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The transition metal surface passivated edges of hexagonal boron nitride (h-BN) and the mechanism of h-BN's chemical vapor deposition (CVD) growth

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Contents:

1. Tests of stable configurations.

Tests of stable configurations are performed carefully with 9-ZZ BNNRs (containing 9 zigzag BN chains) on Cu(111) and Ni(111). Six high symmetric configurations, B_hN_t, B_fN_t, B_hN_f, B_fN_h, B_tN_f, and B_tN_h, which are identified by the positions occupied by B and N atoms, are considered. Figure S1 shows the relative energies of different configurations with respect to that of B_hN_t. From Fig. S1, we can see that for BNNR B_hN_t is the most stable one on Cu(111) while is a little less unstable than B_fN_h. Therefore, the configuration B_hN_t is used to study the edge stabilities of h-BN on metals in our simulations.

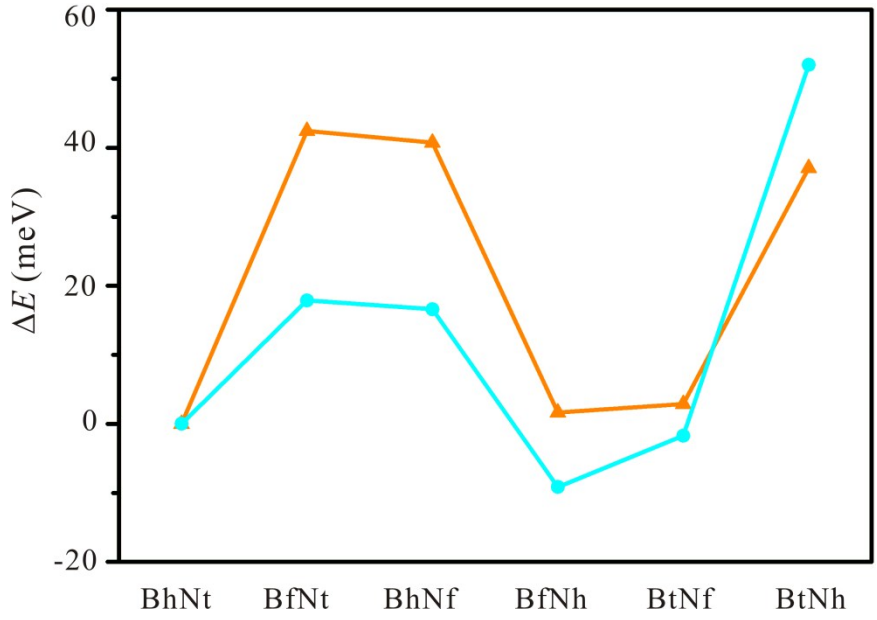

Fig. S1 Relative energies (ΔE) of different configurations of 9-ZZ BNNR with respect to that of B_hN_t on the (111) facets of Cu(▲) and Ni(●).

2. Edge energies of free standing h-BN and h-BN on different metals.

Table S1 Edge energies of free standing h-BN and h-BN on Cu(111), Ni(111), and Rh(111) at different chemical potential differences ($\Delta\mu$).

Edge types	Edge energies (eV/nm)					
	γ^0 ($\Delta\mu = 0$)					γ^0 ($\Delta\mu \neq 0$)
	Bare	H-terminated	Cu(111)	Ni(111)	Rh(111)	
ZZN	10.87	5.95	5.5	4.47	3.26	$\gamma^0 + \Delta\mu/3$
ZZN57	10.29	9.95	8.96	6.28	5.42	$\gamma^0 + \Delta\mu/3$
ZZN+B	19.30	14.53	9.13	5.44	3.30	$\gamma^0 - 2\Delta\mu/3$
ZZB	12.96	9.55	7.91	5.7	4.56	$\gamma^0 - \Delta\mu/3$
ZZB57	11.85	11.25	9.43	5.93	6.19	$\gamma^0 - \Delta\mu/3$
ZZB+N	9.87	7.27	4.73	3.29	2.31	$\gamma^0 + 2\Delta\mu/3$
AC	7.57	7.44	6.84	4.49	3.09	γ^0
AC677	11.91	14.09	11.51	9.02	Unstable	γ^0
AC+N	13.14	11.21	7.33	7.17	5.47	$\gamma^0 + \Delta\mu$
AC+B	15.20	17.85	10.75	6.77	4.61	$\gamma^0 - \Delta\mu$
AC−Ns	9.18	14.43	9.57	7.25	5.91	$\gamma^0 + 2\Delta\mu$
AC−Bs	22.58	24.68	16.29	12.08	10.80	$\gamma^0 - 2\Delta\mu$

Notes: The energies of H-terminated edges were calculated with μ_H = -4.74 eV, which is calculated with pressure and temperature of 10^{-4} mbar and 10^3 K.[1]

3. Magnetism in some typical models.

Table S2 Magnetism (μB) summary of BN flakes/BNNRs with bare, H-terminated, and Cu(111)-, Ni(111)-, Rh(111)- passivated edges. The data in parentheses are those of corresponding Ni substrates. The magnetism of Cu(111) and Rh(111) without BN is zero.

Magnetism / Edge types	Bare edges	H-terminated	On Cu(111)	On Ni(111)	On Rh(111)
ZZN	6.00	0.00	0.00	177.70 (188.41)	0.61
ZZN+B	2.00	0.00	0.00	64.00 (67.61)	0.00
ZZB	12.00	0.00	0.00	170.83 (188.41)	0.51
ZZB+N	4.53	0.00	0.00	66.46 (67.61)	0.00
AC-Ns	0.00	0.00	0.00	79.87 (82.19)	0.00
AC	0.00	0.00	0.00	79.81 (82.19)	0.00
AC+B	2.00	2.00	0.00	77.66 (82.19)	0.00
AC-Bs	4.00	0.00	0.00	76.38 (82.19)	0.00

4. Formation energies vs. orientations, Wulff shapes of h-BN on Cu(111), Ni(111) and Rh(111) at different chemical potential difference.

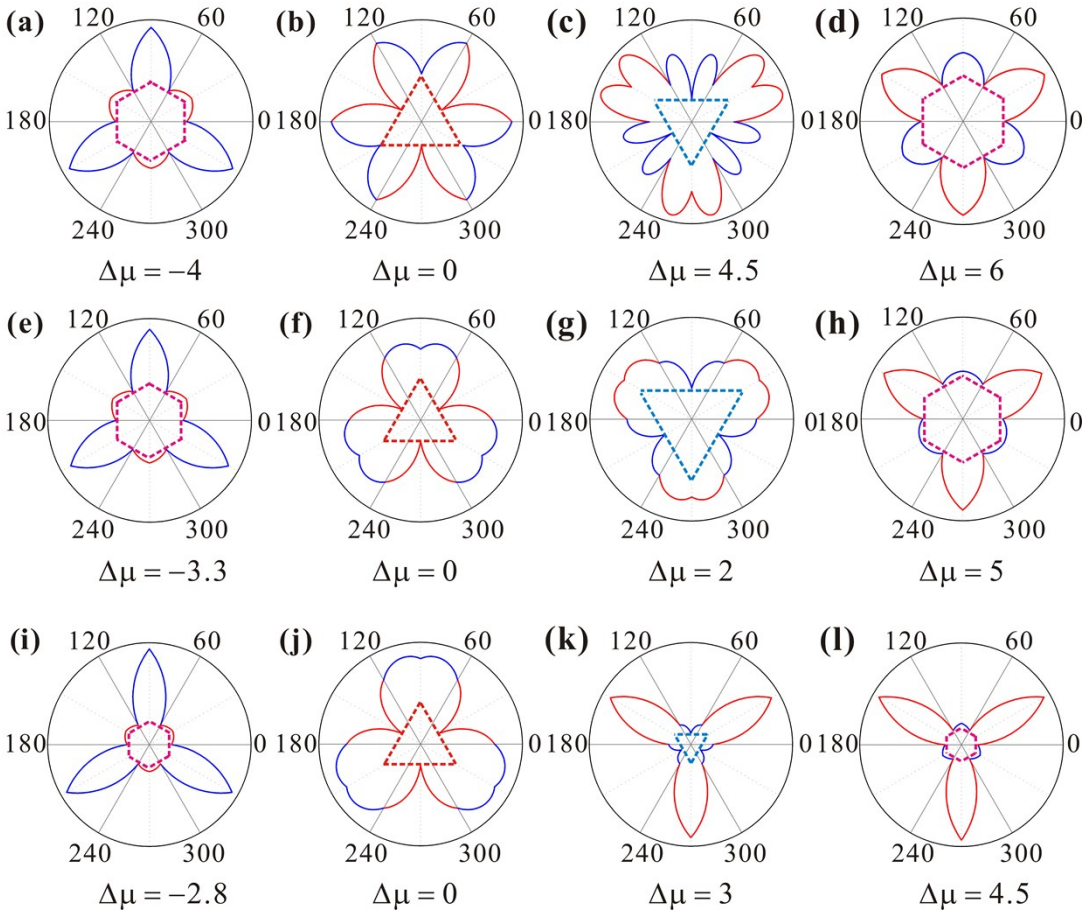

Fig. S2 Formation energies *vs.* orientations of h-BN on Cu(111) (a-d), Ni(111) (e-h) and Rh(111) (i-l) at different chemical potential differences, Δμ. Red and blue solid lines represent the B− and N−rich directions, respectively. The Wulff shapes of h-BN domains are also shown with dashed lines. Red, blue and purple dashed lines represent the shapes constructed with edges along ZZB, ZZN and AC directions, respectively.

(1) Zhao, R.; Gao, J.; Liu, Z.; Ding, F. *Nanoscale* 2015, *7*, 9723.