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Supplementary Materials

Fe_3 Cluster Anchored on the C_2N Monolayer for Efficient Electrochemical Nitrogen Fixation

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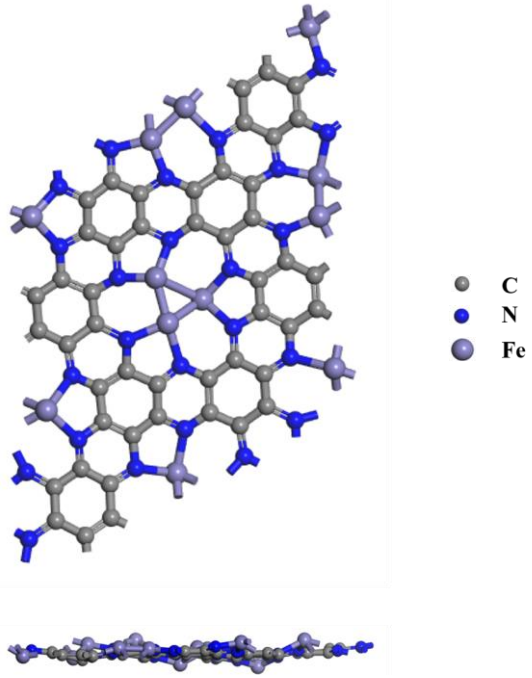

Figure S1. Top and side views of the final structure of $Fe_3@C_2N$ through a 10 ps FPMD simulation at 800 K.

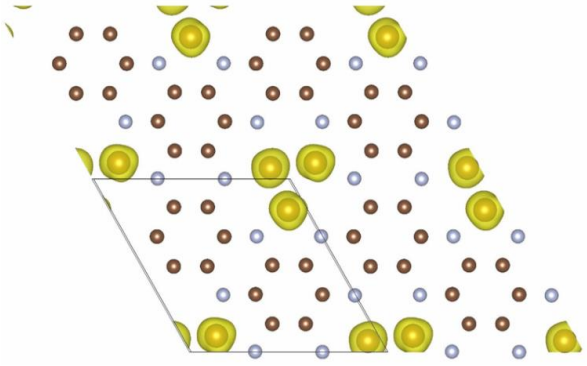

Figure S2. The magnetism distribution of the $Fe_3@C_2N$.

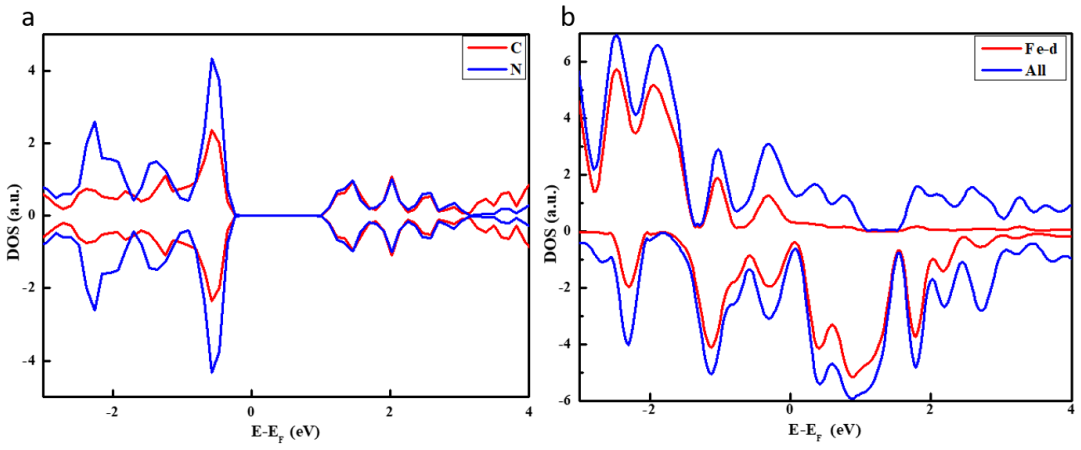

Figure S3. Density of states (DOS) of C_2N (**a**) and $Fe_3@C_2N$ (**b**).

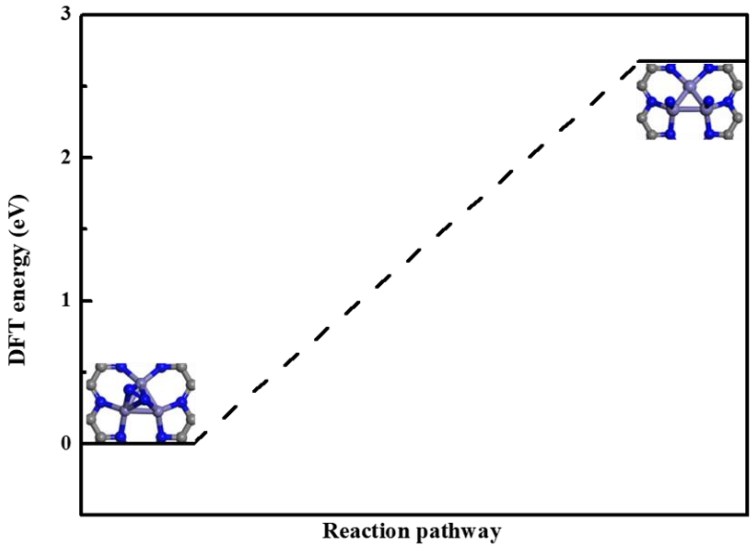

Figure S4. The energy diagram of dissociation mechanism on the $Fe_3@C_2N$.

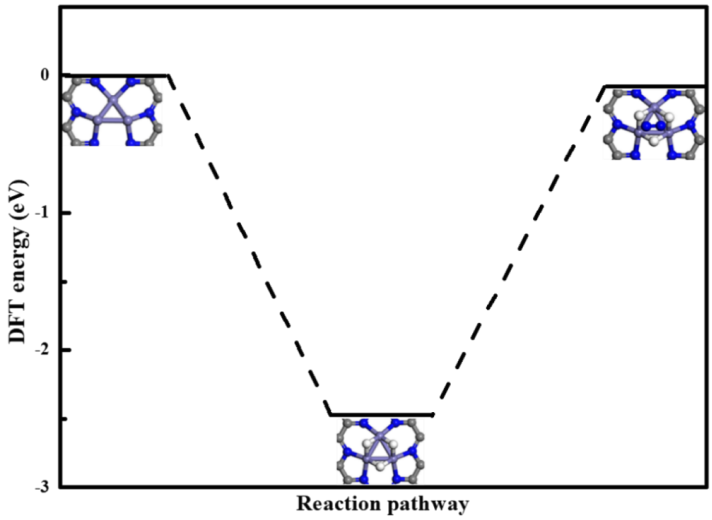

Figure S5. The energy diagram of the surface hydrogenation mechanism on the $Fe_3@C_2N$.

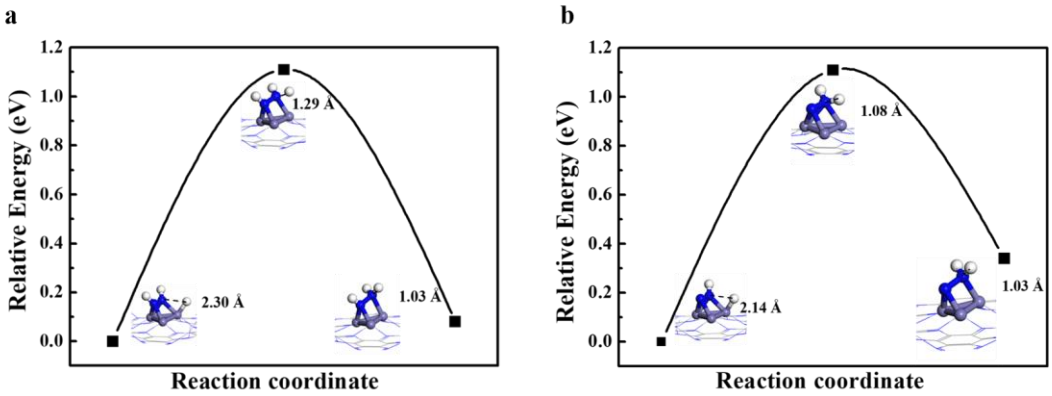

Figure S6. The reaction pathway of the potential limiting step of the enzymatic mechanism (a) and the consecutive mechanism (b).

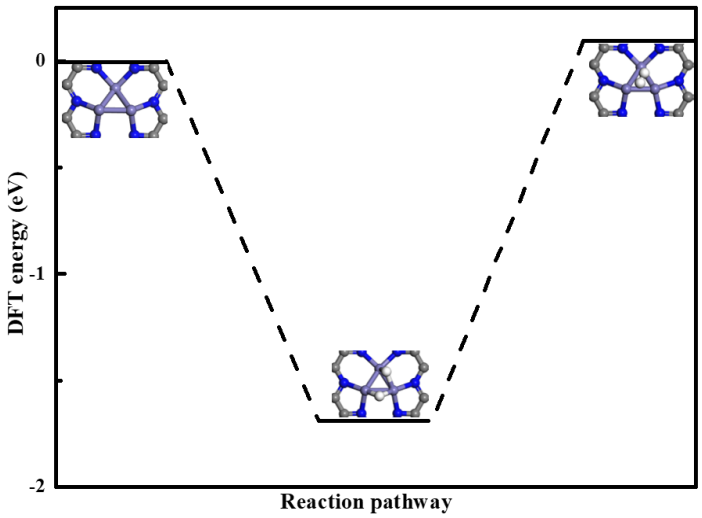

Figure S7. The energy diagram of HER on the $Fe_3@C_2N$.

Table S1 The calculated zero-point energy (ZPE, in eV) and entropy (T = 298.15 K, in eV, taken from the NIST-JANAF thermodynamics table [S1]) of the gas molecules.

Molecules	ZPE	TS
N_2	0.17	0.60
NH_3	0.93	0.60
H_2	0.33	0.41

Table S2 The calculated E(DFT), ZPE and TS of intermediates on different paths (in eV).

Consecutive	**E(DFT)**	**ZPE**	**TS**
***N_2**	-1.45	0.19	0.09
***NNH**	-0.08	0.51	0.09
***NNH_2**	0.46	0.85	0.10
***NNH_3**	-1.74	1.12	0.18
***N**	0.83	0.09	0.03
***NH**	-1.12	0.40	0.04
***NH_2**	0.24	0.72	0.07
***NH_3**	0.18	0.99	0.12
NH_3(g)	0.55	--	--
Enzymatic	**E(DFT)**	**ZPE**	**TS**
***N_2**	-1.45	0.19	0.09
***NNH**	-0.08	0.51	0.09
***HNNH**	-0.37	0.82	0.09
***H_2NNH**	0.20	1.17	0.11
***H_2NNH_2**	-1.99	1.38	0.19
***H_2NNH_3**	-0.14	1.66	0.26
***NH_2**	0.96	0.72	0.07
***NH_3**	0.18	0.99	0.12
NH_3(g)	0.55	--	--

Table S3 The estimated reaction rate of each step on different paths (k_0 is the prefactor of the estimated reaction rate $k = k_0\exp(-\Delta G/kT)$).

Consecutive	**T = 300 K**	**T = 800 K**
***NN + H → *NNH**	$1.98\times10^{-5}\ k_0$	$1.72\times10^{-2}\ k_0$
***NNH + H → *NNH$_2$**	$1.14\times10^{-14}\ k_0$	$5.91\times10^{-6}\ k_0$
***NH + H → *NH$_2$**	$8.48\times10^{-10}\ k_0$	$3.96\times10^{-4}\ k_0$
***NH$_2$ + H → * NH$_3$**	$4.06\times10^{-8}\ k_0$	$1.69\times10^{-3}\ k_0$
Enzymatic	**T = 300 K**	**T = 800 K**
***NN + H → *NNH**	$1.98\times10^{-5}\ k_0$	$1.72\times10^{-2}\ k_0$
***HNNH + H → *H$_2$NNH**	$2.66\times10^{-10}\ k_0$	$2.57\times10^{-4}\ k_0$
***H$_2$NNH$_2$ + H → *H$_2$NNH$_3$**	$1.42\times10^{-2}\ k_0$	$2.03\times10^{-1}\ k_0$
***NH$_2$ + H → * NH$_3$**	$4.06\times10^{-8}\ k_0$	$1.69\times10^{-3}\ k_0$

Reference

S1. Chase, M. W. NIST-JANAF Thermochemical Tables. American Chemical Society, New York, **1998**.