto de Química, Universidade Federal da Bahia, Campus Universitário da Federação, 40170-280 Salvador, Bahia, Brazil.
[d] Instituto Nacional de Ciência e Tecnologia em Energia e Ambiente – INCT&EA, Campus Universitário da Federação, Universidade Federal da Bahia, 40170-280 Salvador, Bahia, Brazil.

† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

1 J. Cai, P. Ruffieux, R. Jaafar, M. Bieri, T. Braun, S. Blankenburg, M. Muoth, A. P. Seitsonen, M. Saleh, X. Feng, K. Müllen and R. Fasel, *Nature*, 2010, **466**, 470.
2 B. J. Schultz, R. V. Dennis, V. Lee and S. Banerjee, *Nanoscale*, 2014, **6**, 3444.
3 V. Barone, O. Hod and G. E. Scuseria, *Nano Lett.*, 2006, **6**, 2748.
4 Y. W. Son, M. L. Cohen and S. G. Louie, *Nature*, 2006, **444**, 347.
5 K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov and A. K. Geim, *Proc. Natl. Acad. Sci. USA*, **2005**, 102, 10451.
6 A. K. Geim, *Science*, 2009, **324**, 1530.
7 P. Vogt, P. De Padova, C. Quaresima, J. Avila, E. Frantzeskakis, M. C. Asensio, A. Resta, B. Ealet and G. L. Lay, *Phys. Rev. Lett.*, 2012, **108**, 155501.
8 A. O'Hare, F. V. Kusmartsev and K. I. Kugel, *Nano Lett.*, 2012, **12**, 1045.
9 S. Cahangirov, M. Topsakal, E. Aktürk, H. Şahin and S. Ciraci, *Phys. Rev. Lett.*, 2009, **102**, 236804.
10 A. Hansson, F. de B. Mota and R. Rivelino, *Phys. Rev. B*, 2012, **86**, 195416.
11 A. Hansson, F. de B. Mota and R. Rivelino, *Phys. Chem. Chem. Phys*. 2014, **16**, 14473.
12 J. Yu and W. Guo,. *J. Phys. Chem. Lett*. 2013, **4**, 1856.
13 M. Xu, T. Liang, M. Shi, H. Chen, *Chem. Rev*., 2013, **113**, 3766.
14 S.-H. Lee, H.-J. Chung, J. Heo, H. Yang, J. Shin, U.-In Chung and S. Seo, *ACS Nano*, 2011, **5**, 2964.
15 E. V. Castro, K. S. Novoselov, S. V. Morozov, N. M. R. Peres, J. M. B. L. dos Santos, J. Nilsson, F. Guinea, A. K. Geim and A. H. C. Neto, *Phys. Rev. Lett*., 2007, **99**, 216802.
16 J. B. Oostinga, H. B. Heersche, X. Liu, A. F. Morpurgo and L. M. K. Vandersypen, *Nat. Mater*., 2008, **7**, 151.
17 M. Y. Han, B. Ozyilmaz, Y. B. Zhang and P. Kim, *Phys. Rev. Lett*., 2007, **98**, 206805.
18 C. Stampfer, S. Fringes, J. Güttinger, F. Molitor, C. Volk, B. Terrés, J. Dauber, S. Engels, S. Schnez, A. Jacobsen, S. Dröscher, T. Ihn and K. Ensslin, *Front. Phys*., 2011, **6**, 271.
19 D. C. Elias, R. R. Nair, T. M. G. Mohiuddin, S. V. Morozov, P. Blake, M. P. Halsall, A. C. Ferrari, D. W. Boukhvalov, M. I. Katsnelson, A. K. Geim and K. S. Novoselov, *Science*, 2009, **323**, 610.
20 L. Britnell, R. V. Gorbachev, R. Jalil, B. D. Belle, F. Schedin, A. Mishchenko, T. Georgiou, M. I. Katsnelson, L. Eaves, S. V. Morozov, N. M. R. Peres, J. Leist, A. K. Geim, K. S. Novoselov and L. A. Ponomarenko, *Science* 2012, **335**, 947.
21 R. R. Nair, W. Ren, R. Jalil, I. Riaz, V. G. Kravets, L. Britnell, P. Blake, F. Schedin, A. S. Mayorov, S. Yuan, M. I. Katsnelson, H.-M. Cheng, W. Strupinski, L. G. Bulusheva, A. V. Okotrub, I. V. Grigorieva, A. N. Grigorenko, K. S. Novoselov and A. K. Geim, *Small*, 2010, **6**, 2877.
22 J. T. Robinson, J. S. Burgess, C. E. Junkermeier, S. C. Badescu,; T. L. Reinecke, F. K. Perkins, M. K. Zalalutdniov, J. W. Baldwin, J. C. Culbertson, P. E. Sheehan and Eric S. Snow, *Nano Lett*., 2010, **10**, 3001.
23 K. J. Koski and Y. Cui, *ACS Nano*, 2013, **7**, 3739.
24 P. V. C. Medeiros, F. de B. Mota, A. J. S. Mascarenhas and C. M. C. de Castilho, *Nanotechnology*, 2010, **21**, 115701.
25 P. V. C. Medeiros, A. J. S. Mascarenhas, F. de B. Mota and C. M. C. de Castilho, *Nanotechnology*, 2010, **21**, 485701.
26 E. Bianco, S. Butler, S. Jiang, O. D. Restrepo, W. Windl and J. E. Goldberger, *ACS Nano*, 2013, **7**, 4414.
27 Y. Wang, X. Xu, J. Lu, M. Lin, Q. Bao, B. Özyilmaz and K. P. Loh, *ACS Nano*, 2010, **4**, 6146.
28 J. O. Sofo, A. S. Chaudhari and G. D. Barber, *Phys. Rev. B*, 2007, **75**, 153401.
29 D. Haberer, D. V. Vyalikh, S. Taioli, B. Dora, M. Farjam, J. Fink, D. Marchenko,T. Pichler,O K. Ziegler, S. Simonucci, M. S. Dresselhaus, M. Knupfer, B. Büchner and A. Grüneis, *Nano Lett*., 2010, **10**, 3360.
30 D. Haberer, C. E. Giusca, Y. Wang, H. Sachev, A. V. Fedorov, M. Farjam, S. A. Jafari, D. V. Vyalikh, D. Usachov, X. Liu, U. Treske, M. Grobosch, O. Vilkov, V. K. Adamchuk, S. Irle, S. R. P. Silva, M. Knupfer, B. Büchner and A. Grüneis, *Adv. Mater.*, 2011, **23**, 4497.
31 A. Paris, N. Verbitskiy, A. Nefedov, Y. Wang, A. Fedorov, D. Haberer, M. Oehzelt, L. Petaccia, D. Usachov, D. Yyalikh, H. Sachdev, C. Wöll, M. Knupfer, B. Büchner, L. Caliari, L. Yashina, S. Irle and A. Grüneis, *Adv. Funct. Mater*., 2013, **23** 1628.
32 S. Ryu, M. Y. Han, J. Maultzsch, T. F. Heinz, P. Kim, M. L. Steigerwald, L. E. Brus, *Nano Lett*., 2008, **8**, 4597.
33 A. K. Singh, E. S. Penev and B. I. Yakobson, *ACS Nano*, 2010, **4**, 3510.
34 L. A. Chernozatonskii, P. B. Sorokin and J. W. Brüning, *Appl. Phys. Lett*., 2007, **91,** 183103.
35 L. A. Chernozatonskii, D. G. Kvashnin, P. B. Sorokin, A. G. Kvashnin and J. W. Brüning, *J. Phys. Chem. C*, 2012, **116**, 20035.
36 J. M. de Almeida, A. R. Rocha, A. K. Singh, A. Fazzio and A. J. R. da Silva, *Nanotechnology*, 2013, **24**, 495201.
37 A. J. M. Giesbers, U. Zeitler, S. Neubeck, F. Freitag, K. S. Novoselov and J. C. Maan, *Solid State Commun*., 2008, **147**, 366.
38 A. Bhattacharya, S. Bhattacharya, C. Majumder and G. P. Das, *Phys. Rev. B*, 2011, **83**, 033404.
39 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett*., 1996, **77**, 3865.

40 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188.

41 J. Soler, E. Artacho, J. D. Gale, A. Garcia, J. Junquera, P. Ordejon and D. Sanchez-Portal, *J. Phys.: Condens. Matter*, 2002, **14**, 2745.

42 E. Artacho, E. Anglada, O. Dieguez, J. D. Gale, A. García, J. Junquera, R. M. Martin, P. Ordejón, J. M. Pruneda, D. Sánchez-Portal and J. M. Soler, *J. Phys.: Condens. Matter*, 2008, **20**, 064208.

43 I. Kaur, M. Jazdzyk, N. N. Stein, P. Prusevich and G. P. Miller, *J. Am. Chem. Soc.*, 2010, **132**, 1261.

44 A. H. C. Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov and A. K. Geim, *Rev. Mod. Phys.*, 2009, **81**, 109.

45 P. V. C. Medeiros, F. de B. Mota, A. J. S. Mascarenhas and C. M. C. de Castilho, *Solid State Commun.*, 2011, **151**, 529.