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

Efficient Nitric Oxide Reduction to Ammonia on Metal-Free Electrocatalyst

Qian Wu, Hao Wang, Shiying Shen, Baibiao Huang, Ying Dai*, Yandong Ma*

School of Physics, State Key Laboratory of Crystal Materials, Shandong University, Shandanan Str. 27, Jinan 250100, China

*Email: daiy60@sina.com (Y.D.); yandong.ma@sdu.edu.cn (Y.M.)

Computational methods

HER mechanism

$$H^+ + e^- \rightarrow 1/2\ H_2\ (g)$$

The Gibbs free energy of hydrogen adsorption (ΔG_{H*})[1] under standard condition can be obtained by

$$\Delta G_{H*} = \Delta E_{H*} + \Delta E_{ZPE} - T\Delta S_H$$

where ΔE_H is the hydrogen adsorption energy, ΔE_{ZPE} and $T\Delta S_H$ are the zero-point energy difference and entropy difference between adsorbed H* atom and gas-phase H_2, respectively. In detail, ΔE_H, ΔE_{ZPE} and ΔS_H are given by

$$\Delta E_H = E_{H*} - E^* - \frac{1}{2}E_{H_2}$$

$$\Delta E_{ZPE} = E_{ZPE}^{H*} - \frac{1}{2}E_{ZPE}^{H_2}$$

$$\Delta S_H = S_{H*} - \frac{1}{2}S_{H_2}$$

where E_{H*}, E^*, and E_{H_2} are the energies of catalyst with one adsorbed H*, the free electrocatalyst, and gas-phase H_2, respectively. E_{ZPE}^{H*} and $E_{ZPE}^{H_2}$ are the zero-point energies of adsorbed H* without the contribution of catalyst and gas-phase H_2, respectively. S_{H*} and S_{H_2} represent the entropies of adsorbed H* atom and gas-phase H_2 at standard condition, respectively.

The entropy is given by[2]

$$S(T) = \sum_{i=1}^{3N}\left[-R\ln\left(1 - e^{-\frac{hv_i}{k_BT}}\right) + \frac{N_A hv_i\ e^{-hv_i/k_BT}}{T\ \ 1 - e^{-hv_i/k_BT}}\right]$$

where R stands for the universal gas constant, k_B is the Boltzmann constant, h is Plank's constant, N_A is Avogadro's number, v_i represents the frequency and N is the number of adsorbed atoms.

NORR mechanism

The Gibbs free energy of each elemental step (ΔG) of the NORR is adopted following the works of Nørskov et al[3,4].

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S + \Delta G_U$$

where ΔE is the changed energy, ΔE_{ZPE} and ΔS are the change of zero point vibrational energy and the change of entropy, respectively, which can be obtained by the vibrational frequency of the optimized structures. T is the temperature and set to 298.15 K. The $\Delta G_U = -eU$, where e and U are

the transferred charge and the electrode potential, respectively.

Microkinetic modeling

The reaction rate constant k is calculated by the Arrhenius-type based equation[5]

$$k = \frac{k_b T}{h} e^{\frac{-\Delta G_{TS}}{k_b T}}$$

where k_b is the Boltzmann constant, h represents the Planck constant and T is the temperature in kelvin. ΔG_{TS} is the Gibbs free energy difference between the initial state and transition state and can be calculated by CI-NEB method.

Table S1. Charge transfers (ΔQ) between NO and P for NO adsorbed 1P@C_2N and 2P@C_2N.

	1P@C_2N (end-on)	2P@C_2N (end-on)	2P@C_2N (side-on)
ΔQ (e)	0.23	1.44	1.80

Table S2. Elementary reactions for all the considered mechanisms for NORR to NH_3 synthesis.

End-on adsorption		Side-on adsorption	
Reaction Pathway	Reaction Steps	Reaction Pathway	Reaction Steps
N-distal	NO(g) → *NO (end-on) *NO + H^+ + e^- → *HNO *HNO + H^+ + e^- → *H_2NO *H_2NO + H^+ + e^- → *H_2NOH *H_2NOH + H^+ + e^- → *NH_2 + H_2O *NH_2 + H^+ + e^- → NH_3(g)	O-first	NO(g) → *NO (side-on) *NO + H^+ + e^- → *NOH *NOH + H^+ + e^- → *N + H_2O *N + H^+ + e^- → *NH *NH + H^+ + e^- → *NH_2 *NH_2 + H^+ + e^- → NH_3(g)
N-alternating	NO(g) → *NO (end-on) *NO + H^+ + e^- → *HNO *HNO + H^+ + e^- → *HNOH	O-enzymatic	NO(g) → *NO (side-on) *NO + H^+ + e^- → *NOH *NOH + H^+ + e^- → *HNOH

	*HNOH + H^+ + e^- → *H_2NOH *H_2NOH + H^+ + e^- → *NH_2 + H_2O *NH_2 + H^+ + e^- → NH_3(g)		*HNOH + H^+ + e^- → *NH + H_2O *NH + H^+ + e^- → *NH_2 *NH_2 + H^+ + e^- → NH_3(g)
O-alternating	NO(g) → *NO (end-on) *NO + H^+ + e^- → *NOH *NOH + H^+ + e^- → *HNOH *HNOH + H^+ + e^- → *NH + H_2O *NH + H^+ + e^- → *NH_2 *NH_2 + H^+ + e^- → NH_3(g)	N-enzymatic	NO(g) → *NO (side-on) *NO + H^+ + e^- → *NOH *NOH + H^+ + e^- → *HNOH *HNOH + H^+ + e^- → *H_2NOH *H_2NOH + H^+ + e^- → *NH_2 + H_2O *NH_2 + H^+ + e^- → NH_3(g)
O-distal	NO(g) → *NO (end-on) *NO + H^+ + e^- → *NOH *NOH + H^+ + e^- → *N + H_2O *N + H^+ + e^- → *NH *NH + H^+ + e^- → *NH_2 *NH_2 + H^+ + e^- → NH_3(g)	N-first	NO(g) → *NO (side-on) *NO + H^+ + e^- → *NOH *NOH + H^+ + e^- → *H_2NO *H_2NO + H^+ + e^- → *O *O + H^+ + e^- → *OH *OH+ H^+ + e^- → H_2O

Table S3. Computed total energies (E_{tot}), zero-point energies (E_{ZPE}) and entropy (TS) of intermediates for NORR on NO adsorbed 1P@C_2N with end-on configuration.

	E_{tot} (eV)	E_{ZPE} (eV)	TS (eV)	G (eV)
*NO	646.55	0.15	0.22	646.62
*NOH	640.46	0.49	0.15	650.12
*HNO	650.77	0.47	0.18	650.48
*HNOH	655.14	0.81	0.16	654.49
*H_2NO	654.50	0.81	0.17	653.86
*H_2NOH	658.47	1.09	0.31	657.69
*N	640.45	0.07	0.12	640.50
*NH	645.47	0.37	0.08	645.18
*NH_2	650.22	0.69	0.10	649.63
NH_3	653.60	0.96	0.27	652.91

Table S4. Computed total energies (E_{tot}), zero-point energies (E_{ZPE}) and entropy (TS) of intermediates for NORR on NO adsorbed 2P@C_2N with end-on configuration.

	E_{tot} (eV)	E_{ZPE} (eV)	TS (eV)	G (eV)
*NO (end-on)	651.64	0.18	0.11	651.57
*NOH	655.98	0.50	0.10	655.58
*HNO	655.26	0.48	0.16	654.93
*N	646.88	0.11	0.02	646.79
*NH	650.90	0.40	0.05	650.55
*NH_2	654.94	0.68	0.11	654.37
NH_3	658.53	0.96	0.25	657.82

Table S5. Computed total energies (E_{tot}), zero-point energies (E_{ZPE}) and entropy (TS) of intermediates for NORR on NO adsorbed 2P@C_2N with side-on configuration.

	E_{tot} (eV)	E_{ZPE} (eV)	TS (eV)	G (eV)
*NO (side-on)	651.81	0.18	0.09	651.72
*NOH	655.21	0.47	0.16	654.90
*HNO	656.23	0.51	0.09	655.84
*N	646.89	0.11	0.02	646.80
*HNOH	659.74	0.80	0.16	659.10
*H_2NO	660.16	0.81	0.20	659.55
*H_2NOH	665.92	1.07	0.17	665.02
*NH	650.90	0.40	0.05	650.55
*NH_2	654.73	0.68	0.13	654.18
NH_3	658.53	0.96	0.25	657.82
*O	645.83	0.09	0.05	645.79
*OH	649.90	0.36	0.08	649.62
H_2O	653.15	0.61	0.29	652.83

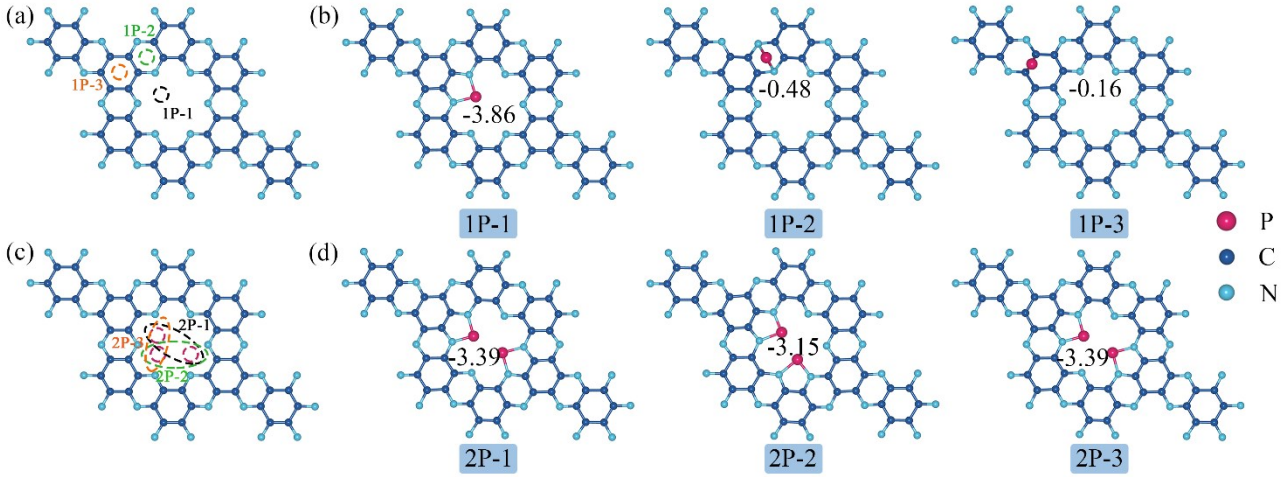

Figure S1. Possible doping sites of (a) single and (c) double P atoms on C_2N. Optimized structures of (b) single and (d) double P atoms doped C_2N, the corresponding adsorption energies are included.

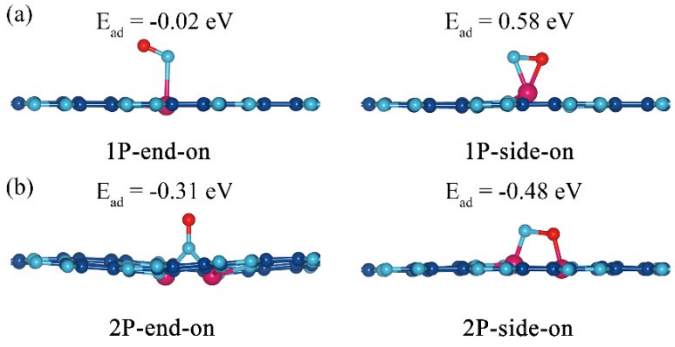

Figure S2. Crystal structures of NO adsorbed (a) 1P@C_2N and (b) 2P@C_2N with end-on and side-on configurations, the corresponding adsorption energies (E_{ad}) are included.

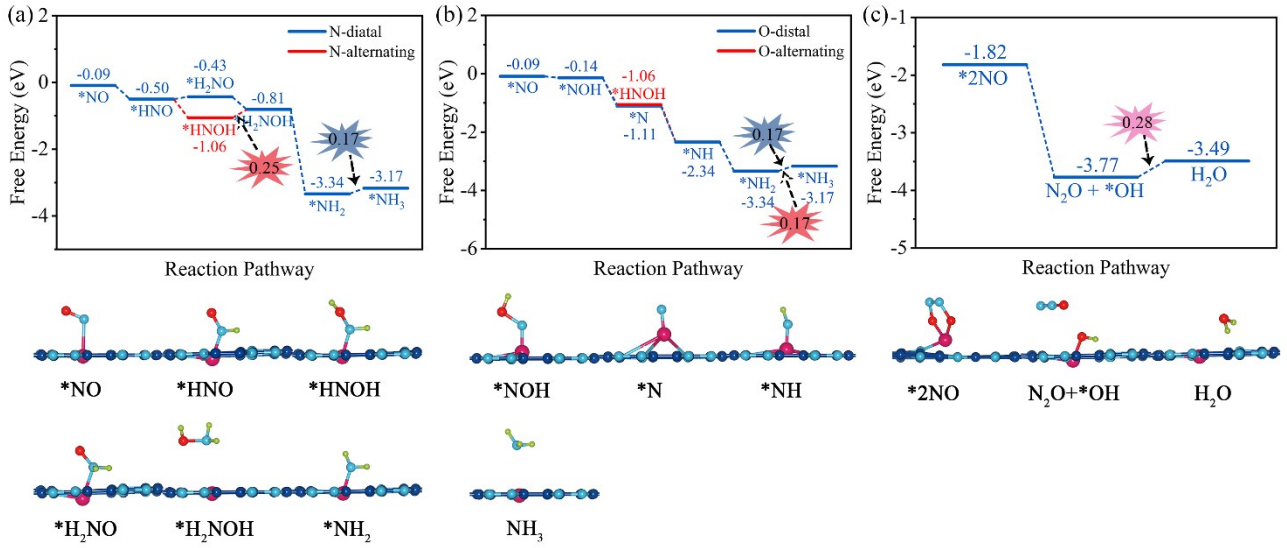

Figure S3. Optimized intermediates and calculated Gibbs free energy diagrams of NORR for NH_3 synthesis through (a) N-distal/alternating and (b) O-distal/alternating reaction pathways on $2P@C_2N$ at U = 0 V. (c) Optimized intermediates and calculated Gibbs free energy diagrams of NORR for N_2O synthesis on $2P@C_2N$ at U = 0 V.

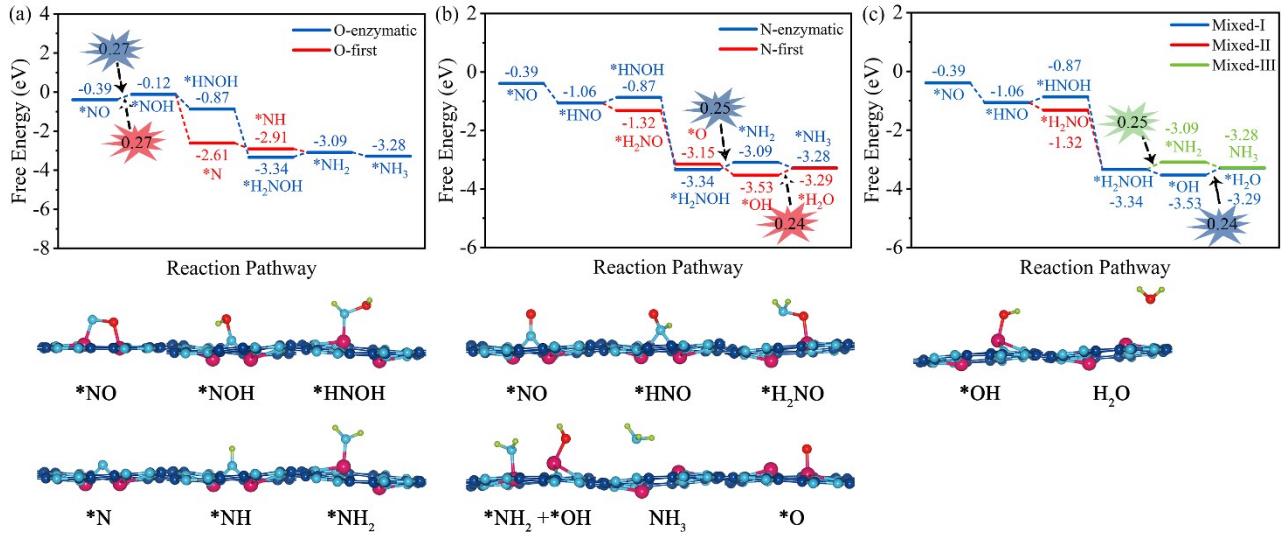

Figure S4. Optimized intermediates and calculated Gibbs free energy diagrams of NORR for NH_3 synthesis through (a) O-first/enzymatic, (b) N-first/enzymatic and (c) Mixed-I/II/III reaction pathways on $2P@C_2N$ at U = 0 V.

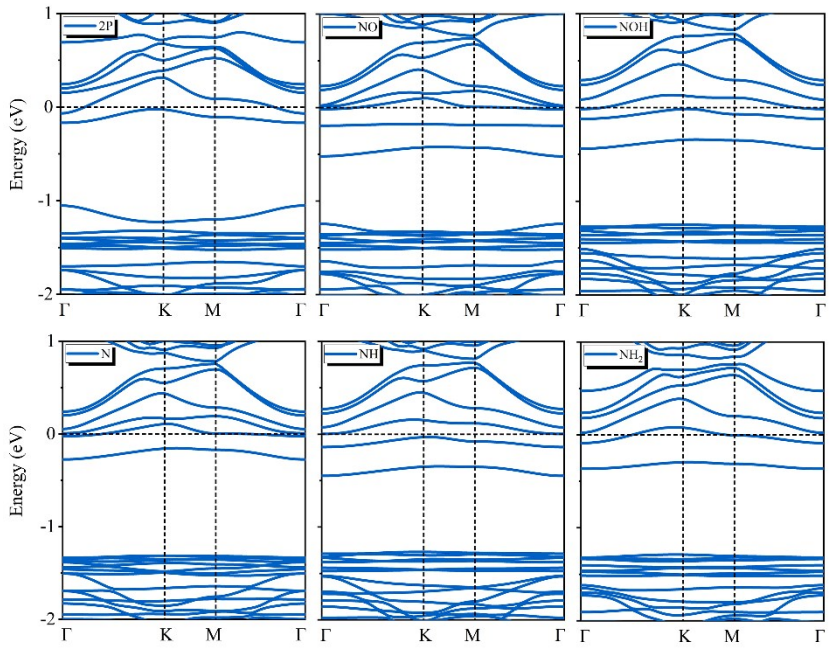

Figure S5. Band structures of intermediates for NORR on 2P@C_2N through O-distal pathway.

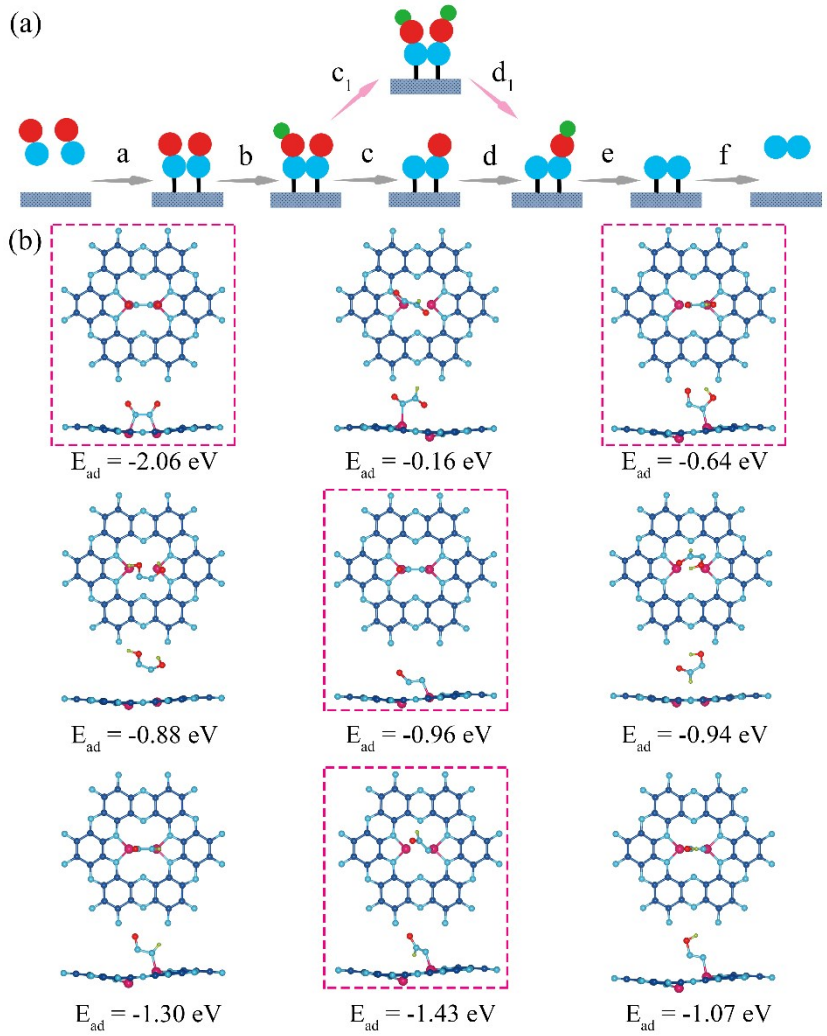

Figure S6. (a) Schematic illustration of the possible reaction pathways of NORR for N_2 synthesis. (b) Possible configurations and the corresponding adsorption energies for the intermediates. The dotted box marks the most stable adsorption configuration in each reaction step.

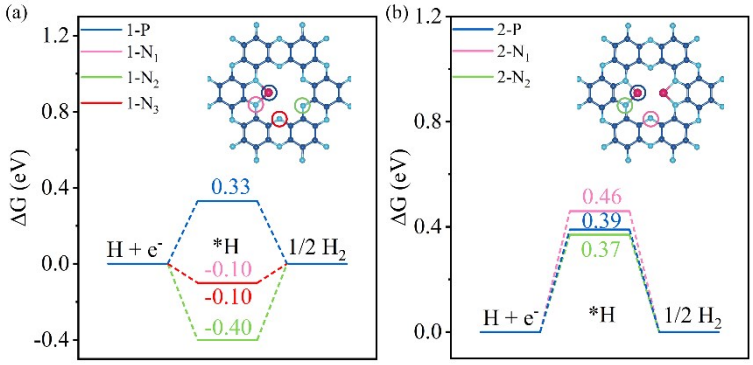

Figure S7. Gibbs free energy diagrams for HER on possible adsorption sites of (a) 1P@C_2N and (b) 2P@C_2N. Inserts illustrate the possible adsorption sites of H atom on 1P@C_2N and 2P@C_2N.

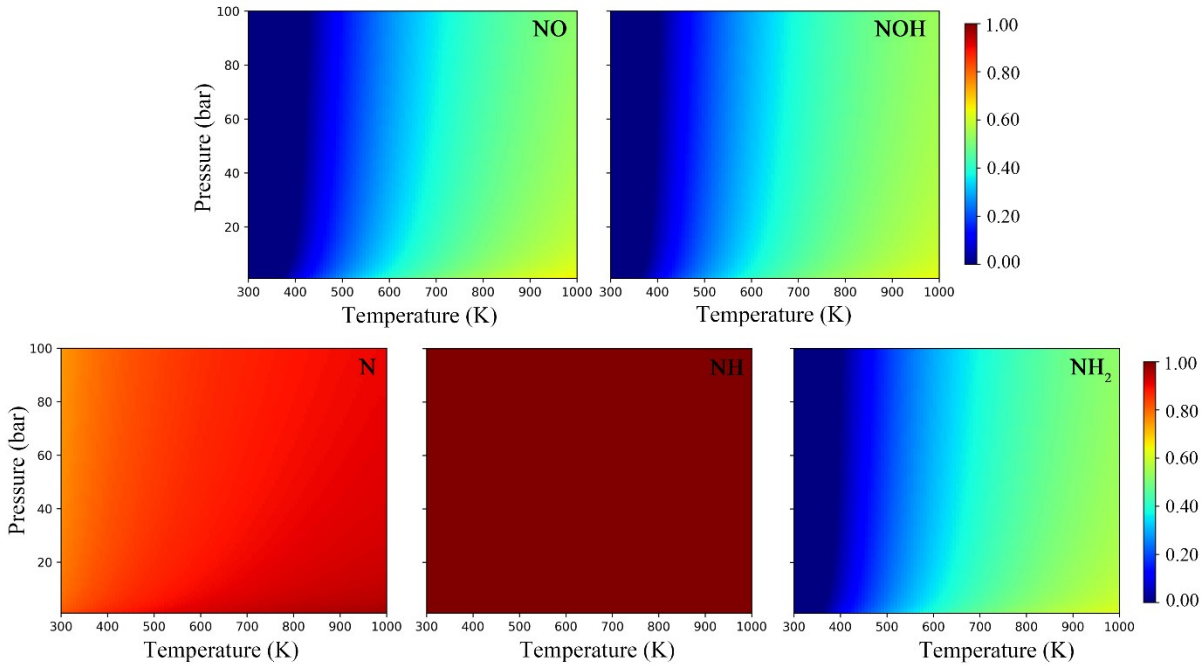

Figure S8. Coverage for surface species, i.e., *NO, *NOH, *N, *NH and *NH_2 on 2P@C_2N various with pressure (1–100 bar) and temperature (300–1000 K). H^+:NO ratio is fixed at 10.

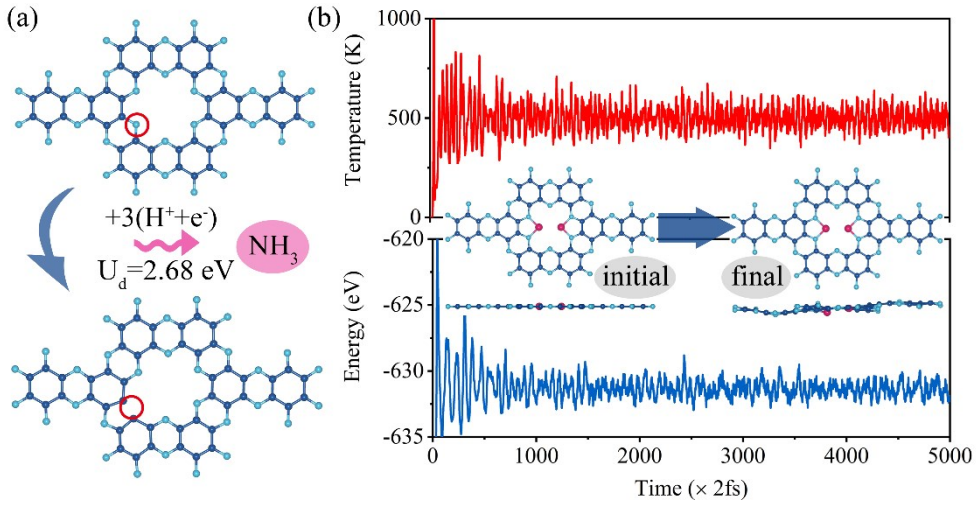

Figure S9. (a) Decomposition mechanism of C_2N substrate. (b) Variations of temperature and energy against the time for AIMD simulations of 2P@C_2N, insert are top and side views of the snapshot of initial and final structures. The simulation is run under 500 K for 10 ps with a time step of 2 fs.

References

1. Tsai, C., Abild-Pedersen, F. & Nørskov, J. K. *Nano Lett.* **14**, 1381–1387 (2014).
2. Zhu, Y. A., Chen, D. Zhou, X. G. & Yuan, W. K. *Catal. Today* **148**, 260–267 (2009).
3. Nørskov, J. K. et al. *J. Phys. Chem. B* **108**, 17886−17892 (2004).
4. Peterson, A. A. Abild-Pedersen, F. Studt, F. Rossmeisl, J. & Nørskov, J. K. *Energy Environ. Sci.* **3**, 1311−1315 (2010).
5. Lynggaard, H. Andreasen, A. Stegelmann, C. & Stoltze, P. *Prog. Surf. Sci.* **77**, 71–137 (2004).