Electronic Supplementary Information

Dissociation of ammonia borane and its subsequent nucleation on the Ru(0001) surface revealed by density functional theoretical simulations

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Contents

1. Relaxed configurations and relative energies of ammonia borane on the Ru(0001) surface calculated with PBE and vdw-D3 functionals.

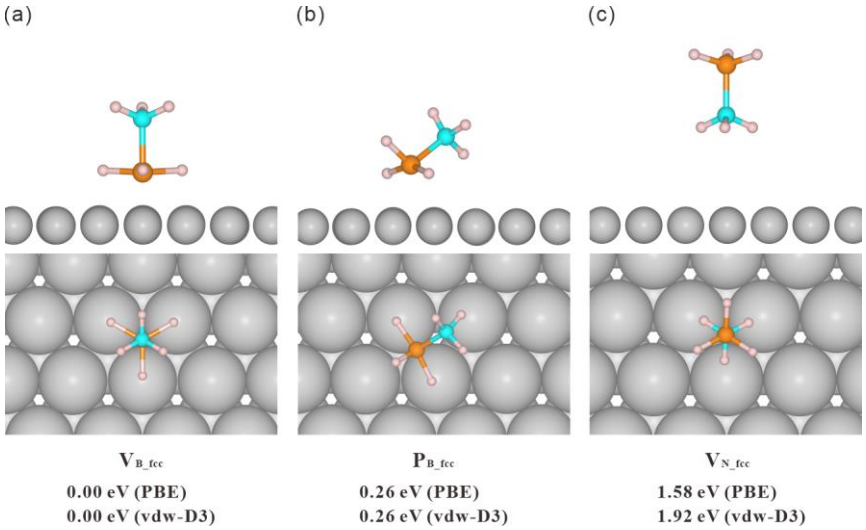

Fig. S1 Relaxed configurations and relative energies of three typical configurations of ammonia borane on Ru(0001) surface calculated by PBE and vdw-D3: (a) V_{B_fcc}, (b) P_{B_fcc} and (c) V_{N_fcc}.

The results show that van der Walls correction has influence on stability of the configuration V_{N_fcc} while almost no influence in the other two configurations, V_{B_fcc} and P_{B_fcc}. As will be discussed in the main text, only physical adsorption exists in V_{N_fcc}. In other words, the influence from van der Walls force can be neglected in configurations having more charge transfer between underlying metal substrate. Therefore, PBE functional is used to simulate the stabilities of the intermediates and and its subsequent nucleation.

2. Side and top views of relaxed geometries of ammonia borane on Ru(0001) surface.

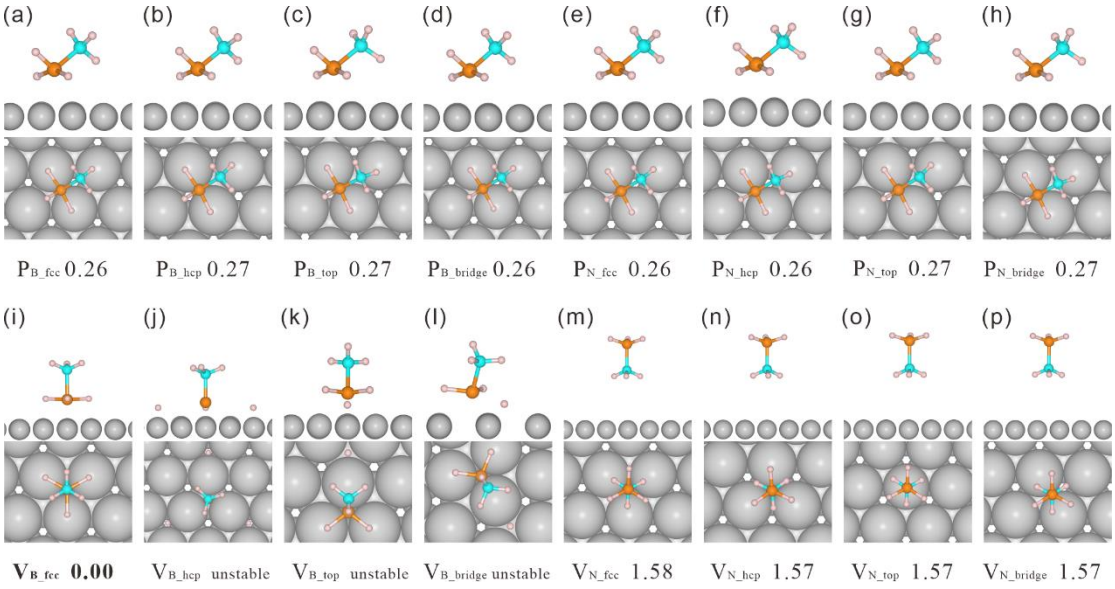

Fig. S2 Side (upper) and top (lower) view of the optimized structures of ammonia borane on Ru(0001) surface. P and V represents the parallel and vertical alignment of ammonia borane molecule on metal surface. The subscripts represent the adsorption sites occupied by B or N atoms before optimization. The relative energy, ΔE (defined as $\Delta E = E_{other} - E_{min}$) is also listed under each panel. The structure with the lowest energy is highlighted in bold.

Considering the adsorption sites, the polarity of ammonia borane (AB) and two adsorption modes, 16 conformations (see Fig. S1) are constructed totally. The configurations are named with P_{x_y} or V_{x_y} (x = B, N; y = fcc, hcp, top, and bridge, respectively). Here, P and V represents the B-N bond is parallel or vertical to underlying metal surface, respectively. The relative energy is also listed in each panel. For configurations with AB parallel to Ru(0001), it clearly shows that B atoms move towards to Ru(0001) while N atoms are away from underlying surface (see Fig. S2a-h). After full relaxation, all configurations with AB molecule parallelling to Ru(0001) surface almost have the same stabilities. For configurations with AB vertical to Ru(0001), the one with B atom possessing fcc site is the most stable while the configurations with B docking hcp, top, and bridge are unstable with H dissociated from B (see Fig. S2i-l). The configurations with N possessing different docking sites remain complete and the AB molecule move away from underlying substrate after full relaxation (see Fig. S2m-p). All configurations of V_N have almost the same adsorption energy. Therefore, the most stable configuration, V_{B_fcc} is used to simulate the dissociation of AB molecule on Ru(0001) surface.

3 The configurations of the intermediate species in the dissociation process of ammonia borane on Ru(0001) surface.

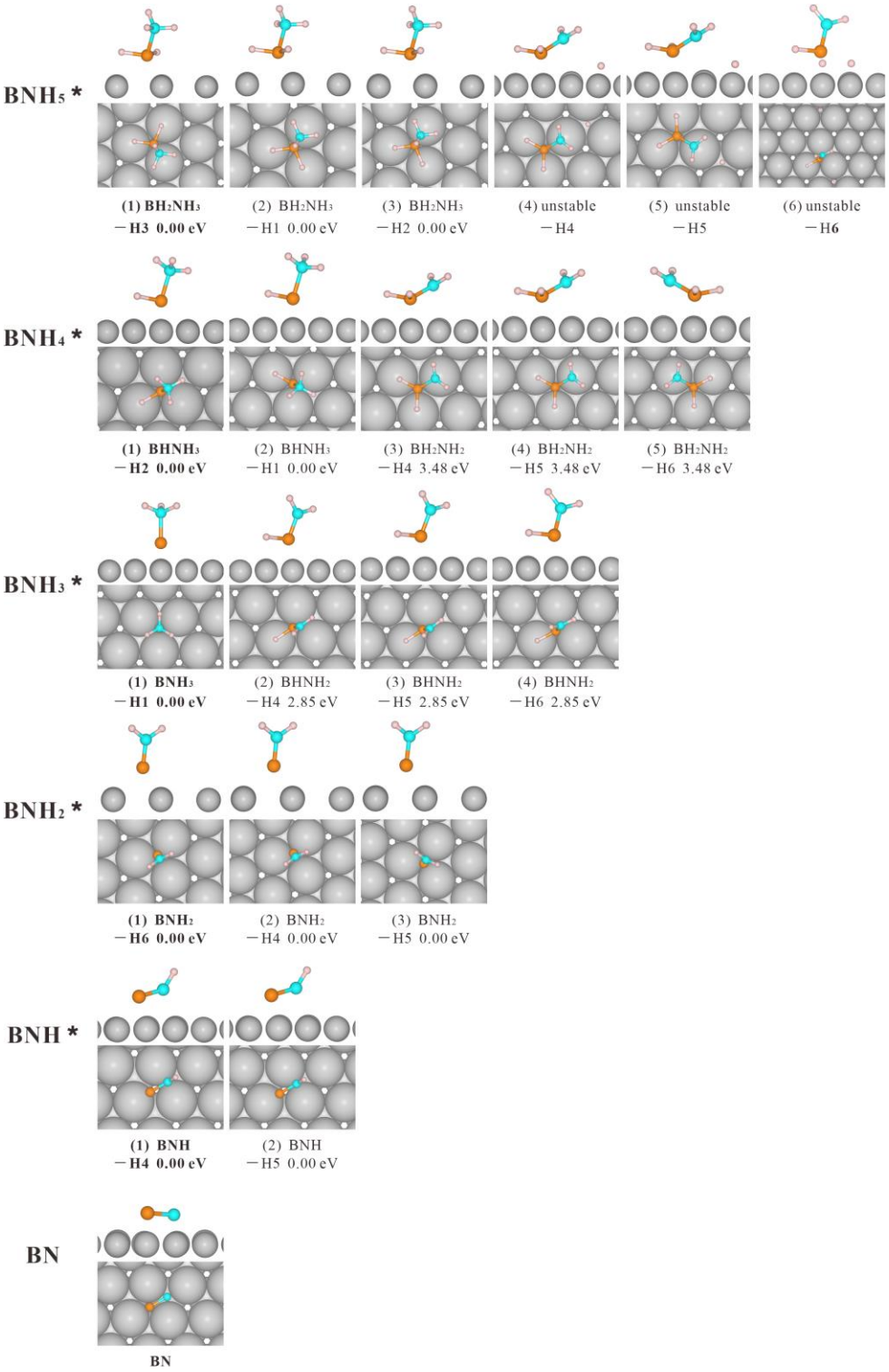

Fig. S3 The optimized configurations of the intermediates in dissociation of ammonia borane on Ru(0001) surface. The nominal formula and relative energies of each configurations are summarized under each panel.

4 The electron density difference and the partial density of states of the intermediate BNH_3* on Ru(0001) surface.

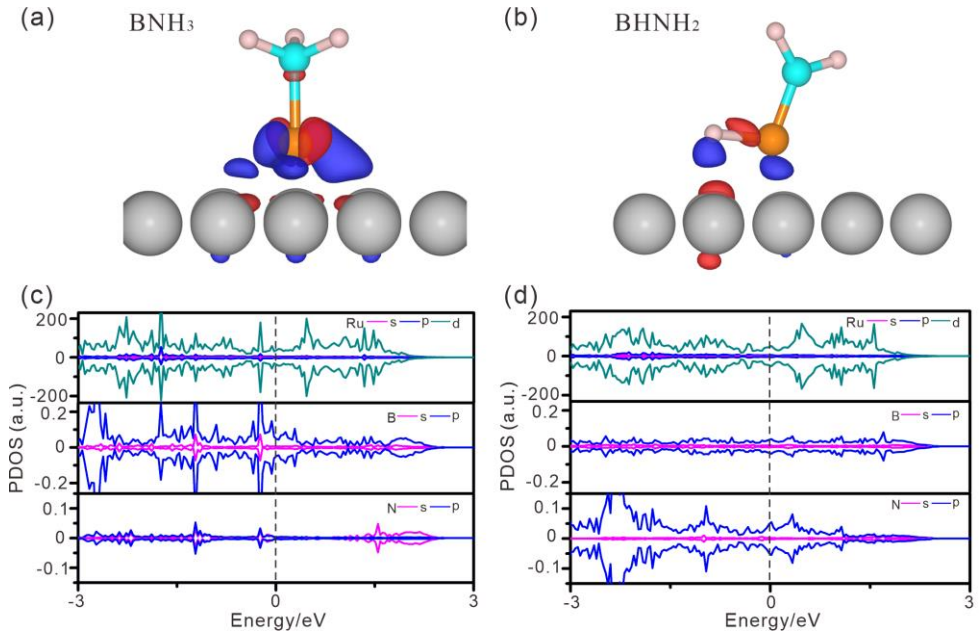

Fig. S4 The electron density difference (EDD) and the partial density of states (PDOS) of the configurations of intermediate BNH3* on Ru(0001) surface: (a) and (c) BNH_3, (b) and (d) $BHNH_2$. The isosurface in (a) and (b) is 0.014 $eÅ^{-3}$, and red and blue represent electron depletion and accumulation, respectively.

5 Relaxed geometries and formation energies of chain-like, ring-shaped and honeycomb configurations of $(BN)_n$ (n = 1-12) clusters on Ru(0001) surface.

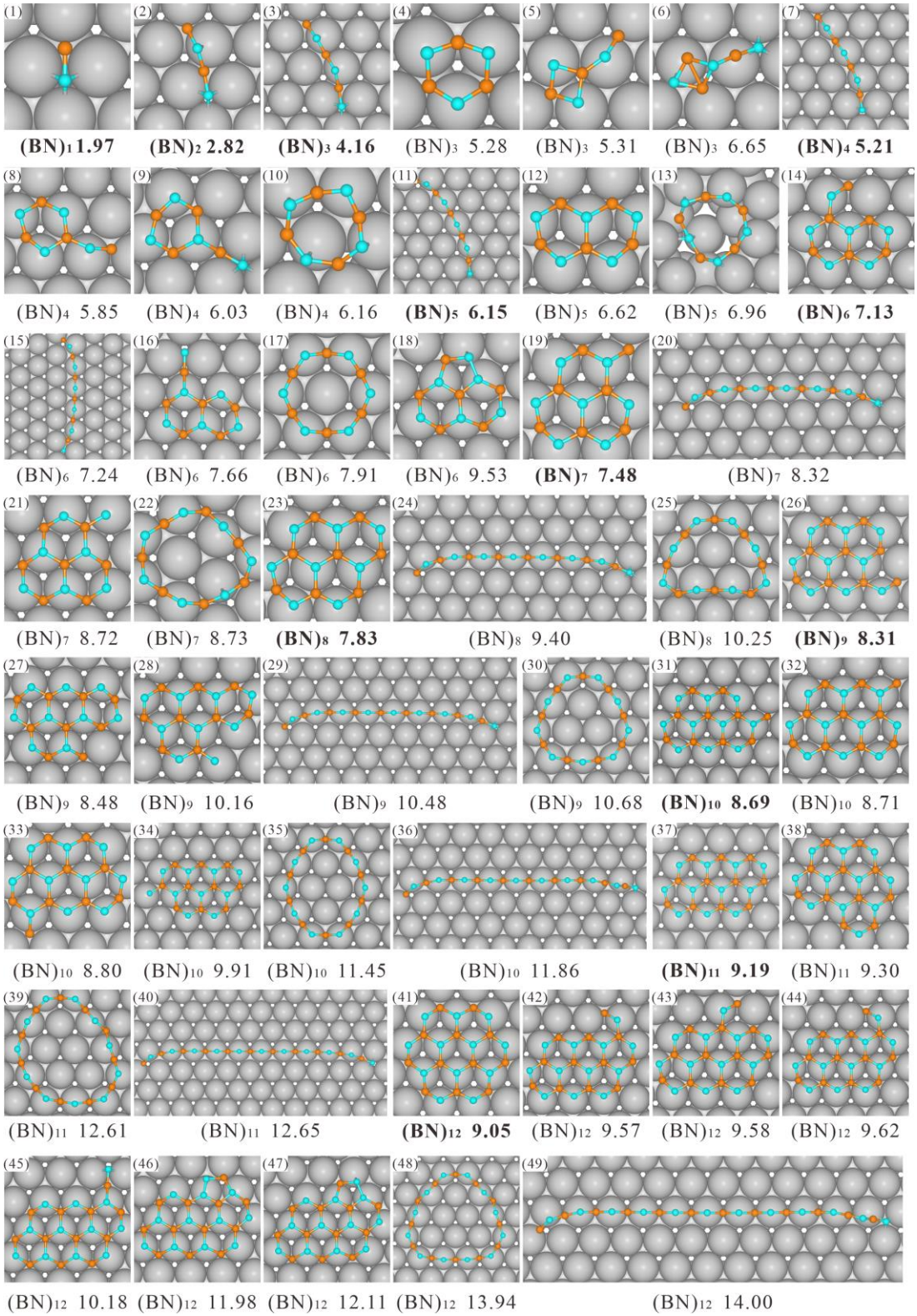

Fig. S5 Relaxed geometries and formation energies of chain-like, ring-shaped and honeycomb configurations of $(BN)_n$@Ru(0001) (n = 1-12). The most stable geometry of cluster with identical size is highlighted with bold.

6 Band structures of free standing BN film, BN film on Ru(0001) and electron density difference of BN film on Ru(0001).

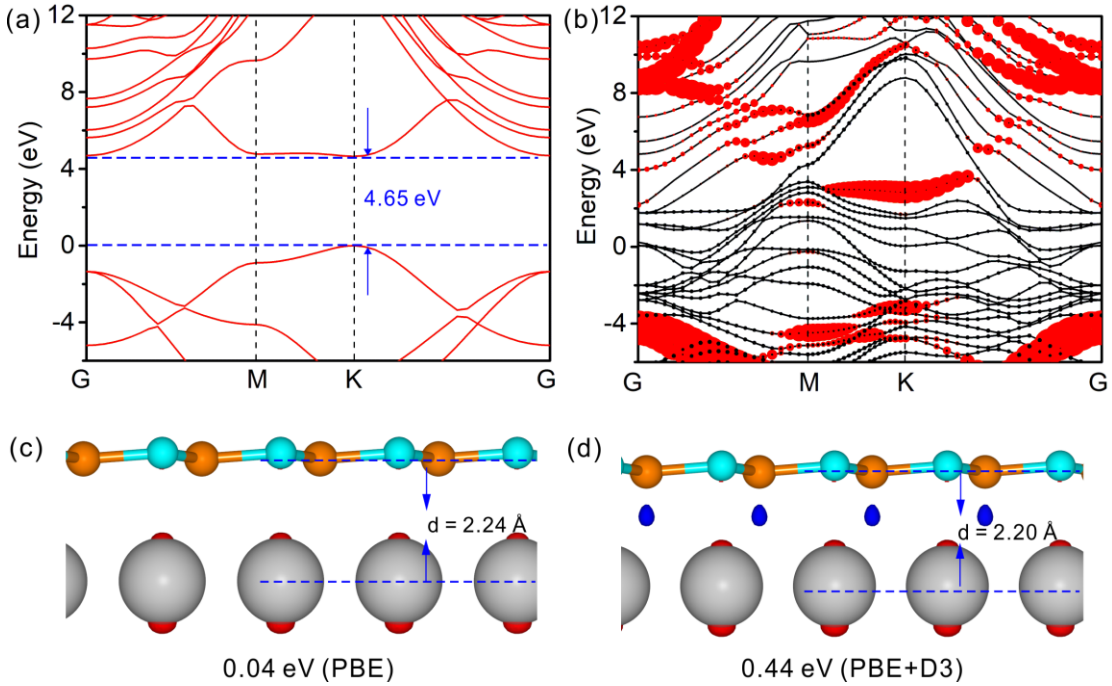

Fig. S6 Band structures of (a) free BN film and (b) BN film on Ru(0001) calculated with PBE+D3 functional. (c and d) Differential charge density between BN film and Ru(0001) obtained from PBE (c) and PBE+D3 (d) functionals. The isosurface is 0.008 eÅ^{-3}. Red and blue represent electron depletion and accumulation, respectively. The distance between BN film and Ru(0001) surface and the binding energy (defined as $E_{BN@Ru(0001)} - E_{BN} - E_{Ru(0001)}$) are also presented.