Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Supplementary Information

Design of 3*d* Transition Metal Anchored B_5N_3 Catalysts for Electrochemical CO_2 Reduction to Methane

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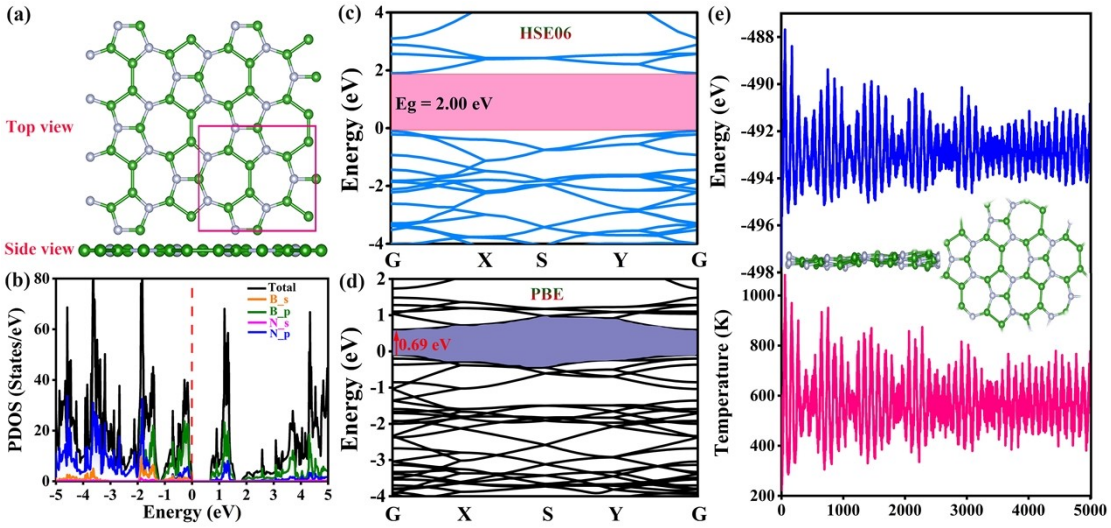

Fig. S1. (a) Optimized structure and (b) projected density of states (PDOS) of a B_5N_3 monolayer. B and N atoms are denoted by green and silver spheres, respectively. The Fermi level (red dashed line) was shifted to zero. (c-d) Band structures of B_5N_3 monolayer computed *via* the (c) HSE06 and (d) PBE functionals. (e) The energy fluctuations and temperature of B_5N_3 monolayer during 15 ps of AIMD. The insets are the side and top views of the B_5N_3 monolayer after 15 ps AIMD simulation at 600 K.

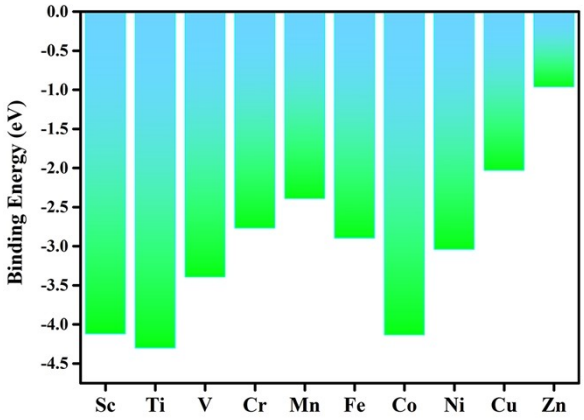

Fig. S2. Binding energy of various transition metal atoms (Sc~Zn) at a 2D-B_5N_3 monolayer.

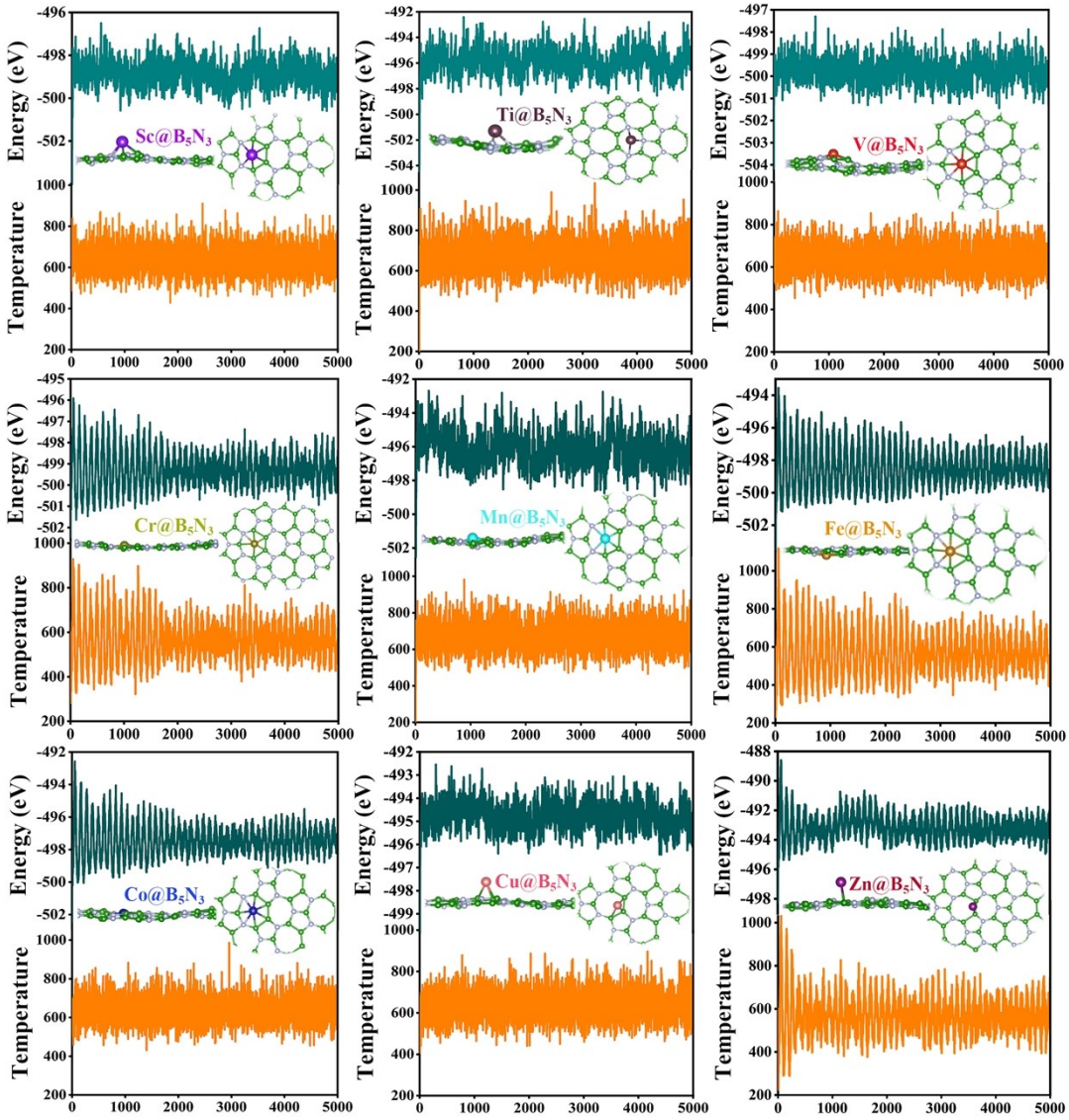

Fig. S3. Snapshots of the equilibrium structure of the TM@B_5N_3 (TM= Sc, Ti, V, Cr, Mn, Fe, Co, Cu, and Zn) at 600 K after 15 ps AIMD simulations.

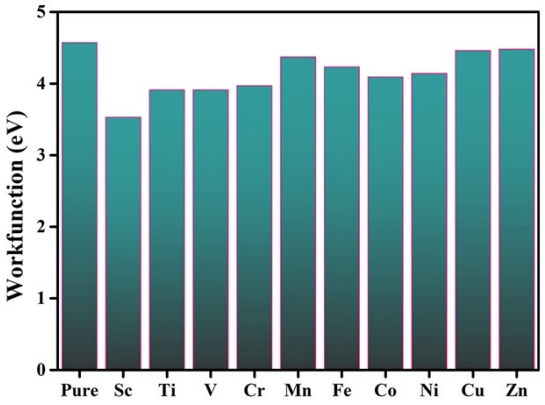

Fig. S4. Calculated work functions of B_5N_3 and the TMs (Sc~Zn)@B_5N_3.

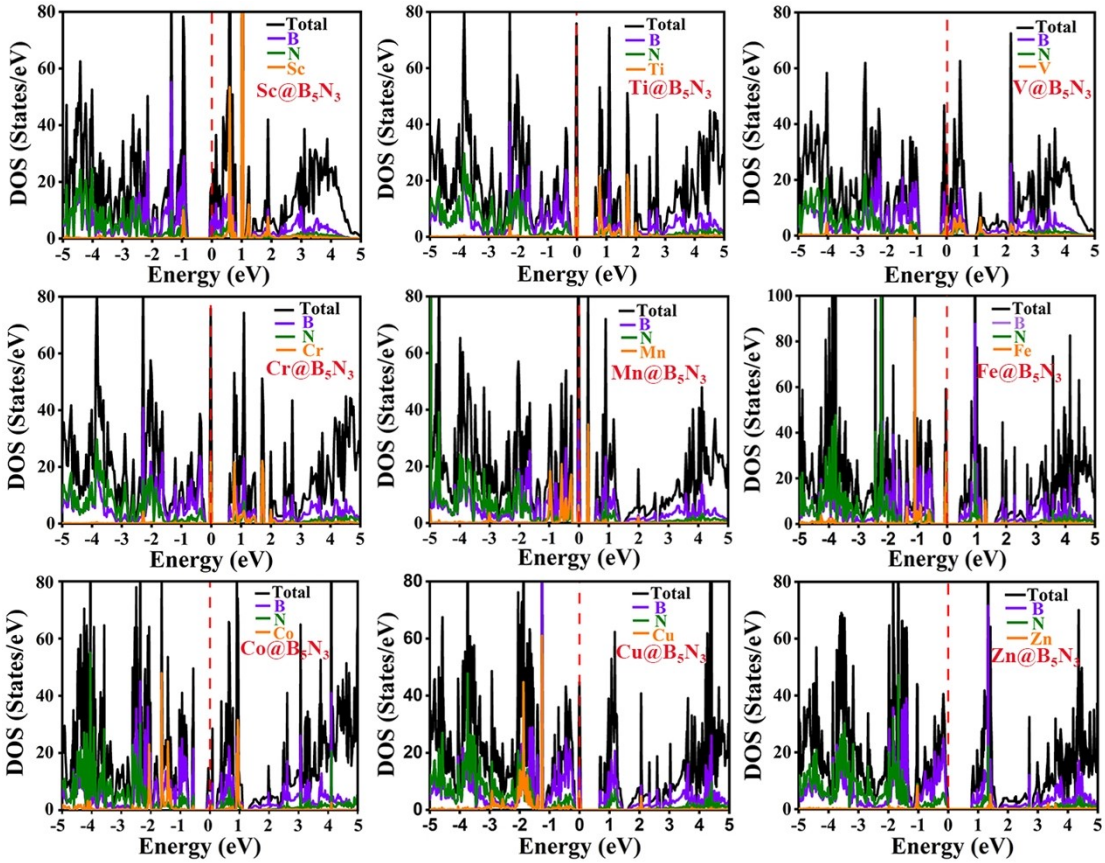

Fig. S5. Calculated PDOS of TMs (Sc~Zn)@B_5N_3. The Fermi levels (red dashed lines) were shifted to zero.

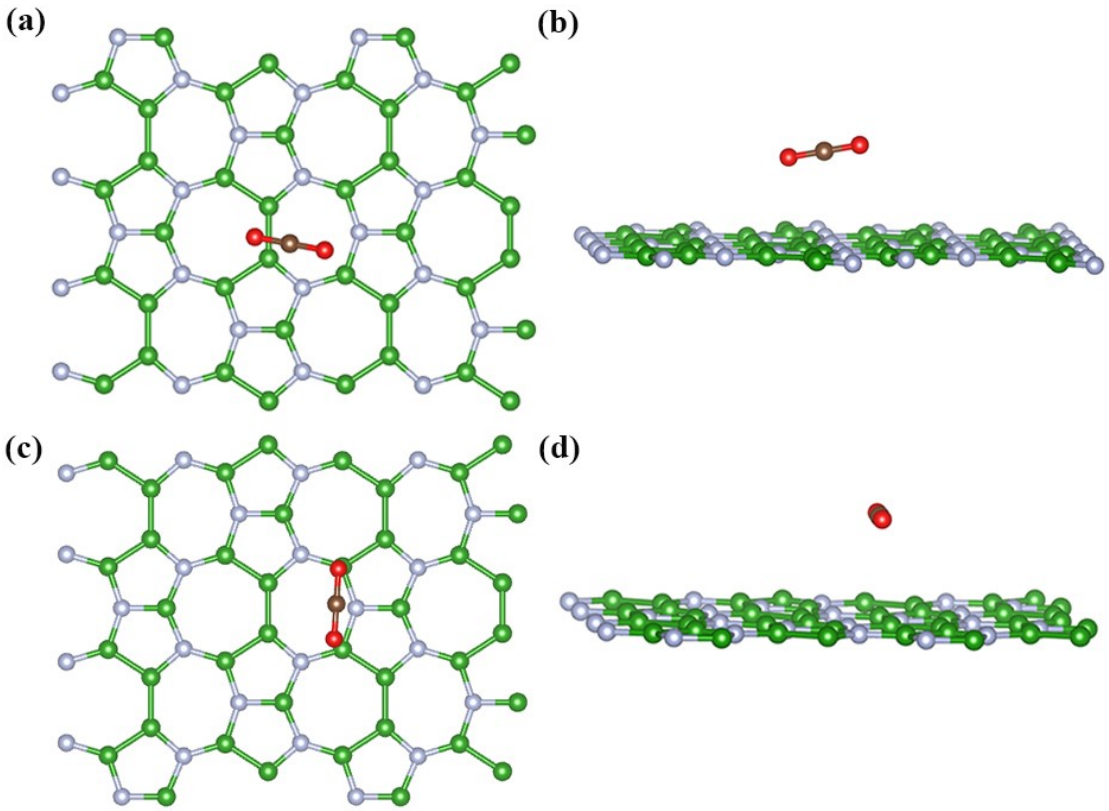

Fig. S6. Optimized structures of CO_2 adsorption on B_5N_3. (a) and (c) are the top views, (b) and (d) are the side views. B, N, C, and O are denoted by green, silver, gray, and red spheres, respectively.

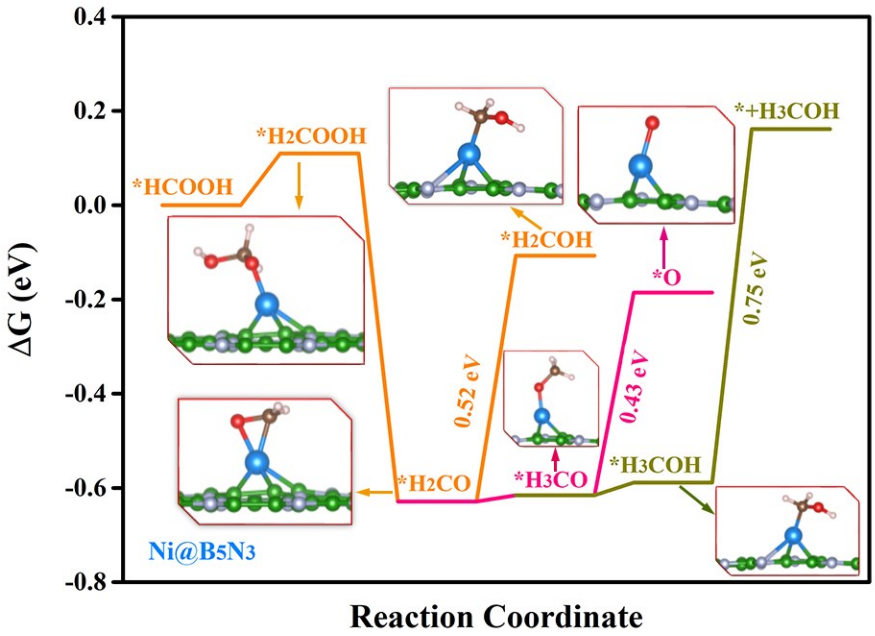

Fig. S7. Free energy diagram of further protonation of the *HCOOH intermediate and the corresponding intermediate configurations on Ni@B_5N_3. B, N, C, H, O, and Ni are denoted by green, silver, gray, white, red, and cyan spheres, respectively.

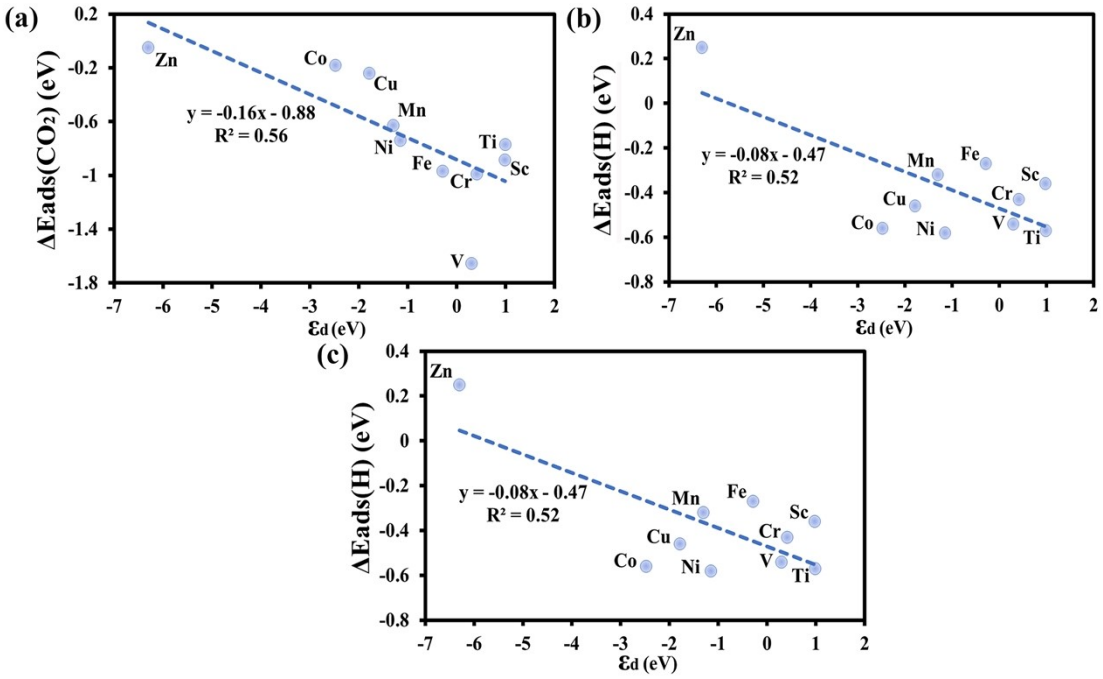

Fig. S8. Correlations between the *d*-band centers of TMs *vs* adsorption energies of (a) *CO_2, (b)*HCOOH, and (c) *H.

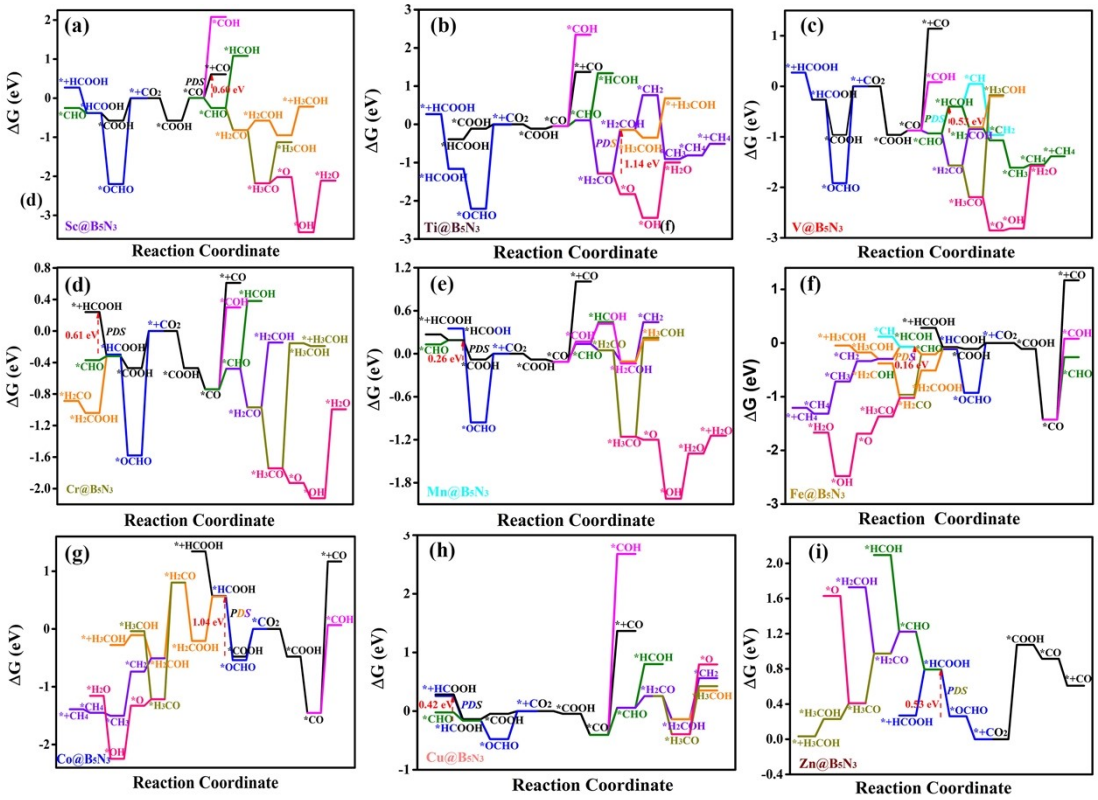

Fig. S9. Free-energy diagrams of CO_2RR *via* diverse paths on (a) $Sc@B_5N_3$, (b) $Ti@B_5N_3$, (c) $V@B_5N_3$, (d) $Cr@B_5N_3$, (e) $Mn@B_5N_3$, (f) $Fe@B_5N_3$, (g) $Co@B_5N_3$, (h) $Cu@B_5N_3$, and (i) $Zn@B_5N_3$ at 0 V *vs* RHE. The red dotted arrows mark the positions where occur. The values in red are the free energies of the preferred path.

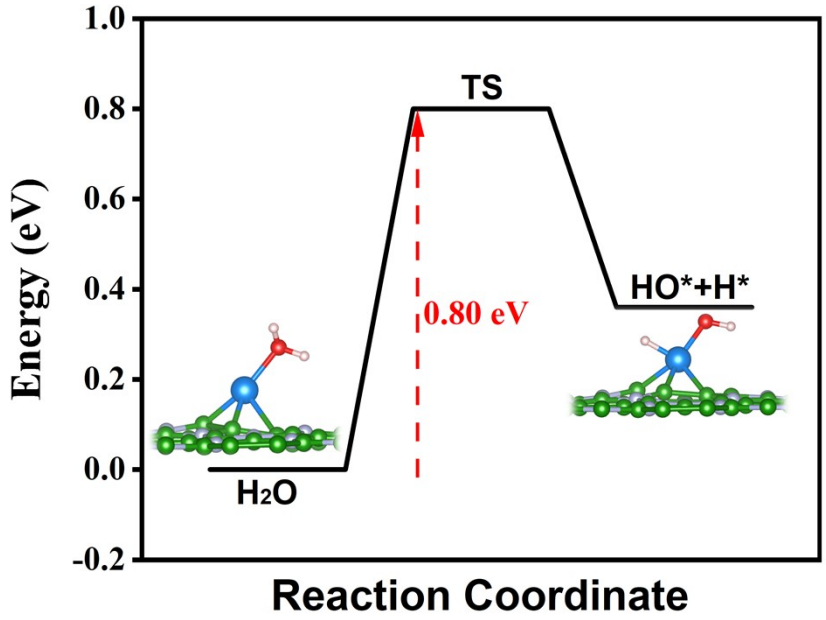

Fig. S10. Free energy profile of water activation over the Ni@B_5N_3 catalyst. B, N, Ni, H, and O are denoted by green, silver, blue, pink, and red spheres, respectively.

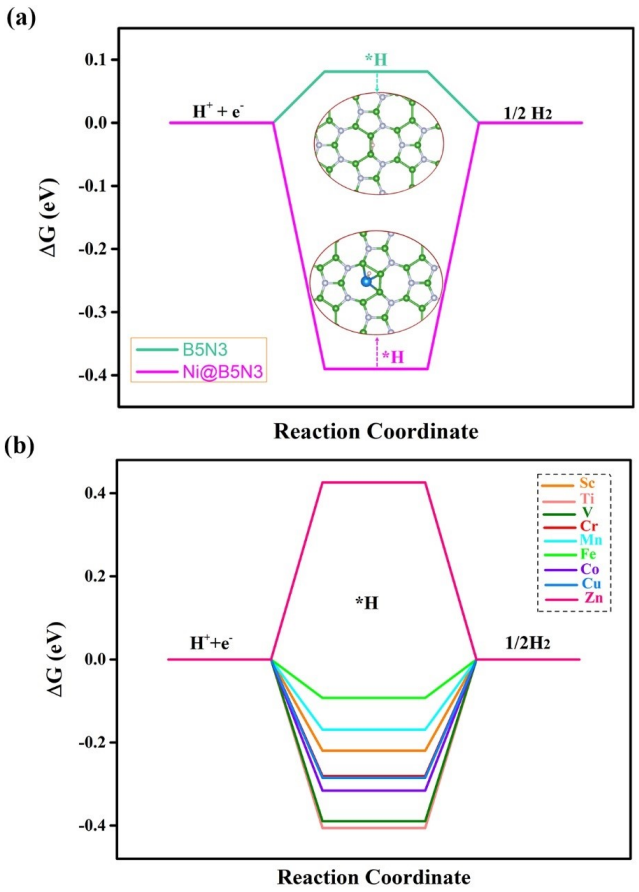

Fig. S11. Free energy diagrams of HER on (a) B_5N_3 and Ni@B_5N_3 and (b) the remaining 3*d* TMs@B_5N_3 at 0 V *vs* RHE.

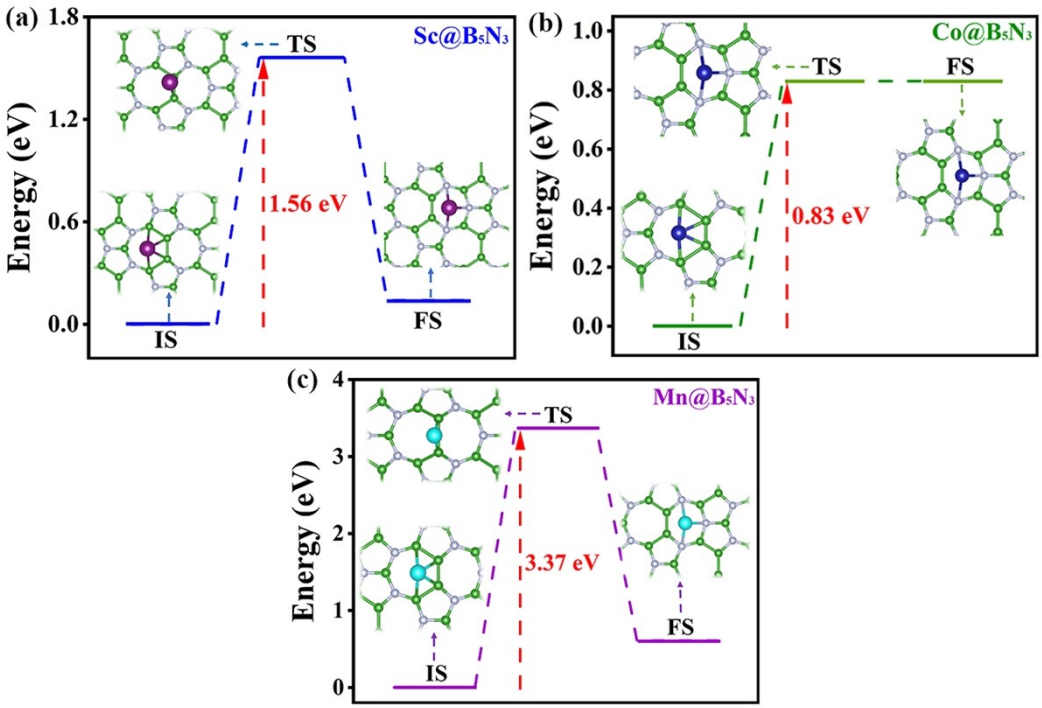

Fig. S12. Diffusion free energy pathways of (a) Sc, (b) Co, and (c) Mn to the adjacent binding sites. B, N, Sc, Co, and Mn are denoted by green, silver, purple, deep blue, and light blue spheres, respectively.

Table S1: Calculated zero-point energy corrections (unit: eV).

B_5N_3		$Sc@B_5N_3$		$Ti@B_5N_3$		$V@B_5N_3$	
Adsorbate	ZPE (eV)	Adsorbate	ZPE (eV)	Adsorbate	ZPE (eV)	Adsorbate	ZPE (eV)
*COOH	0.64	*COOH	0.61	*COOH	0.62	*COOH	0.61
*OCHO	0.67	*OCHO	0.61	*OCHO	0.61	*OCHO	0.61
*CO	0.23	*CO	0.18	*CO	0.20	*CO	0.19
*HCOOH	0.89	*HCOOH	0.88	*HCOOH	0.91	*HCOOH	0.89
*COH	0.55	*COH	0.42	*COH	0.49	*COH	0.50
*CHO	0.49	*CHO	0.45	*CHO	0.46	*CHO	0.47
*H_2CO	0.71	*H_2CO	0.73	*H_2CO	0.72	*H_2CO	0.78
*H_2COOH	1.27	*HCOH	0.72	*HCOH	0.76	*HCOH	0.76
*HCOH	0.84	*H_2COH	1.10	*H_2COH	1.06	*H_2COH	1.08
*H_2COH	1.08	*CH	0.28	*CH_2	0.56	*CH	0.41
*CH	0.40	*CH_2	0.54	*CH_3	0.88	*CH_2	0.60
*CH_2	0.73	*CH_3	0.87	*CH_4	1.24	*CH_3	0.88
*CH_3	0.97	*CH_4	1.23	*H_2COOH	1.22	*CH_4	1.23
*H_3COH	1.37	*H_3COH	1.39	*H_3COH	1.41	*H_3COH	1.38
*CH_4	1.20	*H_3CO	1.10	*H_3CO	1.08	*H_3CO	1.09
*H_3CO	1.09	*O	0.08	*O	0.09	*O	0.08
*O	0.08	*OH	0.38	*OH	0.39	*OH	0.39
*OH	0.40	*H_2O	0.64	*H	0.18	*H_2O	0.64
*H_2O	0.66	*H	0.19	*H_2O	0.63	*H	0.18
*H	0.25						

Cr@B_5N_3		**Mn@B_5N_3**		**Fe@B_5N_3**		**Co@B_5N_3**	
Adsorbate	ZPE (eV)	Adsorbate	ZPE (eV)	Adsorbate	ZPE (eV)	Adsorbate	ZPE (eV)
*COOH	0.63	*COOH	0.60	*COOH	0.62	*COOH	0.63
*OCHO	0.65	*OCHO	0.63	*OCHO	0.62	*OCHO	0.60
*CO	0.19	*CO	0.18	*CO	0.25	*CO	0.22
*HCOOH	0.90	*HCOOH	0.90	*HCOOH	0.93	*HCOOH	0.92
*COH	0.48	*COH	0.41	*COH	0.48	*COH	0.49
*CHO	0.46	*CHO	0.43	*CHO	0.46	*H_2CO	0.79
*H_2CO	0.77	*H_2CO	0.71	*H_2CO	0.78	*HCOH	0.80
*HCOH	0.77	*HCOH	0.78	*HCOH	0.80	*H_2COH	1.06
*H_2COH	1.14	*H_2COH	1.06	*H_2COH	1.22	*H_2COOH	1.22
*CH_2	0.62	*CH_2	0.57	*CH	0.35	*CH_2	0.59
*CH_3	0.89	*CH_3	0.90	*CH_2	0.62	*CH_3	0.92
*H_2COOH	1.22	*CH_4	1.18	*CH_3	0.93	*CH_4	1.22
*CH_4	1.24	*H_3COH	1.35	*CH_4	1.23	*H_3COH	1.42
*H_3COH	1.37	*H_3CO	1.08	*H_3COH	1.39	*H_3CO	1.09
*H_3CO	1.08	*O	0.08	*H_3CO	1.09	*O	0.08
*O	0.09	*OH	0.38	*O	0.08	*OH	0.39
*OH	0.38	*H_2O	0.66	*OH	0.40	*H_2O	0.63
*H_2O	0.64	*H	0.19	*H_2O	0.64	*H	0.21
*H	0.17			*H	0.18		

Ni@B_5N_3		**Cu@B_5N_3**		**Zn@B_5N_3**	
Adsorbate	ZPE (eV)	Adsorbate	ZPE (eV)	Adsorbate	ZPE (eV)
*COOH	0.62	*COOH	0.62	*COOH	0.61
*OCHO	0.61	*OCHO	0.60	*OCHO	0.60
*CO	0.21	*CO	0.19	*CO	0.17
*HCOOH	0.93	*HCOOH	0.91	*HCOOH	0.90
*CHO	0.46	*CHO	0.46	*CHO	0.48
*COH	0.43	*COH	0.49	*COH	0.50
*H_2CO	0.78	*H_2CO	0.75	*H_2CO	0.73
*H_2COH	1.08	*H_2COH	1.02	*H_2COH	0.96
*HCOH	0.81	*HCOH	0.82	*HCOH	0.79
*H_2COOH	1.21	*H_2COOH	1.19	*H_2COOH	1.20
*CH	0.33	*CH_2	0.60	*CH_2	0.58
*CH_2	0.63	*CH_3	0.93	*CH_3	0.93
*CH_3	0.92	*CH_4	1.22	*CH_4	1.19
*CH_4	1.26	*H_3COH	1.38	*H_3COH	1.37
*H_3COH	1.42	*H_3CO	1.11	*H_3CO	1.10
*H_3CO	1.08	*O	0.07	*O	0.08
*O	0.09	*OH	0.38	*OH	0.39
*OH	0.40	*H_2O	0.64	*H_2O	0.65
*H_2O	0.65	*H	0.19	*H	0.18
*H	0.20				