Electronic Supplementary Information

Defective h-BN Sheet Embedded Atomic Metals as Highly Active and Selective Electrocatalysts for NH_3 Fabrication via NO Reduction

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Table S1. The binding energy of Mo atom on defective h-BN with B-vacancy and the adsorption energy of NO on Mo-embedded h-BN. The unit is eV.

	4*4 supercell	5*5 supercell	6*6 supercell
E_b	-9.74	-9.71	-9.75
$E_{ads(NO,end-on)}$	-3.09	-3.12	-3.13

Table S2. Charge transfer between TM atoms and the defective h-BN sheet by Bader charge analysis.

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Mo
ΔQ (e^-)	1.33	1.30	1.27	1.25	1.04	0.91	0.89	0.92	1.22

Table S3. Bond lengths in units of Å and adsorption energies for NO on TMs @h-BN in units of eV.

	Side-on adsorption				End-on adsorption		
	N-O	N- TM	O- TM	E_{ads}	N- O	N- TM	E_{ads}
Ti	1.27	2.17	2.08	-2.34	1.21	1.98	-2.67
V	1.30	1.92	1.91	-3.11	1.21	1.78	-3.05
Cr	1.28	1.88	1.94	-1.64	1.21	1.74	-2.08
Mn	-	-	-	-	1.20	1.71	-2.63
Fe	1.24	1.81	2.09	-1.89	1.19	1.69	-2.50
Co	-	-	-	-	1.19	1.71	-1.87
Ni	-	-	-	-	1.19	1.72	-1.67
Cu	-	-	-	-	1.18	1.75	-1.17
Mo	1.35	1.89	1.97	-3.49	1,21	1.83	-3.09

Table S4. Atom charge of NO gas molecule and adsorbates on the Cu doped defective h-BN sheet based on Bader charge analysis.

	NO	*NO	*HNO	*NOH
N	0.45	0.23	-0.14	-0.13
O	-0.45	-0.38	-0.40	-0.71

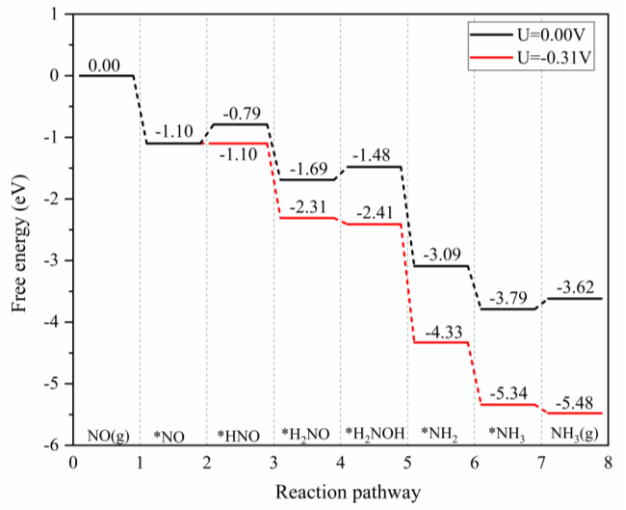

Figure S1. Free-energy diagram for the NOER on Ni@h-BN at low coverage along the most energetically favorable (Path II) pathway.

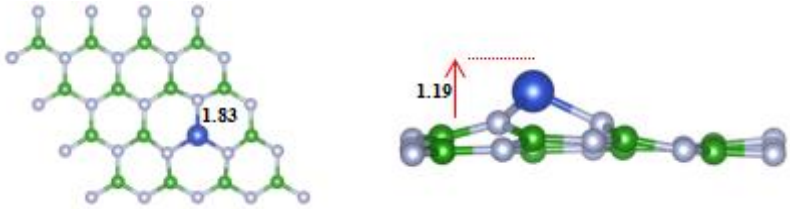

Figure S2. Optimized structure of Cu-embedded h-BN sheet.The unit of bond length is Å.

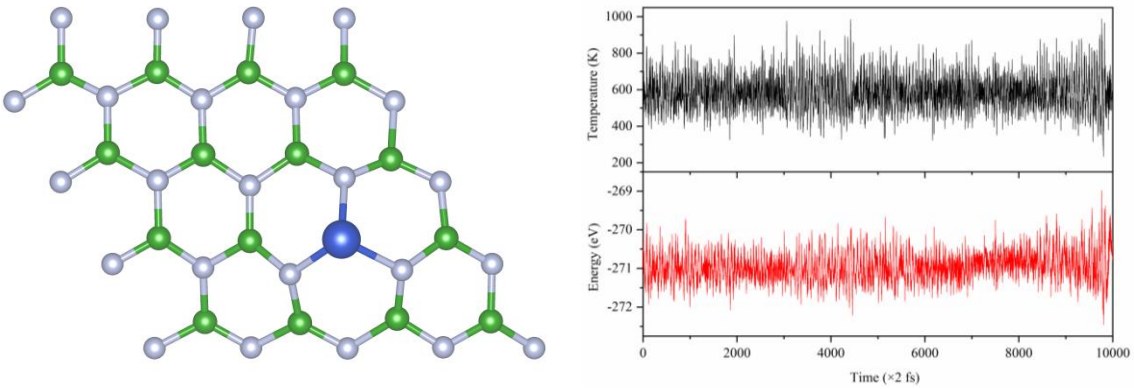

Figure S3. (a) Geometry snapshot (b)Variation of temperature and total energy of single Cu atom decorated defective h-BN during AIMD simulation. The simulation was running under 600 K for 20 ps with a time step of 2 fs. Green, white and blue balls represent B, N, and Cu atoms, respectively

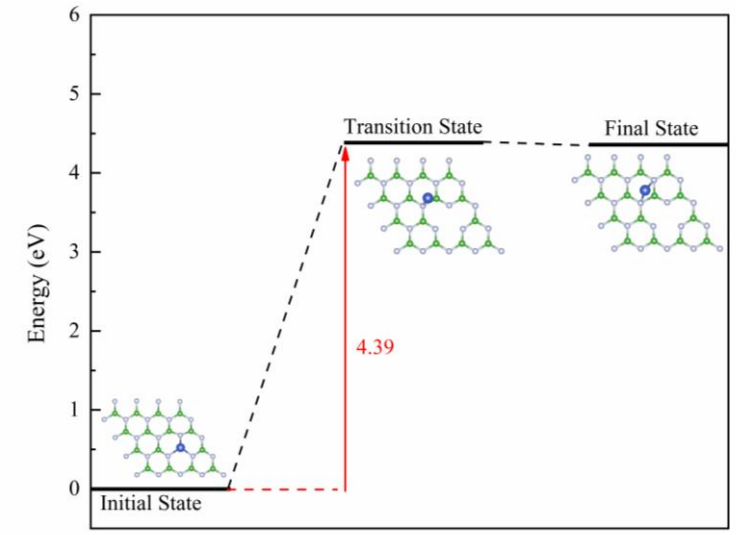

Figure S4. The minimum energy path (MEP) for the diffusion of the embedded Cu atom from the defect B vacancy to a neighboring hollow site.

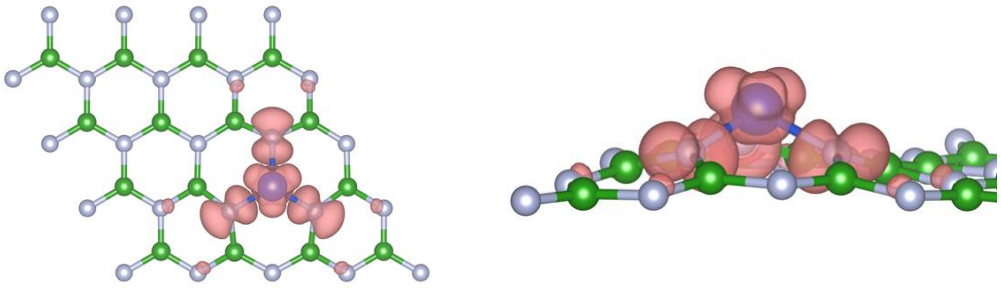

Figure S5. spin-polarized density for Cu-embedded h-BN sheet in the 3D isosurface version with a value of 0.00623 electrons $Å^{-3}$.

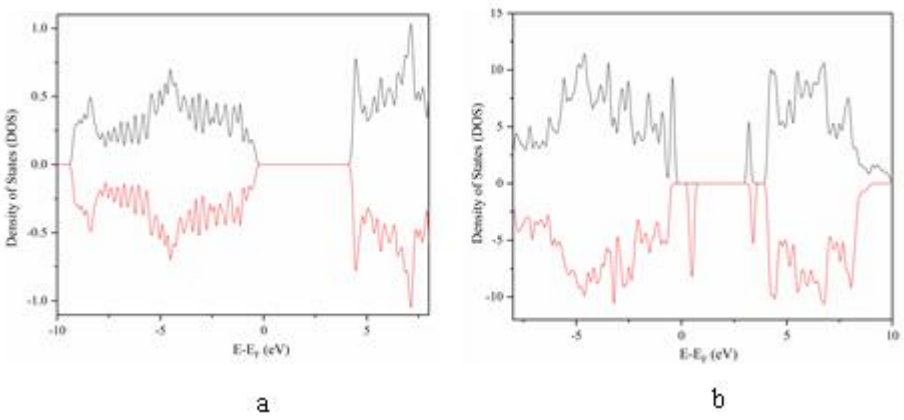

Figure S6. Density of states profiles of (a) perfect h-BN and (b) Cu-doped h-BN sheet with B-vacancy. The Fermi level was shifted to zero.

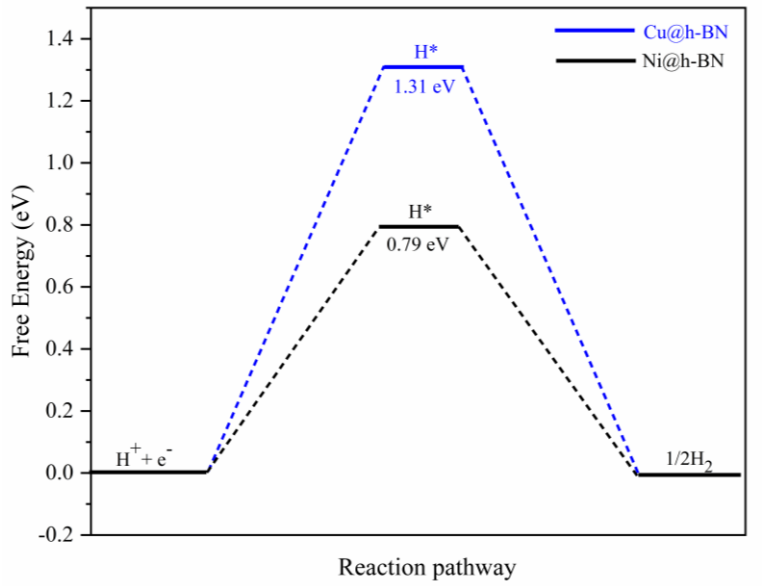

Figure S7. Gibbs free energy diagram of Cu@h-BN and Ni@h-BN for HER.