

Chemically decorated boron-nitride nanoribbons

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Motivated by recent studies of graphenene nanoribbons (GNRs), we explored electronic properties of pure and chemically modified boron nitride nanoribbons (BNNRs) using the density functional theory method. Pure BNNRs with both edges fully saturated by hydrogen are semiconducting with wide band gaps. Values of the band gap depend on the width and the type of edge. The chemical decoration of BNNRs' edges with four different functional groups, including $-F$, $-Cl$, $-OH$, and $-NO_2$, was investigated. The band-gap modulation by chemical decoration may be exploited for nanoelectronic applications.

Keywords boron–nitride nanoribbons, chemical modification

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Graphene, a single layer of graphite, has attracted considerable research attention recently due to its intriguing physical properties and potential applications in nanoelectronics [1–5]. Both experimental and theoretical studies have shown that, by carving a graphene sheet into one-dimensional nanoribbons, the electronic band gap of the graphene nanoribbon (GNR) opens up and is dependent on its width and crystallographic orientation [6–16]. These findings render graphene-based band-structure engineering conceivable [14–21]. Moreover, theoretical calculations have shown that half-metallicity may be realized in GNR either by applying an external in-plane electric field or by chemically functionalizing zigzag-edges of GNR with different groups such as H, COOH, OH, NO₂, NH₃, CH₃, etc. [23–26]. Half-metallic GNR may find application in spintronics.

Two-dimensional hexagonal boron nitride (h-BN) is structurally similar to graphene, and has been fabricated experimentally [27]. Unlike graphene, the h-BN has a large energy band gap due to strong ionicity of BN. Hence, it is expected that nanoribbons carved out of h-BN also have large band gaps. It has been shown that the band gap of boron nitride nanoribbons (BNNRs) whose zigzag edges are passivated by hydrogen decreases with increasing width, while that of BNNRs with armchair edges oscillate periodically with the width [28–34]. Moreover, recent calculations indicate that electronic properties of BNNRs can be modulated by apply-

ing external transversal electric field, and BNNRs may undergo metallic to semiconducting to half-metallic transition [29–33]. The half-metallicity is also found in BNNRs with only one edge passivated with hydrogen [34]. These findings suggest potential applications of BNNRs in nanoelectronic devices. In this work, we show, through density functional theory (DFT) calculations, that electronic properties of BNNRs can be modulated by chemical decoration at the ribbons' edges. Four chemical functional groups were considered, including $-H$, $-NO_2$, $-F$, and $-Cl$. Our studies suggest that edge decoration is a viable way to tailor electronic properties of BNNRs.

The first-principles calculations were based on the linear combination of atomic orbital DFT method implemented in DMol³ package[†] [35, 36]. The generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) form as well as an all-electron double numerical basis set with polarized function (DNP) were chosen for the spin-unrestricted DFT calculation [37]. The real-space global cutoff radius was set to be 3.70 Å. To simulate chemically modified BNNRs, a tetragonal supercell was selected. BNNRs with either zigzag or armchair edges were considered for pristine models. The nearest distance between two neighboring BNNRs is greater than 30 Å. The k -points sampling was employed using the Monkhorst–Pack scheme with spacing of 0.04 Å⁻¹ [38]. The structures were fully optimized with no constrain, and the forces on atoms were less than

[†]DMol³ is a density functional theory quantum mechanical package available from Accelrys. Delley Software, Inc.

$0.05 \text{ eV} \cdot \text{\AA}^{-1}$ after geometric optimization.

We first computed the electronic properties of pure BNNRs with zigzag and armchair edges, respectively, all passivated with hydrogen atoms, as shown in Figs. 1 and 2. The width of BNNR w is defined as the number of rings along the direction normal to the ribbon axis. For BNNR with zigzag edges, the optimized periodic length of the ribbon is 2.514 \AA . The average B–N bond length is 1.454 \AA for $w = 4$, the same as that within a BN sheet (1.454 \AA with the same level of calculation). The N–H and B–H bond lengths are 1.016 and 1.202 \AA , respectively. The Hirshfeld charge analysis indicates that average charge transfer from B to N is about $0.19 e$ inside the ribbon. At the edges, average charge transfer from H to N is about $0.12 e$, and $-0.052 e$ from H to B. The latter charge is too small to be of qualitative significance. For BNNR with armchair edges, the optimized periodic length along the ribbon direction is 4.382 \AA . The average B–N bond length is 1.452 \AA for $w = 4$, and the N–H and B–H bond lengths are 1.016 and 1.209 \AA , respectively, similar to those in BNNR with zigzag edges. The charge analysis indicates that the charge transfer from B to N is about $0.19 e$ inside the ribbon, about $0.11 e$ from H to N, and $-0.056 e$ from B to H at the edges. Clearly, the edge shape of BNNRs does not affect the structures and

charge transfer behavior inside the BNNR.

In Figs. 1 and 2, electronic band structures and energy band gaps of BNNR with zigzag or armchair edges are presented. Pure BNNRs with zigzag edges are semiconducting with indirect band gaps $> 4.0 \text{ eV}$, so are those with armchair edges but with direct band gaps $> 4.5 \text{ eV}$. Near the Fermi level, profiles of electronic structures depend on BNNR's edge structure, but are independent of their width w . The band gap of BNNRs with zigzag edges decreases monotonically with increasing w , while those with armchair edges oscillates periodically with a period of $w = 1.5$ in width. These results are consistent with previous theoretical studies [28, 29]. It is well known that the DFT–PBE method always underestimate the band gap of semiconductors, but this will not affect the following discussion on tailoring electronic properties of BNNRs through chemical decoration.

Next, chemically modified BNNRs with zigzag edges were studied. The modification was realized by decorating BNNR's edges with functional groups, such as $-\text{Cl}$, $-\text{F}$, $-\text{NO}_2$, and $-\text{OH}$. Here, we chose BNNR with $w = 4$ as the pristine model. Both edges of the BNNR are chemically functionalized with the same or different functional groups. As shown in Fig. 3, " $\text{Cl}_{(N)}\text{-H}_{(B)}$ " denotes that the BNNR is decorated with Cl and H atoms at top (N)

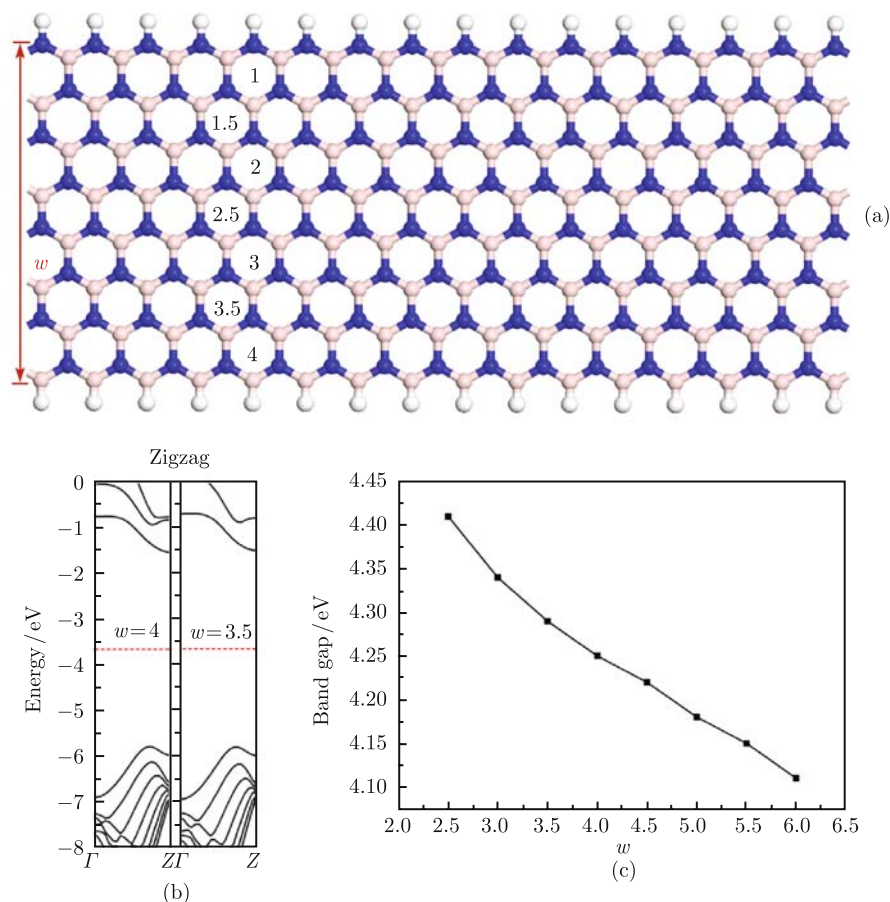


Fig. 1 (a) Optimized structure of BNNR with zigzag edges. The width (w) of BNNR is 4. (b) Calculated band structures of BNNR with $w = 4$ and 3.5. (c) A relationship between band gap and w is plotted. The Fermi level is plotted with a red dotted line. The blue, pink and white balls represent N, B and H atoms, respectively.

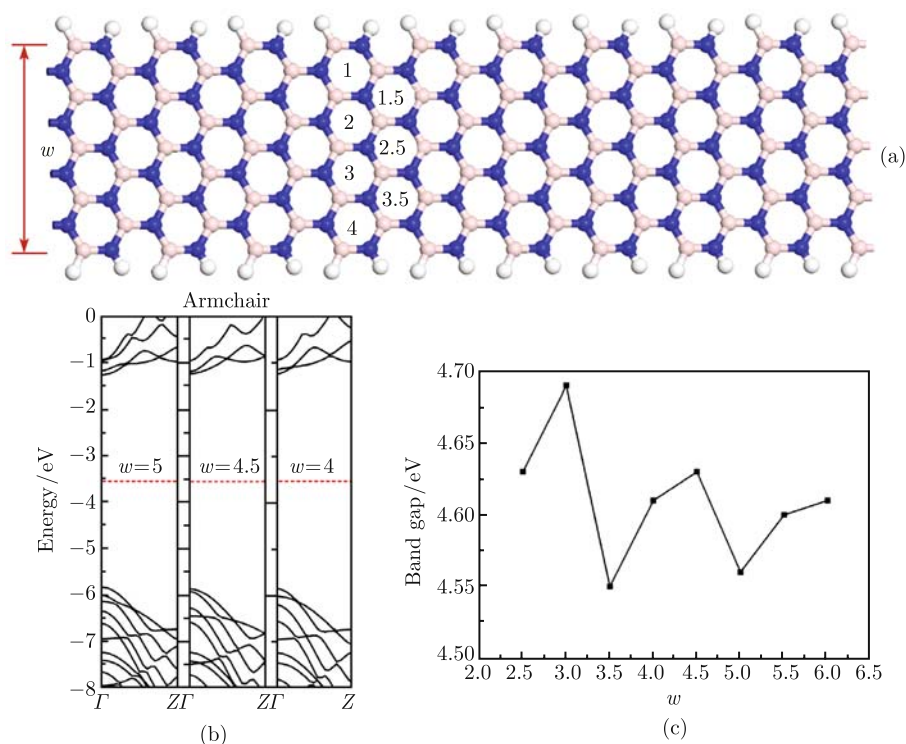


Fig. 2 (a) Optimized structure of BNNR with armchair edges. The width of BNNR is $w=4$. (b) Calculated band structures of BNNRs with $w=4, 4.5$ and 5 . (c) A relationship between band gap and w . The Fermi level is plotted with a red dotted line. The blue, pink and white balls represent N, B and H atoms, respectively.

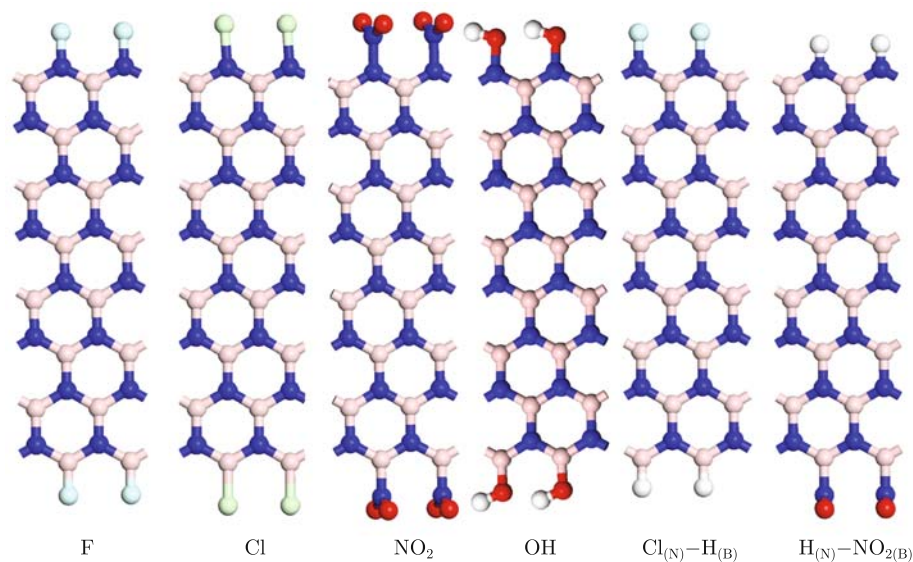


Fig. 3 Optimized structures of BNNRs with chemically modified zigzag edges.

and bottom (B) edge, respectively.

To assess relative stability among these chemically decorated BNNRs, we calculated average adsorption energy for various functional groups to the edges of BNNRs. The average adsorption energy is defined as

$$E = [E_{\text{total}}(\text{BNNR-X}) + nE_{\text{total}}(\text{H}) - E_{\text{total}}(\text{BNNR-H}) - nE_{\text{total}}(\text{X})]/n$$

where $E_{\text{total}}(\text{system})$ is the total energy of the system, and $X = \text{F}, \text{Cl}, \text{NO}_2$, or OH . Average adsorption en-

ergies are summarized in Table 1. Clearly, except OH and F, the replacement reaction of H atom by NO₂ or Cl is endothermic. The B edge of BNNR was more favorable than the N edge for decoration with these functional groups. The most stable configuration is the H_(N)-F_(B), where the B edge of BNNR is saturated with F and the N edge with H. Interestingly, the charge on functional group and corresponding B(N)-X bond length are dependent on the adsorbing sites (B or N edge) and the type of functional groups, as shown in Table 1.

Table 1 Energy band gaps of BNNRs with chemically modified zigzag edges; adsorption energies of chemical functional group at the edge of BNNRs (E in unit of eV/group); and charge analysis results and bond lengths.

	E /(eV/group)	Charge (e)	Gap/eV	Bond length/Å
H	0.00	0.11*, -0.05**	4.25	1.02 ^a , 1.20 ^b
F	-0.696	-0.06, -0.12	4.51	1.40, 1.34
Cl	1.864	0.02, -0.06	0.30	1.73, 1.74
NO ₂	2.783	-0.01, -0.16	1.64	1.50, 1.52
OH	-0.096	-0.08, -0.02	3.86	1.44, 1.39
H _(N/B) -F _(B/N)	-2.81/1.42	0.12, -0.12/-0.06, -0.05	4.56/4.32	1.02, 1.34/1.40, 1.20
H _(N/B) -Cl _(B/N)	0.53/3.20	0.12, -0.06/0.02, -0.05	0.98/0.90	1.02, 1.74/1.73, 1.20
H _(N/B) -NO _{2(B/N)}	1.91/3.56	0.12, -0.16/-0.02, -0.05	1.86/2.21	1.02, 1.52/1.49, 1.20
H _(N/B) -OH _(B/N)	-1.93/1.74	0.11, -0.08/-0.02, -0.05	4.77/3.41	1.02, 1.39/1.44, 1.20
OH _(N/B) -NO _{2(B/N)}	1.84/0.84	-0.01, -0.16/-0.02, -0.08	1.08/2.12	1.44, 1.52/1.49, 1.39

*Charge analysis result for the chemical group connected to the N-edge of BNNR.

**Charge analysis result for the chemical group connected to the B-edge of BNNR.

^a and ^b are lengths of N-X and B-X bond (X= H, F, Cl, NO₂, and OH), respectively.

In Fig. 4, electronic band structures and density of states (DOS) projected onto functional groups are plotted. The chemical decoration of BNNR's edges may alter electronic properties of BNNRs in different fashions. For BNNRs decorated with F and OH, the interaction between functional groups and B or N atoms at the edges

shifts the band states near the Fermi level, resulting in an enlarged (F) or narrowed (OH) energy band gap. For BNNRs decorated with Cl and NO₂, however, the functional groups induce many new states inside the band gap of pure BNNR, resulting in a very narrow band gap. These two distinct changes on the electronic properties of BNNRs offer a chemical way to control the band gap of BNNRs, as demonstrated in Table 1.

We also studied chemically modified BNNRs with armchair edges. In this case, we chose BNNRs with width $w = 6$ as the pristine model. Optimized structures of BNNRs with chemically modified armchair edges are displayed in Fig. 5. Unlike BNNRs with zigzag edges, the fully decorated BNNR with Cl is unstable and Cl atoms tend to escape from the edges spontaneously. A full decoration with OH group will induce a local distortion at the edges. The structural distortion is mainly caused by the short distance between two neighboring decorated sites. However, BNNRs with a 50% edge decoration with Cl or OH groups are very stable without showing any local structural distortion.

In Table 2, adsorption energies of various functional groups to BNNR's edges are summarized. Similar to BNNRs with zigzag edges, B edges are more favorable than N edges for the adsorption. Moreover, the BNNR with B-edge-site decoration (50% decoration) is energetically more stable than pure BNNR, suggesting that the decoration may be realized experimentally.

In Fig. 6, we plotted electronic band structures and DOS of BNNRs with chemically modified armchair edges. The interaction between functional groups and BNNR mainly causes a shift of band states in most cases. An exception is that when only N-edge-site is decorated (50% decoration) with Cl, an unoccupied impurity state is introduced inside the band gap due to the interaction between Cl and the N edge. As listed in Table 2, most BNNRs with chemically modified armchair edges have

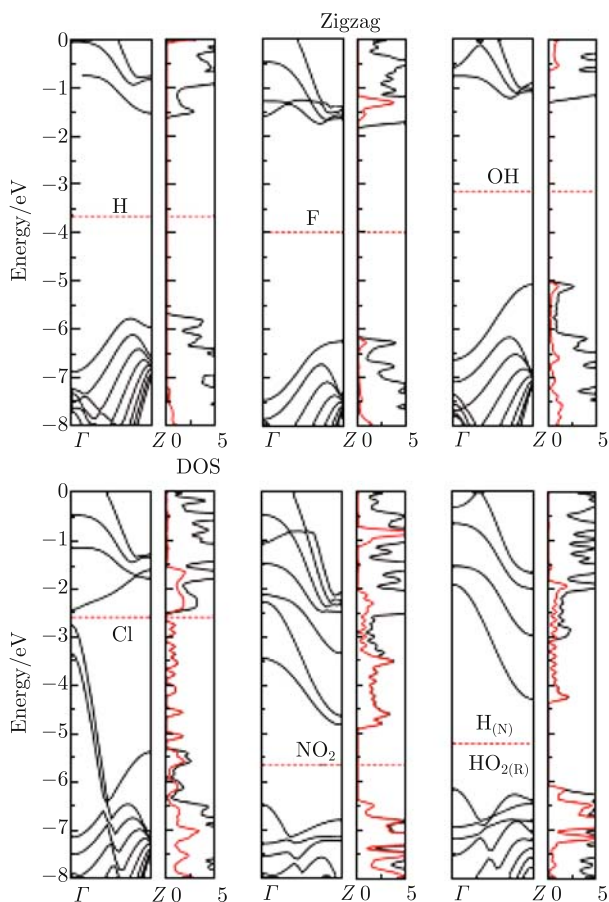


Fig. 4 Electronic band structures and density of states (DOS) of BNNRs with chemically modified zigzag edges. The Fermi level is plotted with a red dashed line. The DOS projected onto functional groups are plotted with red solid lines.

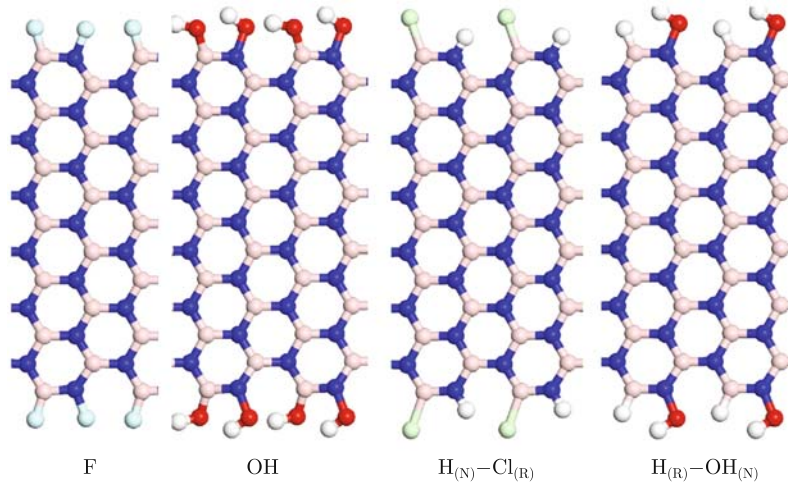


Fig. 5 Optimized structures of BNNRs with chemically modified armchair edges.

Table 2 Energy band gaps of BNNRs with chemically modified armchair edges; the adsorption energies of chemical functional group to BNNR (E in unit of eV/group); and charge analysis results and bond lengths.

	$E/(eV/group)$	Charge (e)	Gap/eV	Bond/ \AA
H	0.00	0.11*, -0.06**	4.61	1.02 ^a , 1.21 ^b
F	-0.30	-0.05, -0.12	4.48	1.39, 1.33
OH	0.19	0.04, 0.13	4.31	1.44, 1.38
$H_{(N/B)}-F_{(B/N)}$	-2.90/1.59	0.10, -0.12/ -0.04, -0.05	4.48/4.73	1.02, 1.37/1.42, 1.18
$H_{(N/B)}-Cl_{(B/N)}$	-0.57/2.77	0.06, -0.04/0.07, -0.08	4.57/3.58	1.01, 1.81/1.76, 1.16
$H_{(N/B)}-OH_{(B/N)}$	-1.24/2.21	0.09, -0.07/0.01, -0.05	4.79/3.87	1.01, 1.40/1.43, 1.19

*Charge analysis result for the chemical group decorating the N-edge of BNNR.

**Charge analysis result for the chemical group decorating the B-edge of BNNR.

^a and ^b are length of N-X and B-X bonds ($X = H, F, Cl$, and OH), respectively.

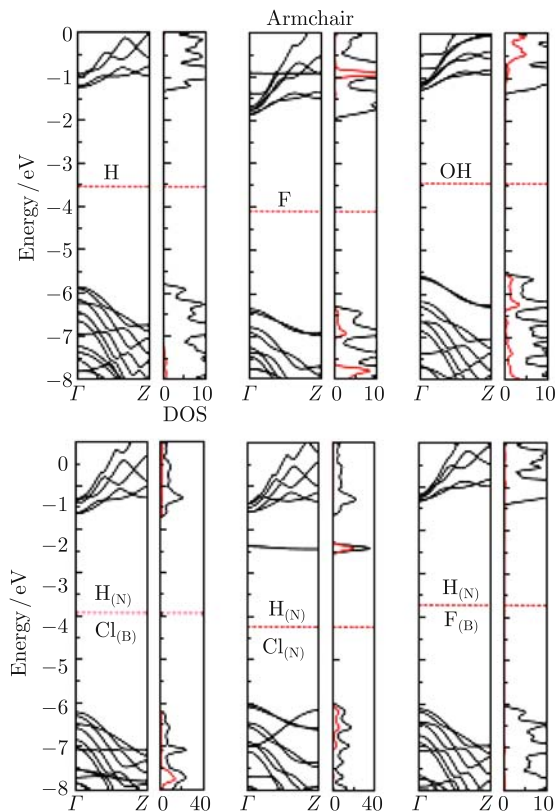


Fig. 6 Electronic band structures and density of states (DOS) of BNNRs with chemically modified armchair edges. The Fermi level is plotted with a red dashed line. The DOS projected onto functional groups are plotted with red solid lines.

a narrowed band gap, except “ $H_{(N)}-OH_{(B)}$ ” and “ $H_{(B)}-F_{(N)}$ ” decorated BNNRs which have a larger band gap than the pure BNNR.

In conclusion, we have studied structural stability and electronic properties of pure and chemically decorated BNNRs using a density functional theory method. Electronic properties of pure BNNRs depend on the type of edges and their widths. BNNRs with either zigzag or armchair edges are semiconducting with wide band gaps. The band gap of BNNRs with zigzag edges decreases monotonically with increasing width, while that of BNNRs with armchair edges oscillates periodically with the width. Chemical decoration of BNNRs’ edges can modify BNNRs’ electronic properties, particularly its band gap. The band-gap modulation by chemical decoration may be exploited for nanoelectronic applications.

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