Electronic Supplementary Information

A Theoretical Study on the Structures, Electronic and Magnetic Properties of New Boron Nitrogen Composite Nanosystems by Depositing Superhalogen Al_{13} on the Surface of Nanosheet/Nanoribbons

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In this work, when adsorbing the superhalogen Al_{13} on the surface of 2D BNML, twenty-one typical adsorption situations have been considered. The optimized geometries and relative energies for all these composite Al_{13}-BNML systems have been presented in Table S1 and Figure S1. For convenience, these new structures have been named according to the following rules:

(1) When the top site of Al atom (T_{Al}) in Al_{13} cluster interacting with the top site of B atom (T_B), top site of N atom (T_N), bridge site over B–N bond ($B_{B\text{-}N}$) and hollow site of BN hexagon ring (H_{BN}) on the surface of BNML, four obtained composite systems are named as X-$Al_{13}(T_{Al})$@BNML (X= T_B, T_N, $B_{B\text{-}N}$ and H_{BN}), in which $Al_{13}(T_{Al})$ represents one single Al atom in Al_{13} cluster is adsorbed on BNML.

(2) When the bridge of Al–Al bond ($B_{Al\text{-}Al}$) in Al_{13} cluster interacting with the surface of BNML, eight Al_{13}-modified BNML systems are obtained, and they are named as X/X'-$Al_{13}(B_{Al\text{-}Al})$@BNML (X or X'= T_B, T_N, $B_{B\text{-}N}$ and H_{BN}), including T_B/T_B-$Al_{13}(B_{Al\text{-}Al})$@BNML, T_N/T_N-$Al_{13}(B_{Al\text{-}Al})$@BNML, $B_{B\text{-}N}/B_{B\text{-}N}$-$Al_{13}(B_{Al\text{-}Al})$@BNML, H_{BN}/H_{BN}-$Al_{13}(B_{Al\text{-}Al})$@BNML, T_B/T_N-$Al_{13}(B_{Al\text{-}Al})$@BNML, T_B/H_{BN}-$Al_{13}(B_{Al\text{-}Al})$@BNML, T_N/H_{BN}-$Al_{13}(B_{Al\text{-}Al})$@BNML and T_B/H_{BN}-$Al_{13}(B_{Al\text{-}Al})$@BNML, respectively. Here, $Al_{13}(B_{Al\text{-}Al})$ represents Al–Al bond of Al_{13} cluster, and X/X' means the adsorption sties on BNML for two Al atoms in Al–Al bond.

(3) When the three-membered ring (H_{Al}) in Al_{13} cluster interacting with the surface of BNML, nine Al_{13}-modified BNML systems are obtained, and they are named as X/X'/X''-$Al_{13}(H_{Al})$@BNML-Y_{center} (X, X' or X''= T_B, T_N, $B_{B\text{-}N}$, H_{BN}; Y_{center} = $T_{Bcenter}$, $T_{Ncenter}$, $B_{B\text{-}Ncenter}$, $H_{BNcenter}$), including $T_B/T_B/T_B$-$Al_{13}(H_{Al})$@BNML-$T_{Ncenter}$, $T_B/T_B/T_B$-$Al_{13}(H_{Al})$@BNML-$B_{B\text{-}Ncenter}$, $T_N/T_N/T_N$-$Al_{13}(H_{Al})$@BNML-$T_{Bcenter}$, $T_N/T_N/T_N$-$Al_{13}(H_{Al})$@BNML-$H_{BNcenter}$, $B_{B\text{-}N}/B_{B\text{-}N}/B_{B\text{-}N}$-$Al_{13}(H_{Al})$@BNML-$T_{Ncenter}$, $B_{B\text{-}N}/B_{B\text{-}N}/B_{B\text{-}N}$-$Al_{13}(H_{Al})$@BNML-$H_{BNcenter}$, $H_{BN}/H_{BN}/H_{BN}$-$Al_{13}(H_{Al})$@BNML-$T_{Bcenter}$, $H_{BN}/H_{BN}/H_{BN}$-$Al_{13}(H_{Al})$@BNML-$T_{Ncenter}$ and $T_B/T_B/T_N$-$Al_{13}(H_{Al})$@BNML-$T_{Ncenter}$, respectively. Here, $Al_{13}(H_{Al})$ means the three-membered ring of Al_{13} cluster, X/X'/X'' represents the adsorption sties on BNML for three Al atoms in the three-membered ring, and Y_{center} means that the center of the adsorbed three-membered ring in Al_{13} cluster locating over the site on the BNML surface.

By comparison, we can find that adsorbing the superhalogen Al_{13} at the top of N atom (T_N) can obtain the most energetically stable configuration for the modified BNML systems (Table S1), which is named as T_N-Al_{13}(T_{Al})@BNML. In this work, therefore, we will mainly focus on the Al_{13}-modified BN nanosystems at the T_N site.

Table S1 The relative energies ΔE (meV) of different magnetic couplings to the ground state, the adsorption energy E_{ad} (eV), the total magnetic moment (M_{tot}) for the obtained composite Al_{13}-BNML systems. The NM and FM represent the nonmagnetic and ferromagnetic spin couplings, respectively.

Systems	ΔE (meV)		E_{ad} (eV)	M_{tot} (μ_B)
	NM	FM		
Al_{13}	108.8	0.0	--	1.0
BNML	0.0	--	--	0.0
T_B-Al_{13}(T_{Al})@BNML	90.3	0.0	-0.601	1.0
T_N-Al_{13}(T_{Al})@BNML	190.0	0.0	-0.851	1.0
$B_{B\text{-}N}$-Al_{13}(T_{Al})@BNML	111.9	0.0	-0.619	1.0
H_{BN}-Al_{13}(T_{Al})@BNML	143.4	0.0	-0.599	1.0
T_B/T_B-Al_{13}($B_{Al\text{-}Al}$)@BNML	110.0	0.0	-0.649	1.0
T_N/T_N-Al_{13}($B_{Al\text{-}Al}$)@BNML	108.0	0.0	-0.715	1.0
$B_{B\text{-}N}$/$B_{B\text{-}N}$-Al_{13}($B_{Al\text{-}Al}$)@BNML	37.7	0.0	-0.672	1.0
H_{BN}/H_{BN}-Al_{13}($B_{Al\text{-}Al}$)@BNML	80.8	0.0	-0.699	1.0
T_B/T_N-Al_{13}($B_{Al\text{-}Al}$)@BNML	108.9	0.0	-0.672	1.0
T_B/H_{BN}-Al_{13}($B_{Al\text{-}Al}$)@BNML	46.5	0.0	-0.693	1.0
T_N/H_{BN}-Al_{13}($B_{Al\text{-}Al}$)@BNML	108.5	0.0	-0.708	1.0
T_B/H_{BN}-Al_{13}($B_{Al\text{-}Al}$)@BNML	106.8	0.0	-0.664	1.0
T_B/T_B/T_B-Al_{13}(H_{Al})@BNML-$T_{Ncenter}$	99.5	0.0	-0.736	1.0
T_B/T_B/T_B-Al_{13}(H_{Al})@BNML-$B_{B\text{-}Ncenter}$	100.7	0.0	-0.759	1.0
T_N/T_N/T_N-Al_{13}(H_{Al})@BNML-$T_{Bcenter}$	106.1	0.0	-0.770	1.0
T_N/T_N/T_N-Al_{13}(H_{Al})@BNML-$H_{BNcenter}$	99.9	0.0	-0.730	1.0
$B_{B\text{-}N}$/$B_{B\text{-}N}$/$B_{B\text{-}N}$-Al_{13}(H_{Al})@BNML-$T_{Ncenter}$	99.3	0.0	-0.718	1.0
$B_{B\text{-}N}$/$B_{B\text{-}N}$/$B_{B\text{-}N}$-Al_{13}(H_{Al})@BNML-$H_{BNcenter}$	100.3	0.0	-0.753	1.0
H_{BN}/H_{BN}/H_{BN}-Al_{13}(H_{Al})@BNML-$T_{Bcenter}$	100.7	0.0	-0.760	1.0
H_{BN}/H_{BN}/H_{BN}-Al_{13}(H_{Al})@BNML-$T_{Ncenter}$	91.9	0.0	-0.761	1.0
T_B/T_B/T_N-Al_{13}(H_{Al})@BNML-$T_{Ncenter}$	100.8	0.0	-0.763	1.0

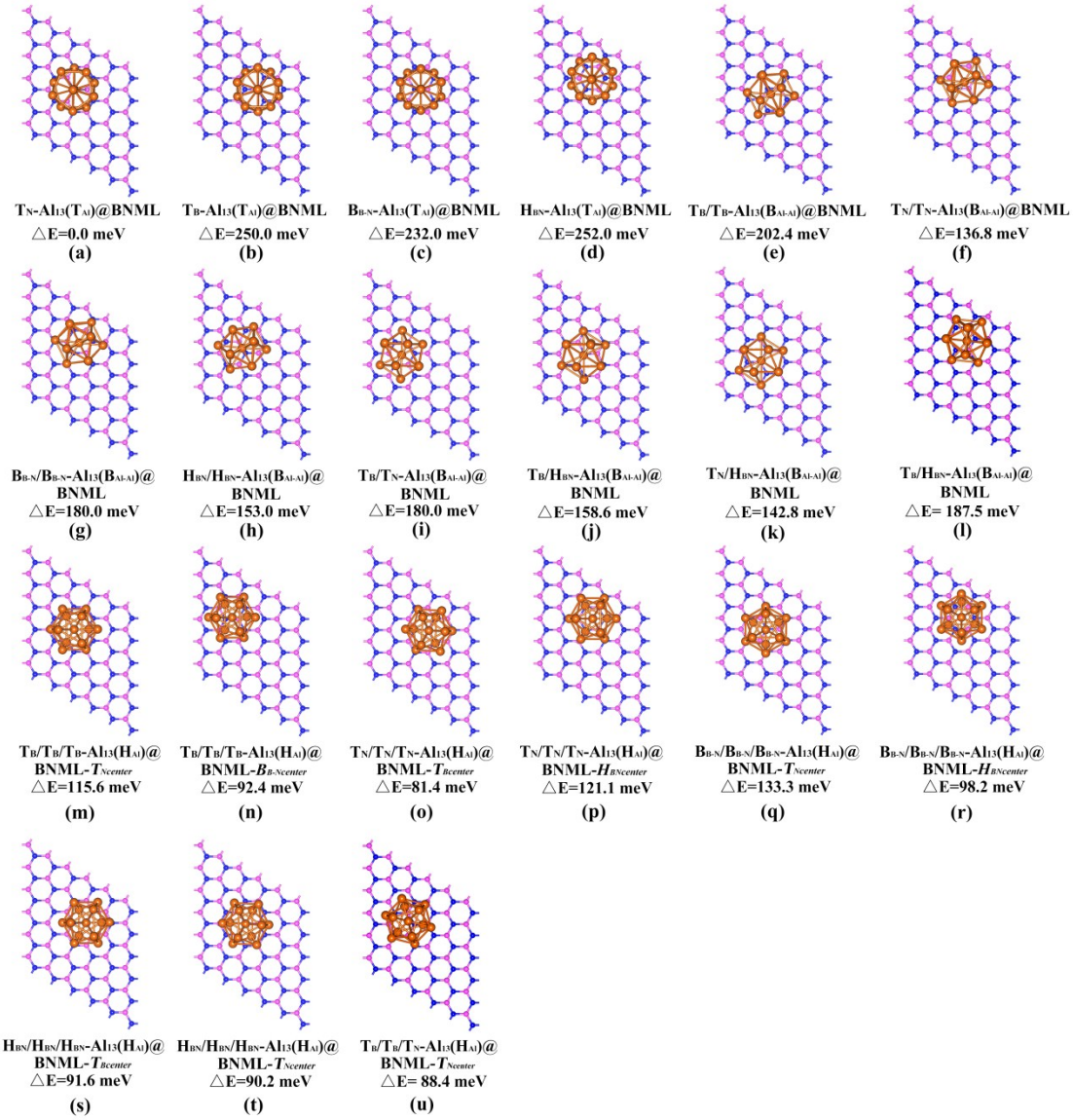

Figure S1. The geometries and relative energies of obtained composite Al_{13}-BNML systems. The brown, pink and blue balls represent Al, B and N atoms, respectively.

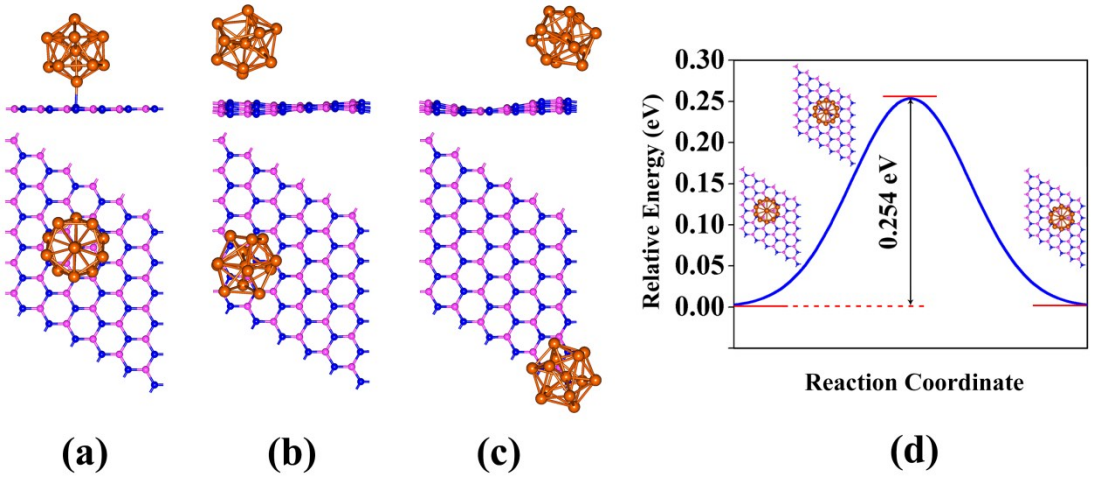

Figure S2. Starting from the initial structure T_N-Al_{13}(T_{Al})@BNML (a), *ab initio* molecular dynamics simulation is run for 2 ps, where increasing the temperature from 0 to 350 K within the first 1.4 ps, the composite configuration T_B/H_{BN}-Al_{13}(B_{Al-Al})@BNML (b) can be obtained, while the composite configuration T_B/T_B/T_N-Al_{13}(H_{Al})@BNML-$T_{Ncenter}$ (c) can be obtained, when keeping at 350 K for 0.6 ps. (d) Minimum-energy pathway for the Al_{13} moving between two T_N sites on the BNML surface. The brown, pink and blue balls represent Al, B and N atoms, respectively.

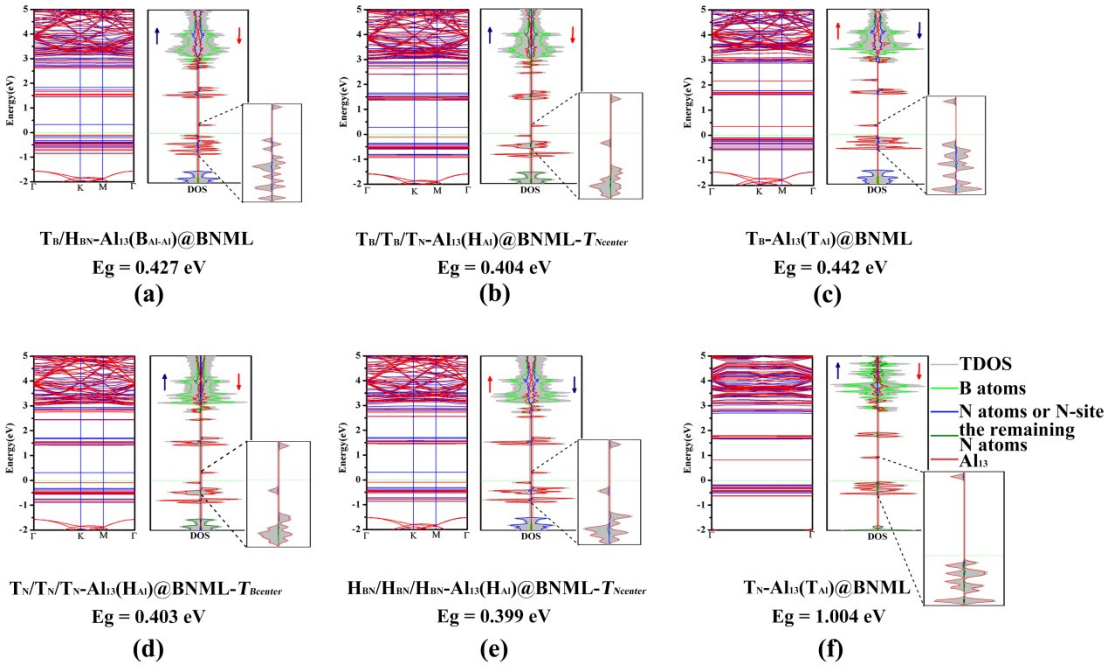

Figure S3. The band structures and corresponding DOSs for T_B/H_{BN}-$Al_{13}(B_{Al\text{-}Al})$@BNML (a), $T_B/T_B/T_N$-$Al_{13}(H_{Al})$@BNML-$T_{Ncenter}$ (b), T_B-$Al_{13}(T_{Al})$@BNML (c), $T_N/T_N/T_N$-$Al_{13}(H_{Al})$@BNML-$T_{Bcenter}$ (d) and $H_{BN}/H_{BN}/H_{BN}$-$Al_{13}(H_{Al})$@BNML-$T_{Ncenter}$ (e), respectively. (f) The calculated band structure using the HSE hybrid functional of T_N-$Al_{13}(T_{Al})$@BNML system. E_g refers to the energy gap between the top valence band (TVB) and the bottom conduction band (BCB). The blue and red lines in the band structures denote the spin-up (↑) and spin-down (↓) channels, respectively. The Fermi-level is set as zero and indicated by the green dotted line. Note that the DOS around the Fermi-level for (a~f) is zoomed in to make it clearer.