Supplementary Information for:

High Intrinsic Catalytic Activity of Two-Dimensional Boron Monolayers for Hydrogen Evolution Reaction

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Table S1. The H-adsorption free energy (ΔG_H) of β_{12} and trigonal BM with respect to H coverage.

β_{12} BM			Trigonal BM		
H-coverage	**ΔE_H (eV)**	**ΔG_H (eV)**	**H-coverage**	**ΔE_H (eV)**	**ΔG_H (eV)**
1/12	-0.19	0.11	1/18	-0.78	-0.48
3/12	-0.19	0.11	2/18	-0.71	-0.41
6/12	-0.18	0.12	3/18	-0.36	-0.06
9/12	0.03	0.33	5/18	-0.16	0.14

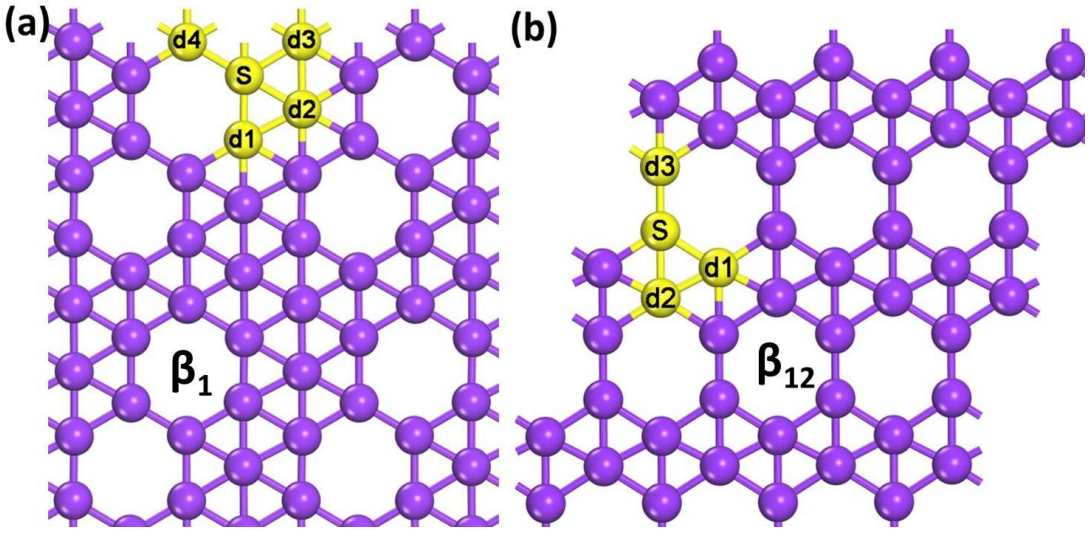

Figure S1. The structures of (a) β_1 and (b) β_{12}, respectively as well as the possible desorption paths for B_2H_6 on BMs: β1-S-d1, β1-S-d2, β1-S-d3, β1-S-d4 and β12-S-d1, β12-S-d2, β12-S-d3 for β1 and β12 BMs, respectively.

Table S2. The calculated free energy difference (ΔG) between the formation of H_2 and B_2H_6 on the BMs.

Compound	defect type	ΔG_H (eV)	ΔG (eV)[1]
β_1-boron monolayer	S-d1	0.10	-1.97
	S-d2		-3.23
	S-d3		-2.12
	S-d4		-2.02
β_{12}-boron monolayer	S-d1	0.01	-3.65
	S-d2		-3.88
	S-d3		-1.60

[1] ΔG is calculated by: $\Delta G = \Delta G_{(3H2)} - \Delta G_{(B2H6)}$, where the $\Delta G_{(3H2)}$ or $\Delta G_{(B2H6)}$ is the formation free energy of 3 H_2 or 1 B_2H_6 molecule on the BM, respectively.

Table S3. The comparison of the calculated free energy of hydrogen adsorption by using PBE-GGA with and without D2 correction. The effect of weak interaction on free-standing BMs is negligible as the DFT-D2 and DFT give very similar results.

ΔG_H (eV)	PBE-GGA	PBE-GGA with D2	PBE-GGA with D2
β_{12}-S1	0.10	0.13	
χ_3-S1	0.03	0.05	
β_{12}@Ag-S_1	-0.34	-0.01	0.02
β_{12}@Ag-S_3	-0.31	-0.13	-0.10

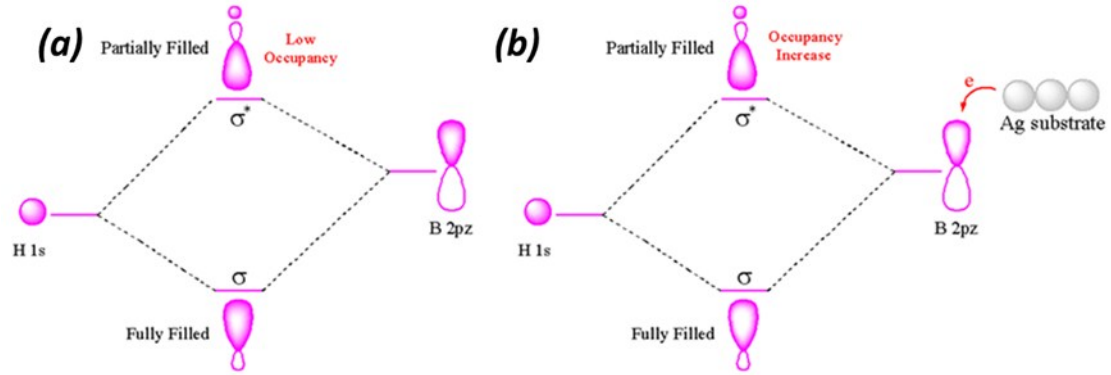

Figure S2. (a) The combination of H 1s orbital and B 2pz orbital forms a fully filled bonding orbital and a partially filled anti-bonding orbital. (b) Charge transfer from Ag to BM will occur when the BM is placed on the Ag substrate. The extra electron gained from Ag will occupy the anti-bonding orbital, leading to weaker H-B bonding strengths and a more positive ΔG_H.