Supporting information

Important role of surface charge on new mechanism of nitrogen reduction

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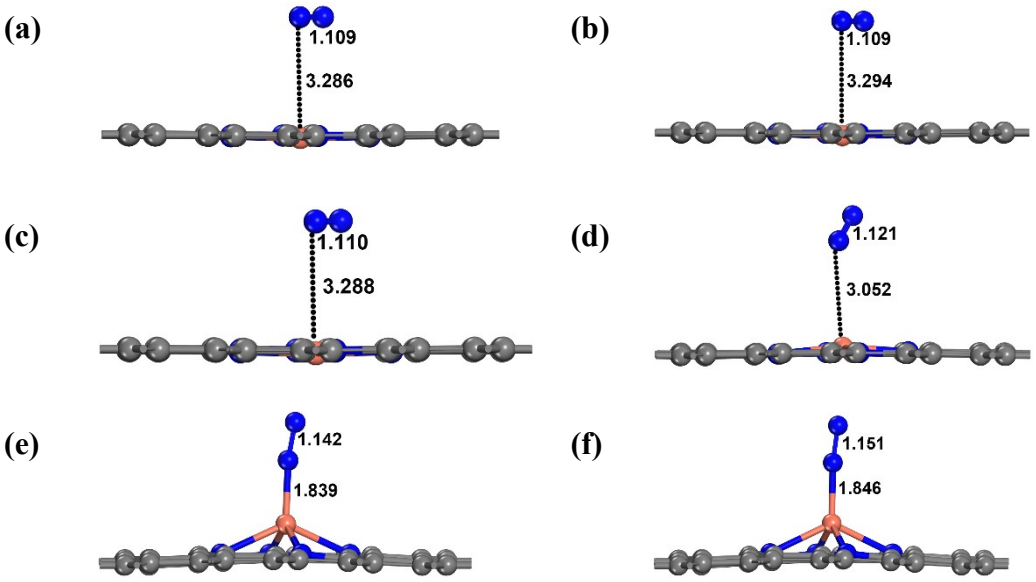

Fig. S1. Side views of the adsorption configurations of N_2 on Cu-N_4-graphene under the charge densities of -0.38 (a), -0.75 (b), -1.13 (c), -1.51 (d), -1.88 (e) and -2.26 × 10^{14} (f) e·cm^{-2}. Date in the figure refer to the atomic distances in Å.

Table S1 Results of E_{ZPE} and TS obtained from vibration computations for all adsorbates

Species	E_{ZPE} (eV)	TS (eV)
*	0.59	1.04
*N_2	0.67	1.18
*NNH	0.67	1.15
*NHNH	0.68	1.21
*NNH_2	0.67	1.16
*N-NH_3	0.71	1.27
*N	0.64	1.12
*$NHNH_2$	0.69	1.22
*NH-NH_3	0.74	1.35
*NH	0.64	1.10
*NH_2	0.67	1.16
*NH_3	0.68	1.23

Notes: E_{ZPE} stands for zero point energy and TS represents the product of temperature and entropy. "*" represents the chemisorbed species.

Table S2 Mulliken net charges (e) on N_2, Cu, the N_4 and Cu-N_4 clusters, and the Cu-N_4-graphene substrate in the optimized configurations of N_2 adsorption on Cu-N_4-graphene under different surface charges

	Charge density	Mulliken net charge (e)				
	(10^{14} e·cm^{-2})	N_2	Cu	N_4	Cu-N_4	Cu-N_4-graphene
0.0	0.00	0.009	0.414	-1.472	-1.058	-0.009
0.5	-3.77	0.004	0.385	-1.521	-1.136	-0.504
1.0	-7.53	-0.002	0.359	-1.938	-1.579	-0.999
1.5	-1.13	-0.018	0.335	-1.953	-1.618	-1.484
2.0	-1.51	-0.140	0.414	-1.495	-1.081	-1.857
2.5	-1.88	-0.254	0.414	-1.511	-1.097	-2.248
3.0	-2.26	-0.352	0.414	-1.925	-1.511	-2.645

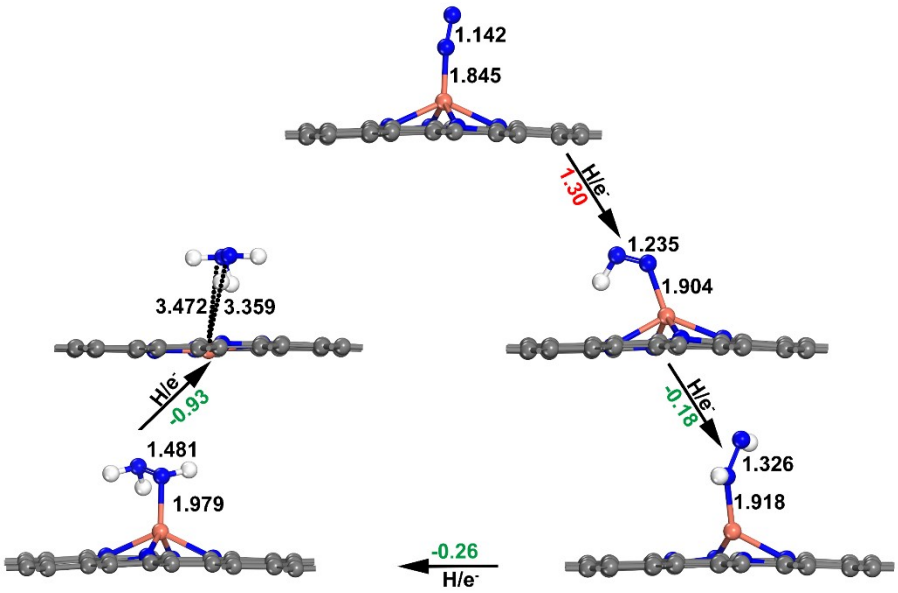

Fig. S2. Side views of the optimized configurations formed in individual hydrogenation processes of NRR under a charge density of -1.88 × 10^{14} e·cm^{-2}, finally forming hydrazine—NH_2NH_2. Data in black represent the bond lengths in Å. Those in red and green refer the changes of Gibbs free energy (Δ*G,* eV) of individual hydrogenation steps (red, endothermic; green, exothermic)

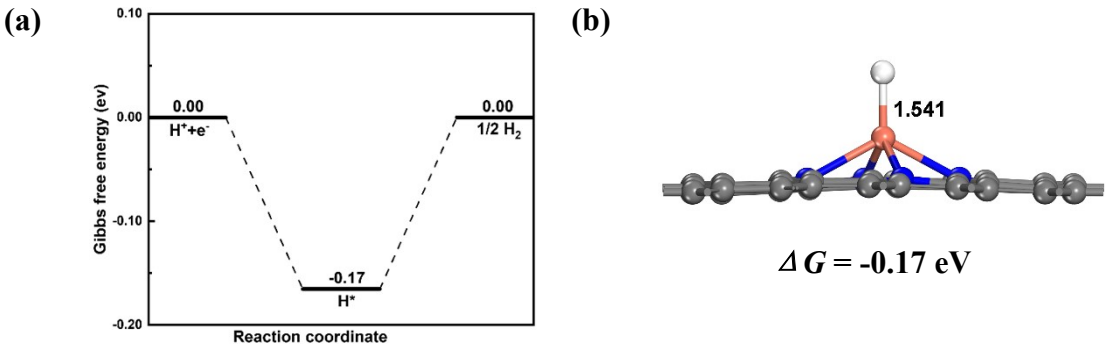

Fig. S3. Gibbs free energy profile (a) and the side view of the optimized configuration (b) of H adsorption on Cu-N_4-graphene under a surface charge density of -1.88 × 10^{14} e·cm^{-2}. The bond length is labeled in Å. Δ*G* refers the change of Gibbs free energy of H adsorbed on Cu-N_4-graphene.