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Communication: Origin of the difference between carbon nanotube armchair and zigzag ends

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In this work, we have found that the difference between armchair and zigzag ends of carbon nanotubes (CNTs) does not pertain at close study for individual bonds and thus alternative strategies need to be developed to reach the ultimate goals in selective growth. Based on first-principles simulations, the difference between binding strengths for CNTs of different chirality was investigated using hydrogen dissociation energies at their passivated ends. When all H atoms are removed collectively we find the well-known difference: that armchair bonds are much weaker than zigzag ones, which is typically seen for both CNT ends and graphene edges. However, when individual H atoms are removed we find almost no difference in hydrogen dissociation energies, small difference in bond lengths, which by association means small difference in C–C and M–C binding energies. We show convincingly that the difference in binding energy between armchair and zigzag ends is due to a fragment stabilization effect that is only manifested when all (or several neighbouring) bonds are broken. This is because at armchair ends/edges neighbouring dangling bonds can pair-up to form C≡C triple bonds that constitute a considerable stabilization effect compared to the isolated dangling bonds at zigzag ends/edges. Consequently, in many processes, e.g., catalytic growth where bonds are normally created/broken sequentially, not collectively, the difference between armchair and zigzag ends/edges cannot be used to discriminate growth of one type over the other to achieve chiral selective growth. Strategies are discussed to realize chirality selective growth in the light of the results presented, including addition of C₂-fragments to favor armchair tubes. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4867744>]

I. INTRODUCTION

During the last two decades, great efforts have been devoted to research on carbon nanotubes (CNTs) to explore and utilize their unique properties.^{1–3} These allotropes of carbon with a cylindrical nanostructure possess excellent mechanical,^{4,5} electrical,^{6,7} and optical properties,⁸ hence have a chance to play an important role in nanotechnology, electronics, optics, and other fields of materials science and technology.^{9–11} For example, the strong but light CNTs are useful as additives to various structural materials. Owing to their extraordinary thermal and electrical conductivities,^{12,13} CNTs also have possible applications in microelectronics.¹⁴ The single-walled carbon nanotubes (SWNTs) can be metallic or semiconducting, which is determined by their chirality.¹⁵ These properties enrich the possible applications, but also raise the challenge to selectively grow SWNTs with suitable conduction for the application at hand.

The controlled chiral selective growth of SWNT is the key to open the gate of CNT applications in information and communication technology (ICT). Although many attempts have been made, at present, state-of-the-art production is only

able to get a narrow diameter and chirality distribution.^{16–19} The best route to achieve chirality-controlled growth of SWNTs is to understand their growth mechanism down to the level of individual atoms and bonds, which is the overall aim with this study. A modified vapor-liquid-solid (VLS) mechanism for the production of nanowires serves to explain the growth mechanism of CNTs in the catalytic chemical vapour deposition (CVD) method on a phenomenological level.^{20–22} The metal-carbon (M–C) binding strength has been shown to play a significant role in growth of CNTs,²³ which can be formalized into three criteria that the metal has to fulfill to be a catalyst: (a) decomposition of the feed-stock gas; (b) formation of graphitic caps on the metal nanoparticle surface; and (c) stabilization of the growing CNT end. Criteria (a) and (b) share common traits with the growth of fibers and relate to freeing up building material on the catalytic metal surface and the strength of the binding of carbon in the metal carbide, respectively. But criterion (c) is specific to tube growth, since the hollow structure results in an unstable growing end that has to be stabilized through a metal that has the M–C binding energy in the required region – not too weak and not too strong, i.e., following a “Goldilocks” principle, which is only fulfilled for a limited number of metals.^{23–25} Thus, metals that can form moderately strong bonds with carbon can be

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used as catalysts. Fe, Co, and Ni are commonly used in their syntheses.^{26–28}

The M–C binding energies are calculated by dividing the CNT-metal adhesion energy/dissociation energy with the number of M–C covalent bonds. Such simulations find that zigzag-like SWNTs have higher M–C binding energies, with around 1 eV, compared to armchair-like SWNT.^{23,29–36} However, the carbon dangling bond (DB) stabilization on the dissociated tube-end accounts for the difference in M–C binding energies between zigzag and armchair SWNT: For armchair tubes the adjacent DBs can interact with each other and form C≡C triple-bonds; For zigzag tubes no triple-bond stabilization is possible since there are no neighbouring DBs (only next-neighbours), and the geometry is unsuitable for triple-bond formation.^{33,36} This is a stabilization effect that only occurs for collective bond breaking and this situation is different in the case of individual DBs and individual bond breaking. It is thus a so-called fragment stabilization energy that lures one to think that there is a large binding energy difference also for the individual bonds for zigzag and armchair SWNTs, and graphene edges. In this study, we give a detailed description of the collective bond-breaking effect, and relate these to the individual bond-breaking, utilizing hydrogen dissociation at the SWNT edges.

II. METHODOLOGY

We have done full structural relaxations with first principles density functional theory (DFT) using the projected augmented wave (PAW) method^{37,38} as implemented in the Vienna *Ab initio* simulation package (VASP).^{39–41} The exchange-correlation interaction was treated at the level of the generalised gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional.⁴² Following convention, we index the SWNT with (n, m). In this work, we have chosen the (n+m=12)-series and (n+m=13)-series, many of which are common products in SWNT synthesis. The SWNTs are all terminated with hydrogen to passivate the unstable ends. The 12-series consists of seven different SWNTs: (12, 0), (11, 1), (10, 2), (9, 3), (8, 4), (7, 5), and (6, 6). The 13-series also consists of seven different SWNTs: (13, 0), (12, 1), (11, 2), (10, 3), (9, 4), (8, 5), and (7, 6). We have used a (20×20×25 Å³) supercell for six layer fragments of the 12-series and 13-series tubes with stoichiometry's C₁₄₄H₂₄ and C₁₅₆H₂₆, respectively. So, the simulation cell has a vacuum region of at least 10 Å in each direction, to decouple the periodic images. The Brillion zone was sampled with the gamma-point only. A plane wave cutoff energy of 700 eV was found sufficient to reach energy convergence. Spin-polarized calculations in an unrestricted framework have been done for all the examined SWNTs to search for the most stable configurations.

In previous work, it has been found that the total energies of hydrogen terminated SWNT fragments do not differ much within one series,³⁶ with all tubes having zigzag character having antiferromagnetic ground states.^{43–45} Also in this study we find that the zigzag-like tube fragments; (12, 0), (11, 1), (10, 2) and (9, 3), and (13, 0), (12, 1), (11, 2) and (10, 3), have antiferromagnetic ground states. In the 12-series and 13-series, the segments are in an energy window of

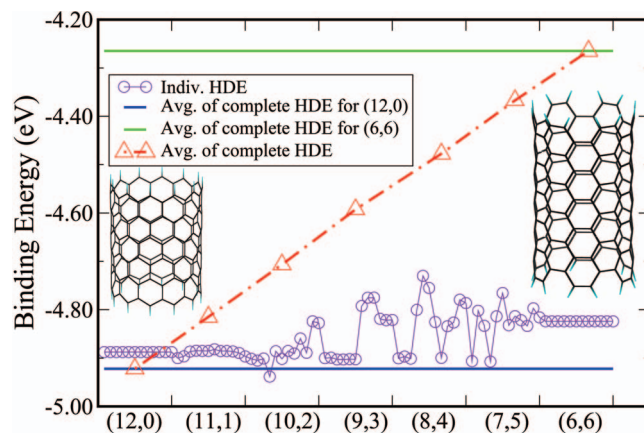


FIG. 1. Individual hydrogen dissociation energies (HDE) and average of complete hydrogen dissociation energies of six-layered fragments of the 12-series.

0.45 eV and 1.39 eV, respectively. The energy window decreases with increasing index (n+m), from the 9-series to the 12-series, cf. Ref. 36. However, the trend stops at the 13-series as it has an energy window comparable to the 9-series. The small energy difference between the SWNTs of different chirality makes the thermodynamic growth control very challenging, and confirms the difficulty of chiral selective growth of SWNTs using ordinary CVD production optimization. Here, instead, the SWNT synthesis strategies have tried to utilize the difference in energy between the ends of tubes with different chirality. In order to properly investigate the well established difference between binding energies at armchair and zigzag ends, we have removed each and every H atom individually at the ends of the SWNTs of the 12- and 13-series, and compared to when all H-atoms are removed collectively, and we have calculated the binding energy and average binding energy for these two different types of dissociation energies (see Figures 1 and 2). The dissociation energies were calculated by the following formula:

$$E_{DE} = E_{SWNT-H} + E_{1/2H_2} - E_{SWNT}, \quad (1)$$

where E_{SWNT} is the total energy of the SWNT passivated by H, E_{SWNT-H} is the total energy of the SWNT with one H

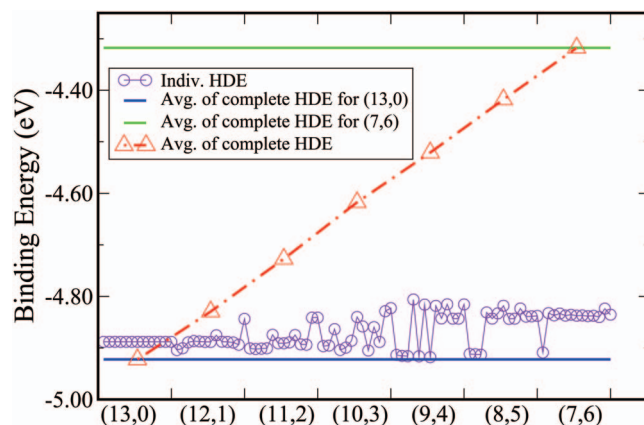


FIG. 2. Individual hydrogen dissociation energies (HDE) and average of complete hydrogen dissociation energies of six-layered fragments of the 13-series.

removed, and $E_{1/2H_2}$ is half the total energy of a hydrogen molecule. Such individual hydrogen dissociation energy was computed for each of the 12 (13) hydrogen atoms at the edge of the tubes in the 12-series (13-series). In addition, we have for each tube computed the average of the complete hydrogen dissociation energy:

$$E_{DE} = (E_{SWNT-mH} + mE_{1/2H_2} - E_{SWNT})/m \quad (2)$$

with $m = 12$ or 13 for the 12-series and 13-series, respectively. $E_{SWNT-mH}$ is the total energy of these SWNTs with m hydrogen atoms removed from one end.

III. RESULTS AND DISCUSSION

Figure 1 shows the results of H dissociation for the 12-series. First, let us examine the dissociation energies when removing all H atoms at one end. The average H–C binding energies calculated through complete H dissociation shows a clear trend and goes up linearly from the most armchair-like tube to the most zigzag-like tube. The average H dissociation energy is 4.26 eV for the (6, 6) armchair tube, while it increases up to 4.92 eV for the (12, 0) zigzag tube. This amounts to a 7.89 eV difference in total energy between zigzag and armchair tubes with one bare end, which is a huge difference in terms of the narrow energy window (0.45 eV) of the passivated 12-series. Such huge and apparent difference in energy lures one to conclude that it would in a straightforward way be possible to use this to achieve chiral selective growth of SWNTs.

However, we are forced to reconsider and to partly give up that idea when we check the H–C binding energies calculated from individual H dissociation energies. As is shown in Figure 1, the individual H dissociation energies are almost the same for the zigzag and armchair tubes, while it oscillates slightly within an energy window of 0.17 eV for the other tubes in the series due to the structural differences. In comparison to the huge difference in the average of complete H dissociation energies, it is easy to conclude there is no pronounced difference in the individual H dissociation energies between tubes of different chirality. The fragment stabilization effect for armchair ends is due to neighbouring dangling bonds pairing-up to form $C\equiv C$ triple bonds that constitute a considerable stabilization effect, which is not possible for the isolated dangling bonds at zigzag ends positioned at next-neighbour carbons. The average of the complete H dissociation is directly affected by how many $C\equiv C$ triple bonds that form on the bare ends (equals m) and how many carbon dangling bonds (radicals) are left (equals $(n-m)$),³⁶ which is clearly seen by the steady decrease in this value from left to right in Figure 1. This fragment stabilization effect caused by the formation of $C\equiv C$ triple bonds is not present in the individual H dissociation energies, which gives a measure of the true H–C binding energies.

The C–C bond lengths are very similar regardless of the tube chirality, and they are hardly affected by removing individual H atoms, leading to similar dissociation energy for all tubes. When removing all H atoms at one end, the C–C bond lengths at the bare end of (12, 0) zigzag tube are 1.39 Å, which is slightly different from 1.41 Å at the other end. While

the lengths of the edge C–C bonds at the bare end of the (6, 6) armchair tube are 1.25 Å, which are significantly decreased from 1.42 Å at the hydrogen terminated end, and apparently in the $C\equiv C$ triple bond length range. The stabilization effect radically decreases the bond length between the adjacent edge carbon atoms and lowers the total energy of the bare-ended tube.

The results for the 12-series compare well with our earlier calculation of individual H-dissociation for the (5,5) and (10,0) tubes in Ref. 36, and are in fact universal as it applies also to the 13-series: As can be seen in Figure 2, the average of the complete H dissociation energy for the different tubes displays the same trend as for the 12-series from the most zigzag-like tube to the most armchair-like tube. The average H dissociation energy is 4.32 eV in the most armchair-like (7, 6) tube, and it increases up to 4.92 eV in the (13, 0) zigzag tube. The difference of the total energies of the completely dissociated tube is as much as that of 12-series. However, the dispersion of the individual dissociation energy is within only 0.12 eV for the 13-series, which is even smaller than for the 12-series. The marked difference in the 13-series between the collective H dissociation energies and the individual H dissociation energies is as significant as in the 12-series. The C–C bonds lengths at the bare end of (7, 6) armchair tube are 1.24 Å, and thus the $C\equiv C$ triple bonds also form in the 13-series causing the same fragment stabilization energies.

We have found that there are very small differences between the individual H–C binding energies of different chiralities, including for armchair and zigzag ends. This means that there are small differences also in individual C–C binding energies and M–C binding energies between zigzag and armchair tubes. Since the difference in binding energy between armchair and zigzag ends also in these cases is due to the same fragment stabilization effect that is only manifested when all (or several neighbouring) bonds are broken. In this study, we use H–C dissociation energies to probe the bond strengths at the edge of different SWNTs. Another reliable measure of bond strength is the bond lengths,^{46,47} which can be used to substantiate the difference in C–C and M–C binding energies between different chiralities. Naturally, all the H–C bonds in the 12- and 13-series are almost equivalent between 1.090 Å and 1.093 Å. For the C–C bond lengths we find the central bonds in the tubes in the 12-series and 13-series the largest differences are 0.004 Å for the shorter C–C bond (1.422–1.426 Å), and 0.009 Å for the slightly longer C–C bond (1.428–1.437). In Ref. 23, the bond lengths are reported to be similar between M_{55} clusters bound to the (5,5) and (10,0). We report here small intrinsic differences in H–C and C–C bond strengths in SWNTs of different chiralities. It should be clear that this means that the individual M–C binding energy differences between armchair and zigzag edges are not substantial due to differences arising from the tubes, even though differences in average M–C binding energies from complete dissociation are reported to be large,^{23,29–36} which are due to the triple-bond fragment stabilization. However, there are differences between individual M–C bond strengths for different chirality tubes on a smaller scale that serve as the physics behind the great achievements already obtained towards index selective growth, e.g., because of differences in

strain due to the metals atomic size/lattice constant. In terms of growth of CNTs, bonds between the tube end and the catalytic metal will normally be created or broken sequentially, not collectively. Thus, we conclude that the difference between armchair and zigzag ends can only be used in a limited way to discriminate growth of one type over another to achieve chiral selective growth. That is, the energy differences due to chirality we report (ca. 20 meV) are too small at growth temperatures (above 600 °C) to be used to reach the ultimate goal of only producing SWNTs of one index.

The conclusion also applies for graphene. The binding energy of an armchair edge of graphene is found to be smaller by 1 eV per edge atom than that of a zigzag edge.⁴⁸ The edge C–C bonds lengths at the armchair edge of graphene are 1.23 Å,⁴⁸ which is equivalent to the C≡C triple bonds in the bare armchair-like tubes ends found in this study. The difference in binding energies between graphene armchair and zigzag edges are thus also only a collective effect caused by fragment stabilization when several neighbouring bonds are broken, which does not persist for individual binding energies. In many cases, the edges of graphene nanoribbons do not prefer armchair termination, but generally has a combination of armchair and zigzag terminations.^{49–51} However, different substrates and possibly different growth mechanisms can be used to achieve growth of only armchair⁵² or only zigzag edges.⁵³ It remains to be seen how this is connected to the small difference in binding energy of armchair and zigzag edges or stability of the formed graphene flake. It should be noted that the interaction between the metal and the carbon nanostructure is different for graphene and CNT growth: For CNT growth the interaction with the metal is mainly in the xy-direction of the carbon structure, while for graphene growth the interaction with the metal is mostly in the z-direction of the sheet/flake.

In view of these results, new strategies are needed to achieve chiral selective growth of SWNTs. It seems there are very little prospect of further success in tuning the catalytic-CVD parameters to reach beyond the present state-of-the-art of narrow SWNT distributions, since this approach relies on thermodynamic differences between products and production steps that does not exist, or are very small. Our suggestion is to realize chiral selective growth of SWNTs through seeding with cap, ring, or belt shaped molecules, chemical synthesis of such molecules could be found in Ref. 54, in a manner similar to the re-growth of SWNTs from cut nanotube fragments,^{55–58} as has been demonstrated recently.⁵⁹ Another plausible strategy would be to try to favor armchair tube production by adding C₂-fragments rather than individual C atoms one-by-one, which recent molecular dynamics simulations indicate to be a possibility.⁶⁰ To achieve C₂-fragment addition at the growing tube edge one could try to use a C₂-fragment containing feed-stock gas combined with parameter optimization of the temperature, pressure, and M–C binding energy (choice of catalytic metal). If these C₂-fragments would survive without decomposition and be added to the tube end the triple-bond stabilization for neighboring carbon atoms at an armchair edge would favor their production.

In conclusion, the differences of binding strengths between carbon nanotubes (CNTs) of different chirality have

been investigated using hydrogen dissociation energies at the passivated tube ends. The well-known difference; that armchair bonds are much weaker than zigzag ones were reproduced when all H atoms are removed collectively, which is typically seen for both CNTs and graphene edges. However, there is almost no difference in hydrogen dissociation energies when individual H atoms are removed, which by association means no difference in individual C–C and M–C binding energies: Since C–C and M–C binding energies in the literature are computed from complete dissociation (average of multiple bonds broken) they are subject to the kind of fragment stabilization effects investigated in this study. The fragment stabilization effect seen for collective bond breaking at armchair ends/edges are due to neighboring dangling bonds pairing-up to form C≡C triple bonds and thus lower the total energy of the system leading to pronounced lower binding energies. This convincingly explains that the difference in binding energy between armchair and zigzag ends is due to the fragment stabilization effect that is only manifested when all (or several neighbouring) bonds are broken. Therefore, the difference between armchair and zigzag ends/edges cannot be used to discriminate growth of one type over another to achieve chiral selective growth through processes where bonds will be created/broken sequentially not collectively, e.g., in traditional catalytic growth. Based on our findings we suggest chiral selective growth via molecular templates/seeding, or growth through addition of C₂-fragments instead of C atoms one-by-one favoring armchair tubes.

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¹S. Iijima, *Nature (London)* **354**, 56 (1991).

²J. W. Mintmire, B. I. Dunlap, and C. T. White, *Phys. Rev. Lett.* **68**, 631 (1992).

³D. Bethune, C. Klang, M. De Vries, G. Gorman, R. Savoy, J. Vazquez, and R. Beyers, *Nature (London)* **363**, 605 (1993).

⁴M.-F. Yu, O. Lourie, M. J. Dyer, K. Moloni, T. F. Kelly, and R. S. Ruoff, *Science* **287**, 637 (2000).

⁵M. Locascio, B. Peng, P. Zapol, Y. Zhu, S. Li, T. Belytschko, and H. Espinosa, *Exp. Mech.* **49**, 169 (2009).

⁶S. Hong and S. Myung, *Nat. Nanotech.* **2**, 207 (2007).

⁷Z. Tang, L. Zhang, N. Wang, X. Zhang, G. Wen, G. Li, J. Wang, C. Chan, and P. Sheng, *Science* **292**, 2462 (2001).

⁸K. Mizuno, J. Ishii, H. Kishida, Y. Hayamizu, S. Yasuda, D. N. Futaba, M. Yumura, and K. Hata, *Proc. Natl. Acad. Sci. U.S.A.* **106**, 6044 (2009).

⁹M. A. Mohamed, N. Inami, E. Shikoh, Y. Yamamoto, H. Hori, and A. Fujiwara, *Sci. Tech. Adv. Mater.* **9**, 025019 (2008).

¹⁰L. P. Zanello, B. Zhao, H. Hu, and R. C. Haddon, *Nano Lett.* **6**, 562 (2006).

¹¹H. W. C. Postma, T. Teepen, Z. Yao, M. Grifoni, and C. Dekker, *Science* **293**, 76 (2001).

¹²T. Yildirim, O. Gülseren, C. Kılıç, and S. Ciraci, *Phys. Rev. B* **62**, 12648 (2000).

¹³M. Zhang, S. Fang, A. A. Zakhidov, S. B. Lee, A. E. Aliev, C. D. Williams, K. R. Atkinson, and R. H. Baughman, *Science* **309**, 1215 (2005).

¹⁴P. G. Collins, M. S. Arnold, and P. Avouris, *Science* **292**, 706 (2001).

¹⁵J.-C. Charlier, X. Blase, and S. Roche, *Rev. Mod. Phys.* **79**, 677 (2007).

- ¹⁶R. Rao, D. Liptak, T. Cherukuri, B. I. Yakobson, and B. Maruyama, *Nat. Mater.* **11**, 213 (2012).
- ¹⁷H. Zhu, K. Suenaga, J. Wei, K. Wang, and D. Wu, *J. Cryst. Growth* **310**, 5473 (2008).
- ¹⁸Y. Yao, C. Feng, J. Zhang, and Z. Liu, *Nano Lett.* **9**, 1673 (2009).
- ¹⁹H. R. Barzegar, F. Nitze, T. Sharifi, M. Ramstedt, C. W. Tai, A. Malolepszy, L. Stobinski, and T. Wågberg, *J. Phys. Chem. C* **116**, 12232 (2012).
- ²⁰R. Wagner and W. Ellis, *Appl. Phys. Lett.* **4**, 89 (1964).
- ²¹R. Baker, M. Barber, P. Harris, F. Feates, and R. Waite, *J. Catal.* **26**, 51 (1972).
- ²²J. Rodríguez-Manzo, M. Terrones, H. Terrones, H. Kroto, L. Sun, and F. Banhart, *Nat. Nanotech.* **2**, 307 (2007).
- ²³F. Ding, P. Larsson, J. A. Larsson, R. Ahuja, H. Duan, A. Rosén, and K. Bolton, *Nano Lett.* **8**, 463 (2008).
- ²⁴J. P. O'Byrne, Z. Li, J. M. Tobin, J. A. Larsson, P. Larsson, R. Ahuja, and J. D. Holmes, *J. Phys. Chem. C* **114**, 8115 (2010).
- ²⁵Z. Li, J. A. Larsson, P. Larsson, R. Ahuja, J. M. Tobin, J. O'Byrne, M. A. Morris, G. Attard, and J. D. Holmes, *J. Phys. Chem. C* **112**, 12201 (2008).
- ²⁶N. S. Kim, Y. T. Lee, J. Park, J. B. Han, Y. S. Choi, S. Y. Choi, J. Choo, and G. H. Lee, *J. Phys. Chem. B* **107**, 9249 (2003).
- ²⁷S. Huang, X. Cai, C. Du, and J. Liu, *J. Phys. Chem. B* **107**, 13251 (2003).
- ²⁸J. Robertson, *J. Mater. Chem.* **22**, 19858 (2012).
- ²⁹F. Ding, A. R. Harutyunyan, and B. I. Yakobson, *Proc. Natl. Acad. Sci. U.S.A.* **106**, 2506 (2009).
- ³⁰H. Dumlich and S. Reich, *Phys. Rev. B* **82**, 085421 (2010).
- ³¹J.-C. Charlier and S. Iijima, in *Carbon Nanotubes*, Topics in Applied Physics Vol. 80, edited by M. Dresselhaus, G. Dresselhaus, and P. Avouris (Springer Berlin, Heidelberg, 2001), pp. 55–81.
- ³²P. Larsson, J. A. Larsson, R. Ahuja, F. Ding, B. I. Yakobson, H. Duan, A. Rosén, and K. Bolton, *Phys. Rev. B* **75**, 115419 (2007).
- ³³Y. Liu, A. Dobrinsky, and B. I. Yakobson, *Phys. Rev. Lett.* **105**, 235502 (2010).
- ³⁴A. Borjesson and K. Bolton, *J. Phys. Chem. C* **115**, 24454 (2011).
- ³⁵S. Reich, L. Li, and J. Robertson, *Chem. Phys. Lett.* **421**, 469 (2006).
- ³⁶J. Baran, W. Kołodziejczyk, P. Larsson, R. Ahuja, and J. A. Larsson, *Theor. Chem. Acc.* **131**, 1270 (2012).
- ³⁷P. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- ³⁸G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- ³⁹G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- ⁴⁰G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996).
- ⁴¹G. Kresse and J. Hafner, *Phys. Rev. B* **48**, 13115 (1993).
- ⁴²J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ⁴³O. Hod and G. E. Scuseria, *Nano Lett.* **9**, 2619 (2009).
- ⁴⁴O. Hod, J. E. Peralta, and G. E. Scuseria, *Phys. Rev. B* **76**, 233401 (2007).
- ⁴⁵A. Rochefort, D. R. Salahub, and P. Avouris, *J. Phys. Chem. B* **103**, 641 (1999).
- ⁴⁶J. A. Larsson and D. Cremer, *J. Mol. Struct.* **485**, 385 (1999).
- ⁴⁷D. Cremer, A. Wu, J. A. Larsson, and E. Kraka, *Mol. Model. Ann.* **6**, 396 (2000).
- ⁴⁸S. Okada, *Phys. Rev. B* **77**, 041408 (2008).
- ⁴⁹C. Casiraghi, A. Hartschuh, H. Qian, S. Piscanec, C. Georgi, A. Fasoli, K. Novoselov, D. Basko, and A. Ferrari, *Nano Lett.* **9**, 1433 (2009).
- ⁵⁰F. Schedin, E. Lidorikis, A. Lombardo, V. G. Kravets, A. K. Geim, A. N. Grigorenko, K. S. Novoselov, and A. C. Ferrari, *ACS Nano* **4**, 5617 (2010).
- ⁵¹M. Ridene, J. Girard, L. Travers, C. David, and A. Ouerghi, *Surf. Sci.* **606**, 1289 (2012).
- ⁵²G. M. Rutter, N. P. Guisinger, J. N. Crain, P. N. First, and J. A. Stroscio, *Phys. Rev. B* **81**, 245408 (2010).
- ⁵³Q. Yu, L. A. Jauregui, W. Wu, R. Colby, J. Tian, Z. Su, H. Cao, Z. Liu, D. Pandey, and D. Wei, *Nat. Mater.* **10**, 443 (2011).
- ⁵⁴T. Kawase and H. Kurata, *Chem. Rev.* **106**, 5250 (2006).
- ⁵⁵Y. Wang, M. J. Kim, H. Shan, C. Kittrell, H. Fan, L. M. Ericson, W.-F. Hwang, S. Arepalli, R. H. Hauge, and R. E. Smalley, *Nano Lett.* **5**, 997 (2005).
- ⁵⁶R. E. Smalley, Y. Li, V. C. Moore, B. K. Price, R. Colorado, H. K. Schmidt, R. H. Hauge, A. R. Barron, and J. M. Tour, *J. Am. Chem. Soc.* **128**, 15824 (2006).
- ⁵⁷T. Iwasaki, J. Robertson, and H. Kawarada, *Nano Lett.* **8**, 886 (2008).
- ⁵⁸J. Liu, C. Wang, X. Tu, B. Liu, L. Chen, M. Zheng, and C. Zhou, *Nat. Commun.* **3**, 1199 (2012).
- ⁵⁹H. Omachi, T. Nakayama, E. Takahashi, Y. Segawa, and K. Itami, *Nat. Chem.* **5**, 527 (2013).
- ⁶⁰D. A. Gómez-Gualdrón, J. M. Beetege, J. C. Burgos, and P. B. Balbuena, *J. Phys. Chem. C* **117**, 10397–10409 (2013).