Half metallicity along the edge of zigzag boron nitride nanoribbons

Fawei Zheng,[1] Gang Zhou,[1] Zhirong Liu,[2] Jian Wu,[1] Wenhui Duan,[1,*] Bing-Lin Gu,[1] and S. B. Zhang[3]
[1]*Department of Physics and Center for Advanced Study, Tsinghua University, Beijing 100084, People's Republic of China*
[2]*College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China*
[3]*Department of Physics, Applied Physics, and Astronomy, Rensselaer Polytechnic Institute, Troy, New York 12180, USA*
(Received 5 May 2008; revised manuscript received 21 October 2008; published 11 November 2008)

First-principles calculations within the local spin-density approximation reveal half metallicity in zigzag boron nitride nanoribbons (ZBNNRs). When the B edge, but not the N edge, of the ZBNNR is passivated, despite being a pure *sp*-electron system, the ribbon shows a giant spin splitting. The electrons at the Fermi level are 100% spin polarized with a half-metal gap of 0.38 eV and its conductivity is dominated by metallic single-spin states. The two states crossing at the Dirac point have different molecular origins, which signal a switch of carrier velocity. The ZBNNR should be a good potential candidate for wide gap spintronics.

DOI: 10.1103/PhysRevB.78.205415 PACS number(s): 73.21.Hb, 71.15.Mb, 73.22.−f

I. INTRODUCTION

Half metallicity is at the forefront of spintronics study.[1–3] Half metallicity occurs when one of the electron spins shows insulating behavior while the other shows metallic behavior.[4] If one drives a current through such a half-metallic system, the current will be 100% spin polarized. Obviously, 100% spin polarization could have many potential spin-related applications.[1,2] For sometime now, it is understood that transition metal (TM)-containing systems such as ferromagnetic manganese perovskite will show half metallicity.[5,6] The TM systems, however, may not be compatible with many of the matured technologies today that rely heavily on main group semiconductors. Heavy TM elements also often act as poison agents in biological systems. Thus, it is highly desirable to develop non-TM half-metallic materials, especially if the half metallicity can be a by-product of the existing electronic materials. To this end, it is quite encouraging to see that the nanoscale zigzag graphene ribbons would show half metallicity under a high in-plane homogeneous electric field,[7] as graphene ribbons could be an ideal conducting material for future nanoelectronic applications.[8] However, an intrinsic half metallicity without any external constraints is yet to be demonstrated and is more desirable in many practical applications.

In search for an intrinsic half metallicity in main group semiconductors, we note that boron nitride (BN) nanoribbons may hold high promises. Boron nitride nanotubes (BNNTs), hexagonal *h*-BN, and boron nitride nanoribbons (BNNRs) are the III-V analogs of the widely studied carbon nanotubes, graphite, and graphene nanoribbons (GNRs). Different from their carbon counterparts, however, the BNNTs have a nearly constant band gap that is independent of radius and chirality.[9] The *h*-BN is, on the other hand, a wide gap semiconductor. Single layer *h*-BN has been successfully fabricated on the surfaces of metals.[10] The BNNRs are expected to be produced, straightforwardly, by using a single layer *h*-BN as the starting material but should have very different physical properties from those of *h*-BN due to quantum size and symmetry effects and, as will be shown below, due to unexpected edge effects. More importantly, the properties of the BNNRs may also be qualitatively different from those of the GNRs because of the relatively large ionicity and significantly larger band gap of the *h*-BN.

In this paper, we predict the intrinsic half metallicity in BNNRs with zigzag edges [zigzag boron nitride nanoribbons (ZBNNRs)] by first-principles calculations within the local spin-density approximation. The half-metal energy gap for ribbons with passivated boron edge is as high as 0.38 eV (about 15 times larger than $k_B T$ at $T = 300$ K). This does not require any applied external electric field, in contrast to the graphene ribbons. Our analysis reveals that the half metallicity is originated from an interesting interplay between the nitrogen edge dangling-bond state and the occupied nitrogen lone-pair state, which is absent in the graphene systems. The crossing between the two states defines the Fermi level and, hence, the degree of half metallicity. The intrinsically different molecular-orbital origins of the two states further suggest a switch of the carrier velocity across the Dirac point that is waiting for an experimental verification. The integration of half metallicity (at the ribbon edge) with a wide gap semiconductivity (of the ribbon backbone) also opens new application potentials whose full extent is yet to be explored.

II. METHOD AND MODELS

The ZBNNRs we considered are schematically illustrated in Fig. 1, which are hexagonally bonded honeycomb ribbons consisting of B and N atoms with zigzag terminated edges under various passivations. In accordance with the previous convention,[11] here, the ZBNNRs are labeled by the number of parallel zigzag chains, which defines the width of the ribbon. The ZBNNR with *n* B-N chains is, thus, named as *n*-ZBNNR. For ZBNNRs, the outmost atoms at one edge (namely, the B edge) are all B atoms, whereas the outmost atoms at the other edge (namely, the N edge) are all N atoms. In terms of hydrogen passivation of the edges, the ZBNNRs are further divided into four subgroups [Figs. 1(a)–1(d)]: (1) both edges are passivated (ZBNNR-2H), (2) only the B edge is passivated (ZBNNR-HB), (3) only the N edge is passivated (ZBNNR-HN), and (4) no edge is passivated (pristine ZBNNR).

Our calculations were performed by using the density-functional theory[12] within the local spin-density approxima-

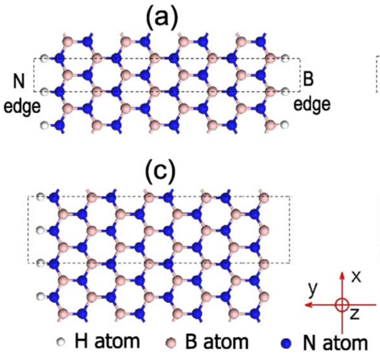

FIG. 1. (Color online) Atomic geometries of the relaxed ZBNNRs with different edge treatments: (a) 8-ZBNNR-2H, (b) 8-ZBNNR-HB, (c) 8-ZBNNR-HN, and (d) pristine 8-ZBNNR, where the number 8 stands for the width of the ribbon, and the suffixes HB and HN stand for the hydrogen termination of the boron and nitrogen edges, respectively. The ribbons are infinitely long along the x direction. The dashed rectangles denote the unit cell of the systems.

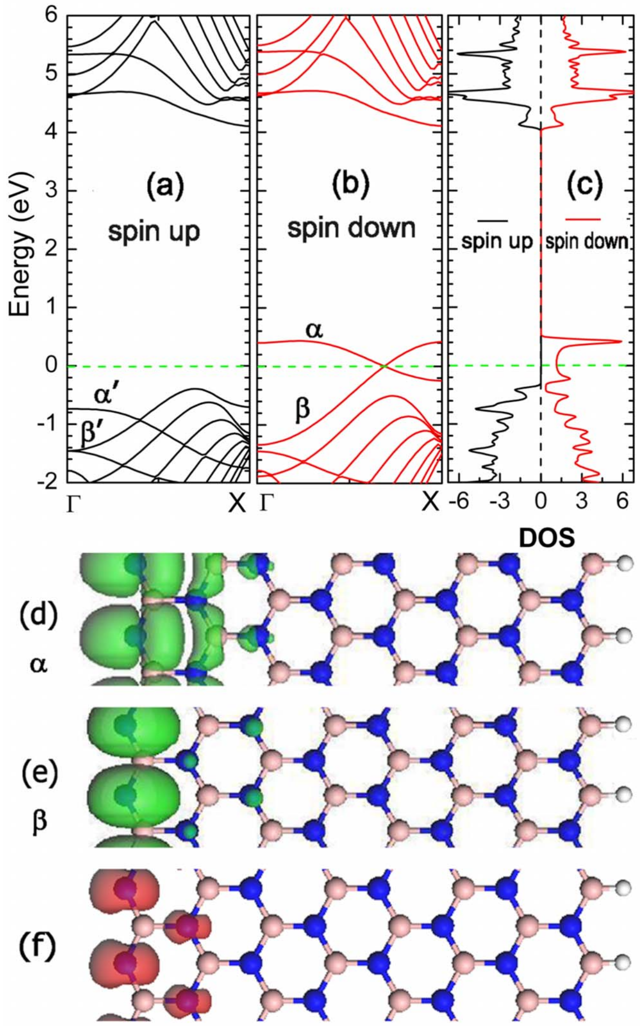

FIG. 2. (Color online) Half metallic and ferromagnetic behaviors of 8-ZBNNR-HB. (a) Spin-up and (b) spin-down energy bands, and (c) the total DOS. Here, the energy zero (i.e., the dot-dashed line) is at the Fermi level. Γ and X denote the center and the boundary of the first Brillouin zone. [(d)–(e)] Partial charge density of the α and β bands at the X point, respectively. The isosurface is $0.003e/\text{Å}^3$. (f) Spatial distribution of the spin difference: red for spin-up and yellow for spin down. The isosurface is $0.03\mu_B/\text{Å}^3$. Due to the small amplitude of the spin-down states, they are not visible from the plot.

tion. In particular, we used the Vanderbilt plane-wave ultrasoft pseudopotential[13] with a 450 eV cutoff energy and the Ceperly-Alder exchange-correlation potential.[14] We adopted a supercell geometry for isolated BNNR sheet in which each two adjacent sheets are separated by at least 11 Å. For n-ZBNNRs, the supercell contains n [Figs. 1(a) and 1(b)] or $2n$ [Figs. 1(c) and 1(d)] B-N chains depending on whether the system is antiferromagnetic. Integration over the one-dimensional Brillouin zone (Γ-X) has been carried out by using 51 and 31 Monkhorst-Pack k points, respectively,[15] with the equivalent k-point scheme. Full optimization of the atomic structures including the atomic positions and lattice parameters has been carried out until the residual forces on atoms are less than 0.01 eV/Å. We have also increased the size of the supercell to make sure that it does not produce any discernible difference on the results.

III. RESULTS AND DISCUSSION

The electronic and magnetic properties of the BN nanoribbons depend critically on how the edges are passivated. Half metallicity is observed when and only when the boron edge is passivated [Fig. 1(b)]. The band structures of the 8-ZBNNR-HB are depicted in Figs. 2(a) and 2(b), which show the marked differences in the spin states; the spin-down electrons are metallic with two bands (α and β) crossing each other at the Fermi level while the spin-up ones are insulating due to the existence of a band gap as large as 4.5 eV. Thus, the charge transport is totally dominated by the spin-down electrons [see the density of states (DOS) in Fig. 2(c)] and the current flow in such a system should be completely spin polarized. The half-metal gap, defined as the difference between the Fermi level and topmost occupied spin-up band, is 0.38 eV. This value is comparable to that of half-metallic graphene nanoribbon under high electric field[7] and is large enough for room-temperature operation. In Figs. 2(d) and 2(e), we plot the partial charge density of the α and β bands (at the characteristic X point). One can see that the α and β bands are almost entirely localized on the N edge. All the ZBNNRs-HB, regardless of their width, have a similar band structure.

In order to understand the band crossing responsible for the half metallicity of ZBNNRs-HB, we have studied how passivation at the N edge affects the electronic structure. With H passivation, the α band shifts down considerably to reside inside the valence band, while the β band is very much unchanged and is, hence, still above the top of the valence band. The projected density of states of the two bands shows that the α band is predominantly composed of the nitrogen p_y and s atomic orbitals, while the β band is composed almost completely of the nitrogen p_z atomic orbitals. In other words, the α band is a dangling-bond state at the N edge and is, hence, strongly affected by the passivation. In

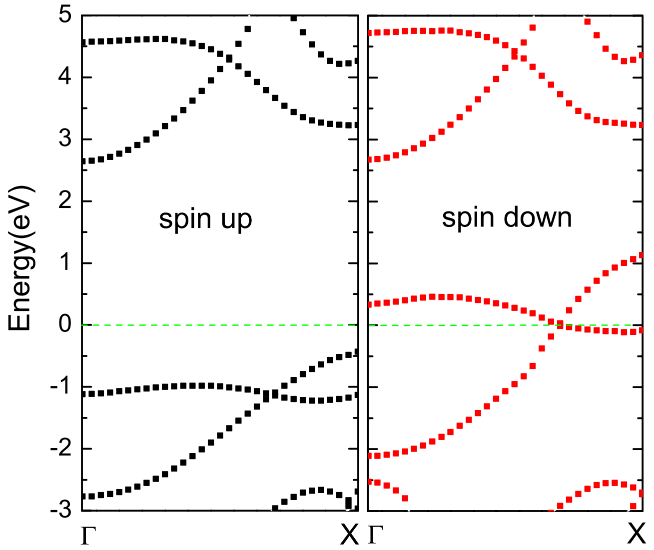

FIG. 3. (Color online) *GW* quasiparticle band structure for 3-ZBNNR-HB. Energy zero is at the Fermi level.

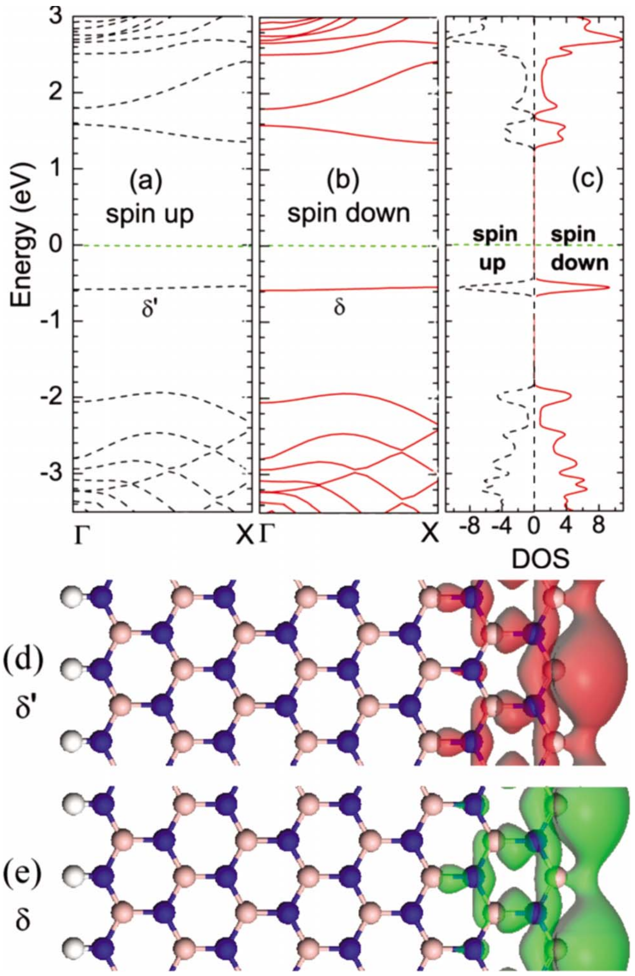

FIG. 4. (Color online) Electronic properties of 8-ZBNNR-HN. [(a)–(c)] Energy band structure. The δ' and δ bands are the highest valence bands. Energy zero is at the nominal Fermi-level position (i.e., the dash-dotted line). [(d)–(e)] Partial charge densities of the δ' and δ bands at the Γ point. The isosurface is $0.03e/\text{Å}^3$.

contrast, the β band is the usual lone-pair state of a threefold coordinated nitrogen and is by in large unaffected by the passivation. The wave functions of the α and β bands have different symmetries: being symmetric and antisymmetric with respect to the basal plane of the BN sheet. These explain why the α and β bands in Fig. 2(b) cross each other without having to create a band gap. However, if we bend the BN sheet or apply an electric field along the z direction to break such a mirror symmetry, the α band will mix with the β band but the total energy of the system also increases. For example, when the 8-ZBNNR-HB ribbon is bent to 90° around the x axis, the total energy increases by 0.2 eV per unit cell. We have checked the spin-up α' and β' bands below the Fermi level to find that they too have the same atomic characters of the spin-down α and β bands.

An essential factor underlying the observed half metallicity is the splitting of the spin states. In fact, Fig. 2(f) shows that the ground state of the ZBNNRs-HB is *ferromagnetic* with a magnetic moment of μ_B per edge N atom. The calculated magnetic interaction is quite large: for instance, the ferromagnetic phase is 0.10 eV per edge N atom more stable than the antiferromagnetic phase, and is also 0.17 eV per edge N atom more stable than the nonmagnetic phase. Importantly, these energy differences are independent of the ribbon width n when $n \geq 5$. A relatively large distance (2.49 Å) between any two adjacent edge N atoms implies that no edge reconstruction has taken place, and there is thus one dangling bond per edge N atom. From such an analysis, we conclude that magnetism is a result of the exchange interaction between the dangling-bond electrons. Similar magnetic ordering in a dangling-bond network was also observed on partially hydrogenated Si(111) surfaces.[16]

An obvious concern with the above discussion is the local-density approximation (LDA) band-gap error, which, in principle, could change the qualitative band structure near the Fermi level in Fig. 2(b). To address such a concern, we studied the band structure of ZBNNRs with the *GW* approximation[17] by using the ABINIT code.[18] The 3-ZBNNR-HB with the width of three B-N chains, instead of eight, was calculated here due to computation cost of the *GW* method. We used the FHI98PP code[19] to generate the pseudopotentials and the integration over the one-dimensional Brillouin zone was carried out by using 31 Monkhorst-Pack k points. The results (Fig. 3) show that the system remains to be half metallic with band crossing at the Fermi level, despite the significant quasiparticle corrections to the LDA band structure, particularly in the conduction bands. The half-metal gap of 0.46 eV is in fact slightly larger than that of LDA, further strengthening our conclusion.[20]

In recent years, graphene has emerged as a new model system in materials science and condensed-matter physics due to its novel physical properties.[21] For example, graphene is the first material where electron transport was found to be governed by the relativistic Dirac equation; namely, energy dispersion $E(k)$ with respect to wave vector k is linear so that charge carriers mimic the relativistic quasiparticles with zero rest mass (the so-called Dirac fermions) and travel with an effective "speed of light" $v = E/k$ on the order of $\sim 10^6$ m/s.[22] Thus, it is important that our ZBNNRs-HB also exhibits such an unusual massless Dirac-fermion behav-

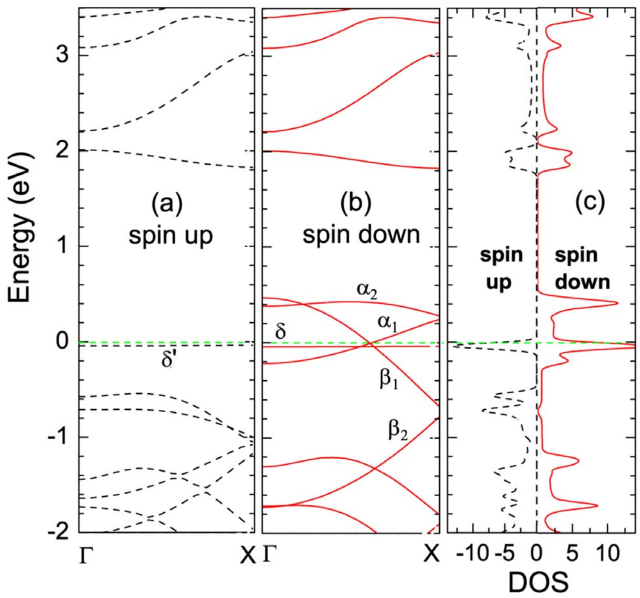

FIG. 5. (Color online) Band structure of the pristine 8-ZBNNR without any edge passivation. (a) Spin up, (b) spin down, and (c) the corresponding DOS for spin-up (black dashed line) and spin-down (red solid line) states. Energy zero is at the Fermi level. Detailed analysis of the partial charge densities reveals that, except for a small spin splitting, the δ (δ') band is very similar to the δ (δ') band in Figs. 4(a) and 4(b). Moreover, the α_1 (α_2) and β_1 (β_2) bands are very similar to the α and β bands in Fig. 2(b).

ior. Due to the intrinsic difference between the α and β bands, however, the two bands at the crossing point will have different slopes, corresponding to different v's. This, combined with the unique one-dimensional characteristics of the edge states, suggests a new physics that cannot exist in the graphene systems with "symmetric" energy dispersion.

When the N edge, and only the N edge, is passivated, the systems, ZBNNRs-HN, behave qualitatively different from ZBNNRs-HB. For example, for 8-ZBNNR-HN, the ground state is antiferromagnetic and is 33 meV/(edge atom) more stable than the ferromagnetic state. The ground-state unit cell is doubled [see Fig. 1(c)] and the band gap is 1.89 eV [see Figs. 4(a)–4(c)]. The calculated partial charge densities for the highest occupied spin-up band (δ') and spin-down band (δ) at the Γ point are shown in Figs. 4(d) and 4(e). They reveal that both states are localized at the bare boron edge. Antiferromagnetism is clearly evidenced by the alternating occupation of the spin-up and spin-down states on alternating neighboring B atoms. Note that the situation here is different from the B-rich mouth of open zigzag BNNTs.[23,24] In the BNNTs, the dimerized paramagnetic state is more stable than the antiferromagnetic state due to a smaller tension at the B-rich mouth. In the current case, however, the antiferromagnetic state is more stable than the dimerized paramagnetic state by 0.14 eV/(edge atom).

For pristine ZBNNRs without the edge passivation, the properties are a combination of ZBNNRs-HB and ZBNNRs-HN; namely, the B edge is antiferromagnetic while the N edge is ferromagnetic. Figure 5 shows the spin-polarized electronic structure of pristine 8-ZBNNR. This system is half metallic but the calculated band gap is negligibly small. Similar results was reported in a recent paper by Barone *et al.*[25] When both edges are passivated, on the other hand, the system [e.g., ZBNNR-2H in Fig. 1(a)] is non-spin-polarized with a large band gap, as revealed by an earlier work of Nakamura *et al.*[26] In total, we can see that the ground states and the energy gaps or half-metal gaps of ZBNNRs are sensitively dependent on the edge passivations, as summarized in Table I.

To experimentally realize half metallicity in ZBNNRs, two key issues must be addressed. (1) The choice of the substrate. Chemical activity of the available substrates is often diverse, which should be utilized to advance our course. For example, if one wishes to minimize the influence of the substrate, an inert substrate should be used as was the case in fabricating single layer *h*-BN.[10] (2) Selective passivation. In the current study, hydrogen has been used as the passivant for its simplicity. The drawback of using H is clear as the selectivity can be rather poor. To optimize the selectivity, one might make good use of the chemical difference between B and N. For example, a more electronegative passivant such as F may be superior for boron passivation to yield the desired half metallicity but may not work at all for nitrogen passivation.

IV. SUMMARY

In summary, first-principles study within the local spin-density approximation reveals half metallicity in ZBNNRs. Specifically, boron edge passivated nanoribbons (ZBNNRs-HBs) is a half metal with a half-metallic gap of 0.38 eV. Non-*d* ferromagnetism and completely spin-polarized current transport may thus be possible. Nitrogen edge passivated nanoribbons (ZBNNR-HNs) are, on the other hand, antiferromagnetic. These unique properties, especially the half metal-

TABLE I. The ground states and the energy gaps or half-metal gaps of 8-ZBNNRs with different kinds of edge passivation.

	8-ZBNNR-2H	8-ZBNNR-HB	8-ZBNNR-HN	8-ZBNNR
Ground state	Semiconductor	Half-metal	Semiconductor	Half-metal
B edge	Nonmagnetic	Nonmagnetic	Antiferromagnetic	Antiferromagnetic
N edge	Nonmagnetic	Ferromagnetic	Nonmagnetic	Ferromagnetic
Energy gap	3.90 eV		1.89 eV	
Half-metal gap		0.38 eV		Negligible

licity, make the BN nanoribbons an attractive candidate for nanoscale wide gap spintronics such as spin-injection electrode, nanomemory elements, and nanotransistors.

ACKNOWLEDGMENTS

S.B.Z. thanks Damien West for the valuable discussions. This work was supported by the National Natural Science Foundation of China (Grants No. 10674077 and No. 10774084) and the Ministry of Science and Technology of China (Grants No. 2006CB605105 and No. 2006CB0L0601). S.B.Z. was supported by the U.S. DOE/BES and EERE under Contract No. DE-AC36-99GO10337.

---

*Author to whom correspondence should be addressed. dwh@phys.tsinghua.edu.cn

[1] G. A. Prinz, Science **282**, 1660 (1998).

[2] S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnar, M. L. Roukes, A. Y. Chtchelkanova, and D. M. Treger, Science **294**, 1488 (2001).

[3] M. Ziese, Rep. Prog. Phys. **65**, 143 (2002).

[4] R. A. de Groot, F. M. Mueller, P. G. van Engen, and K. H. J. Buschow, Phys. Rev. Lett. **50**, 2024 (1983).

[5] J.-H. Park, E. Vescovo, H.-J. Kim, C. Kwon, R. Ramesh, and T. Venkatesan, Nature (London) **392**, 794 (1998).

[6] C. M. Fang, G. A. de Wijs, and R. A. de Groot, J. Appl. Phys. **91**, 8340 (2002).

[7] Y.-W. Son, M. L. Cohen, and S. G. Louie, Nature (London) **444**, 347 (2006).

[8] K. Wakabayashi, Y. Takane, and M. Sigrist, Phys. Rev. Lett. **99**, 036601 (2007).

[9] X. Blase, A. Rubio, S. G. Louie, and M. L. Cohen, Europhys. Lett. **28**, 335 (1994); E. Hernández, C. Goze, P. Bernier, and A. Rubio, Phys. Rev. Lett. **80**, 4502 (1998); Y. Chen, J. Zou, S. J. Campbell, and G. Le Caer, Appl. Phys. Lett. **84**, 2430 (2004); A. P. Suryavanshi, M. Yu, J. Wen, C. Tang, and Y. Bando, *ibid.* **84**, 2527 (2004).

[10] A. Nagashima, N. Tejima, Y. Gamou, T. Kawai, and C. Oshima, Phys. Rev. Lett. **75**, 3918 (1995); M. Corso, T. Greber, and J. Osterwalder, Surf. Sci. **577**, L78 (2005).

[11] K. Nakada, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. B **54**, 17954 (1996); K. Wakabayashi, M. Fujita, H. Ajiki, and M. Sigrist, *ibid.* **59**, 8271 (1999).

[12] Calculations were performed using the Vienna *ab initio* simulation package (VASP). See, G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996), and references therein.

[13] D. Vanderbilt, Phys. Rev. B **41**, R7892 (1990).

[14] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[15] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[16] S. Okada, K. Shiraishi, and A. Oshiyama, Phys. Rev. Lett. **90**, 026803 (2003).

[17] M. S. Hybertsen and S. G. Louie, Phys. Rev. B **34**, 5390 (1986); S. B. Zhang, D. Tomanek, M. L. Cohen, S. G. Louie, and M. S. Hybertsen, *ibid.* **40**, 3162 (1989).

[18] The ABINIT code was developed by the Université Catholique de Louvain, Corning Incorporated and other contributors, http://www.abinit.org

[19] M. Fuchs and M. Scheffler, Comput. Phys. Commun. **119**, 67 (1999).

[20] It should be noted that general gradient approximation (GGA) yields a somewhat different picture here. Our preliminary GGA calculation shows that the N edge spontaneously buckles although the energy lowering of 11 meV/(edge atom) is rather small. This nevertheless causes the opening of an energy gap of 0.39 eV in the down spin and produces an out-of-plane electrical polarization. In DFT calculations, LDA and GGA usually give qualitatively consistent conclusions, but discrepancy does happen in some cases. For example, a DFT study on the stability of bulk BN showed that LDA approach predicts the cubic structure as the ground state while GGA predicts the hexagonal layered structures (Ref. 27). Some works suggested that LDA produces properties slightly closer to experimental values than GGA for BN (Ref. 28). However, to clarify if the predicted half metallicity exists in BNNRs, further experimental works are extremely necessary. Anyway, in consideration of the generality of the mechanism underlying the predicted half metallicity (in fact, half metallicity even exists under the GGA if we constrain all atoms to lie within a plane), we expect it to be also applicable to other similar nanosystems, but not just limited to BNNRs.

[21] A. K. Geim and K. S. Novoselov, Nature Mater. **6**, 183 (2007).

[22] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, and S. V. Dubonos, Nature (London) **438**, 197 (2005).

[23] X. Blase, A. De Vita, J.-C. Charlier, and R. Car, Phys. Rev. Lett. **80**, 1666 (1998).

[24] S. G. Hao, G. Zhou, W. H. Duan, J. Wu, and B. L. Gu, J. Am. Chem. Soc. **128**, 8453 (2006).

[25] V. Barone and J. E. Peralta, Nano Lett. **8**, 2210 (2008).

[26] J. Nakamura, T. Nitta, and A. Natori, Phys. Rev. B **72**, 205429 (2005).

[27] A. Janotti, S. H. Wei, and D. J. Singh, Phys. Rev. B **64**, 174107 (2001).

[28] N. Ooi, V. Rajan, J. Gottlieb, Y. Catherine, and J. B. Adams, Modell. Simul. Mater. Sci. Eng. **14**, 515 (2006); T. E. Mosuang and J. E. Lowther, J. Phys. Chem. Solids **63**, 363 (2002).