Electronic Supplementary Information

The Reconstructed Edges of the Hexagonal BN

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S1. Models, definition and calculations of edge energies.

(a) Illustration of models and tests.

Composed with binary compositions, triangular BN structures with length, L = 2.008 nm (see Fig. S1a,b) were used to calculate the formation energies, γ, of pristine ZZB and ZZN edges, respectively. The influence from the corners (which does not scale with length of L) on γ was tested carefully (Table. S1). More details about calculations of edge energy are discussed below. From Table. S1 we can see that the results are well converged as $L \geq 1.506$ nm. The BNNR models (see Fig. S1c,d) were used to calculate γ of pristine AC edge and other reconstructed ones.

Table S1 Edge energies of ZZB and ZZN of triangular BN patches with different length.

Length of each side of triangular BN patches (nm)	Edge energies of ZZB (eV/nm)	Edge energies of ZZN (eV/nm)
0.502	13.13	11.49
0.753	13.00	11.06
1.004	12.98	10.90
1.255	12.96	10.93
1.506	12.97	10.87
1.757	12.97	10.88

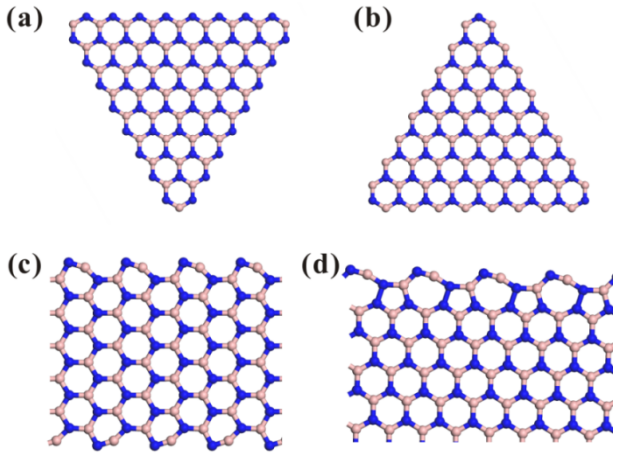

Fig. S1 Representative structures used to calculate formation energies of different edges: (a) pristine zigzag edges terminated with N, (b) pristine zigzag edges terminated with B, (c) pristine and reconstructed armchair edges, (d) reconstructed zigzag edges.

(b) Formation energies of pristine edges.

Unlike graphene, there are three basic edges in BN due to its binary compositions, the edge terminated with N (ZZN), terminated with B (ZZB), and armchair edges (AC). The stabilities of edges can be characterized by their formation energies, i.e., edge energies, γ. A common way to obtain edge energies is to subtract the energy of equivalent material in its bulk from the total slab energy,[1, 2] which can be obtained from density functional theory calculations. Representative structures used to calculate edge energies are shown in Fig. S1. For pristine/reconstructed armchair edges, the energies are defined from equation 1. For pristine zigzag edge terminated with B (N), the energy can be obtained from equation 2 (3).

$$\gamma_{AC} = \frac{E_{AC} - M_{BN}\mu_{BN}}{2L} \quad (1)$$

$$\gamma_{ZZB} = \frac{E_{\Delta} - M_{BN}\mu_{BN} - L\mu_B - \mu_N}{3L} = \gamma_{ZZB}^{0} - \frac{\mu}{3} \quad (2)$$

$$\gamma_{ZZN} = \frac{E_{\nabla} - M_{BN}\mu_{BN} - L\mu_N - \mu_B}{3L} = \gamma_{ZZN}^{0} + \frac{\mu}{3} \quad (3)$$

$$\gamma_{ZZN57} = \frac{E_{ZZ} - M_{BN}\mu_{BN}}{L} - \gamma_{ZZB} \quad (4)$$

where E_{AC}, E_{Δ}, E_{∇}, and E_{ZZ} is the total energy of an optimized BN structure, M_{BN} is the number of BN pairs, μ_{BN} (-17.57 eV) is the energy of BN pair in BN sheet, L is the length of BN edges in units of nanometer, and the factors account for identical edges in each model considered. With edge energies of pristine ZZB and ZZN at hand, it is easy to obtain those of reconstructed zigzag edges. Take ZZN57 as an example, the edge energy can be obtained from equation 4.

(c) Edge energies at different chemical potentials.

Suppose $\mu_{BN} = \mu_B + \mu_N$, the chemical potentials of B and N can be written as $\mu_B = 0.5\mu_{BN} + \Delta\mu$ and $\mu_N = 0.5\mu_{BN} - \Delta\mu$, where $\Delta\mu = (\mu_B - \mu_N)/2$.[3] By choosing the elemental chemical potentials as equal, $\mu_B = \mu_N = 0.5\mu_{BN}$, that is $\Delta\mu = 0$, we determine the values $\gamma_{ZZB}^0 = 12.96\ eV/nm$ and $\gamma_{ZZN}^0 = 10.87\ eV/nm$. Now, we can obtain energies for the basic edges of BN at arbitrary chemical potentials:

$$\gamma_{AC} = 7.57\ eV \tag{5}$$

$$\gamma_{ZZB} = 12.96 - \frac{\Delta\mu}{3} \tag{6}$$

$$\gamma_{ZZN} = 10.87 + \frac{\Delta\mu}{3} \tag{7}$$

For other edges with B/N added, $\Delta\mu$ is added (submitted) from corresponding edge energies. And it is contrary in the case with B (N) substituted. The results are listed in Table S1.

(d) Formation energies of edges terminated with H atoms.

In this work, we also consider the edges terminated with hydrogen atoms to mimic possible situations in experiments. Here, we only consider the case with each edge atom saturated with one H for simplicity although we notice Ding and coworkers have studied the pristine BNNR edges as a function of H−passivation[4]. We find it is efficient enough to eliminate the influence of triple bond on the edges. In this case, take ZZB as another example, the edge energy can be obtained from equation 9, which is similar with equation 2 except that E_Δ is the total energy of BN structure saturated with H, n_H is the number of H atoms, μ_H is the chemical potential of hydrogen, which can be obtained from the DFT calculated energy of H_2 (-6.76 eV),

$$\gamma_{ZZB} = \frac{E_\Delta - M_{BN}\mu_{BN} - L\mu_B - \mu_N - n_H\mu_H}{3L} \tag{9}$$

The chemical potential of hydrogen is highly dependent on the temperature and the pressure. The temperature (and pressure) dependence of μ_H can be written as,[5, 6]

$$2\mu_H = E_{H2} - kTln\left(\frac{kT}{p} \times g \times \zeta_{trans} \times \zeta_{rot} \times \zeta_{vib}\right) \tag{10}$$

where E_{H2} is DFT calculated energy of H_2 (-6.76 eV), k is Boltzmann constant, p is partial pressure of H_2, and g is the degeneracy degree of the electron energy level. ζ_{trans}, ζ_{rot} and ζ_{vib} are the partition functions for translational, rotational, and vibration motions, respectively. Suppose the temperature equals to 1000 K, the pressure of H_2 varies from 10^{-4} mbar to 10^2 mbar, μ_H falls in the range [-4.74 eV, -4.15 eV]. Substitute -4.74 and -4.15 into Eqn.9, we can get edge energies of ZZB at (1000 K, 10^{-4} mbar) and (1000 K, 10^2 mbar) respectively.

(e) Edge energies at different crystallographic directions.

With the basic energies along the armchair and zigzag crystallographic directions, it is convenient to obtain all energies of arbitrary edges using the following analytical expressions,[3, 7]

$$\gamma(\chi) = |\gamma_0| cos(\chi + C) \tag{8}$$

$$|\gamma_0| = 2\sqrt{\left(\gamma_{AC}{}^2 + \gamma_{ZZX}{}^2 - \sqrt{3}\gamma_{AC}\gamma_{ZZX}\right)}$$

$$\tan C = \frac{\sqrt{3}\gamma_{AC} - 2\gamma_{ZZB}}{\gamma_{AC}}, \ 0 < \chi < 30\ °;$$

$$\tan C = -\frac{\sqrt{3}\gamma_{AC} - 2\gamma_{ZZN}}{\gamma_{AC}}, \ -30 < \chi < 0\ °.$$

where γ_{AC}, γ_{ZZB}, and γ_{ZZN} are the basic energies along armchair edges and zigzag edges terminated with B and N, respectively.

S2. Edge energies, band gaps (E_g), electronic and magnetic properties.

Table S2. Edge energies, magnetic properties and band gaps (E_g) of edges.

Edge types	Bare					H-terminated			
	Edge energies (eV/nm)			Magnetic properties	E_g (eV)	Edge energies (eV/nm)			
	γ^0 ($\Delta\mu = 0$)		γ^0 ($\Delta\mu \neq 0$)			μ_H=-3.38		μ_H=-4.74[c]	μ_H=-4.15[c]
	Ours	Ref.				Ours	Ref.		
ZZN	10.87	10.84[a,*]	$\gamma^0 + \Delta\mu/3$	magnetic	metallic	-1.12	~ -1.20[a,*]	5.95	3.13
ZZN57	10.29		$\gamma^0 + \Delta\mu/3$	nonmagnetic	3.41	5.27		9.95	8.07
ZZN57′	13.04		$\gamma^0 + \Delta\mu/3$	magnetic	metallic	7.08		11.75	9.87
ZZN+B	19.30		$\gamma^0 - 2\Delta\mu/3$	nonmagnetic	0.88	9.86		14.53	12.65
ZZN+B+N	12.51		$\gamma^0 + \Delta\mu/3$	magnetic		4.60		9.27	7.39
ZZB	12.96	12.99[a,*]	$\gamma^0 - \Delta\mu/3$	magnetic	metallic	3.39	~3.19[a,*]	9.55	6.73
ZZB57	11.85		$\gamma^0 - \Delta\mu/3$	nonmagnetic	2.61	7.48		11.25	9.37
ZZB57′	Unstable		$\gamma^0 - \Delta\mu/3$			11.52		15.29	13.41
ZZB+N	9.87		$\gamma^0 + 2\Delta\mu/3$	nonmagnetic	0.26	3.50		7.27	5.39
ZZB+B+N	12.23		$\gamma^0 - \Delta\mu/3$	magnetic		6.48		10.25	8.37
AC	7.57	7.57[a,b,*]	γ^0	nonmagnetic	4.25	1.18	~0.80[a,*]	7.44	4.72
AC677	11.91		γ^0	nonmagnetic	3.15	7.84		14.09	11.37
AC677′	12.79		γ^0	nonmagnetic	2.68	7.69		13.93	11.22
AC+N	13.14	12.75[a,*]	$\gamma^0 + \Delta\mu$	nonmagnetic	1.12	4.96		11.21	8.50
AC+B	15.20	15.14[a]	$\gamma^0 - \Delta\mu$	nonmagnetic	0.018	11.60		17.85	15.14
AC−Ns	9.18		$\gamma^0 + 2\Delta\mu$	nonmagnetic	1.31	8.18		14.43	11.72
AC−Bs	22.58		$\gamma^0 - 2\Delta\mu$	magnetic	0.72	18.44		24.68	21.97

[a] data obtained or estimated from ref. 3[3]; [b] data from ref. 6 multiplied with 10;

[c,d] μ_H is calculated from Eq.10 at with pressure of 10^{-4} mbar and 10^2 mbar, respectively; [*] The data taken from literatures was recalculated in the unit of eV/nm.

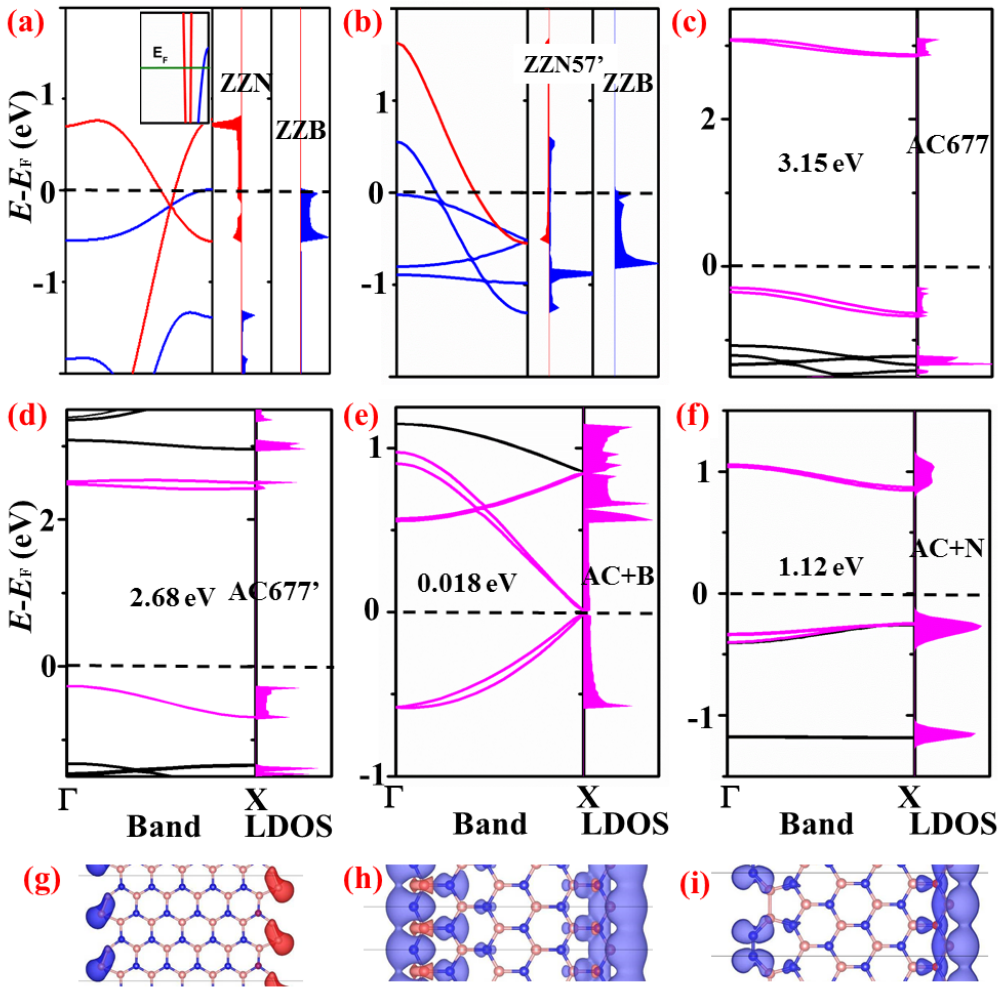

Fig. S2 (a-f) Band structures of BNNRs and LDOS (local density of states) of other edges mentioned in the text. The BNNRs are composed with edges of (a) ZZB and ZZN, (b) ZZB and ZZN57′, (c) AC677, (d) AC677′, (e) AC+B, and (f) AC+N, respectively. Spin density of BNNRs constructed with (g) AC-Bs (AFM, 2.0 u_B/AC site and -2.0 u_B /AC site on the other side), (h) ZZB and ZZN (FM, -1.83 u_B/zz site), and (i) ZZN57′ (FM, 1.61u_B/zz site). The Fermi level (dashed lines) is set to zero. Γ and X denotes the center and the boundary of the first Brillouin zone. The bands near Fermi level and LDOS induced by edges are highlighted with the same color except those possessing magnetism, where red means spin−up and blue represents spin−down.

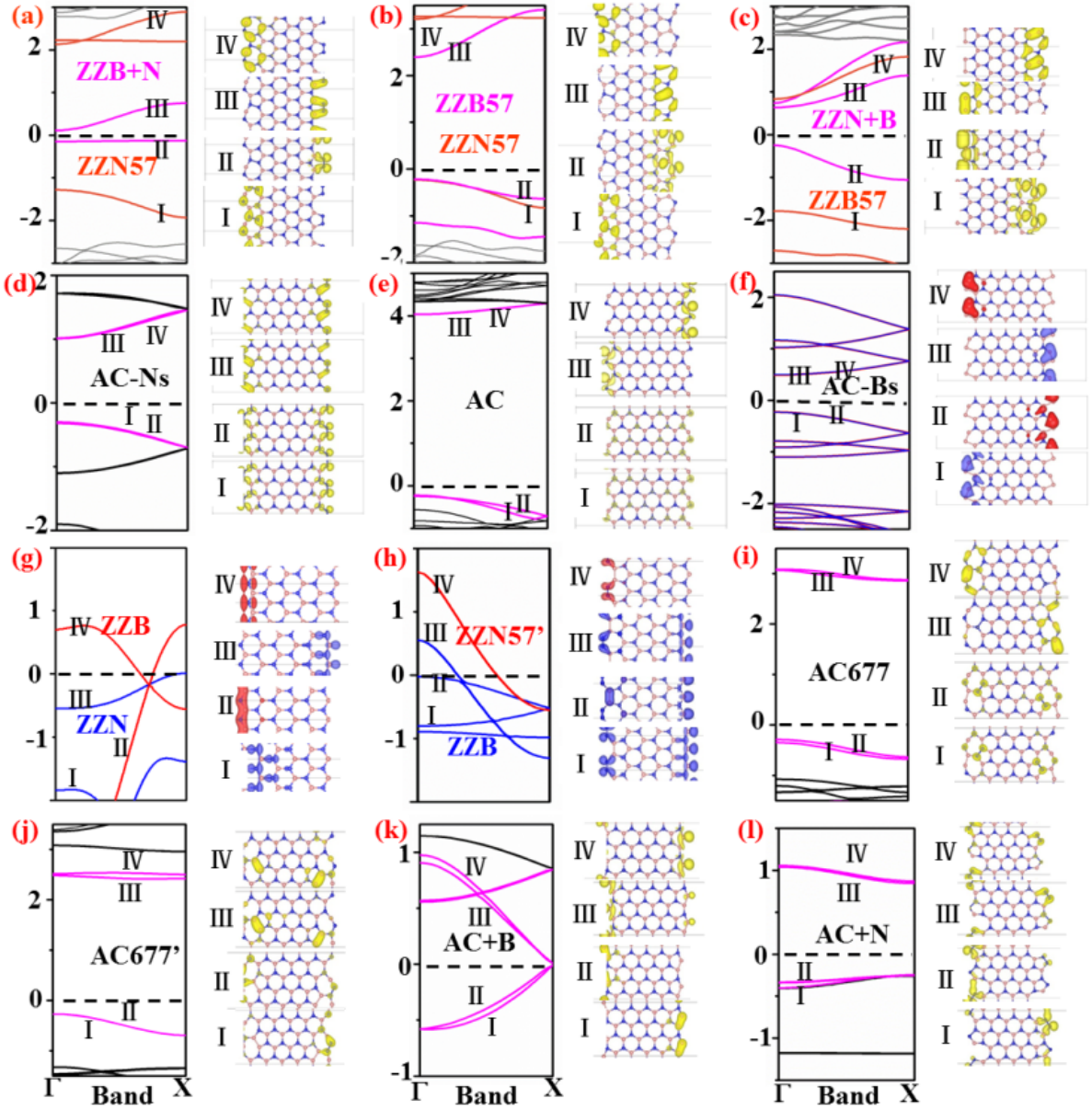

Fig. S3 (a-l) Band structures of BNNRs and partial charge density of specific bands at the Γ point. The Fermi level (dashed lines) is set to zero. Γ and X denotes the center and the boundary of the first Brillouin zone. The isosurface is 0.005e/Å^3.

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