Supplementary Information

Electrochemical reduction of N_2 to ammonia on Co single atoms embedded N-doped porous carbon under ambient conditions

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1. Supplementary Figures

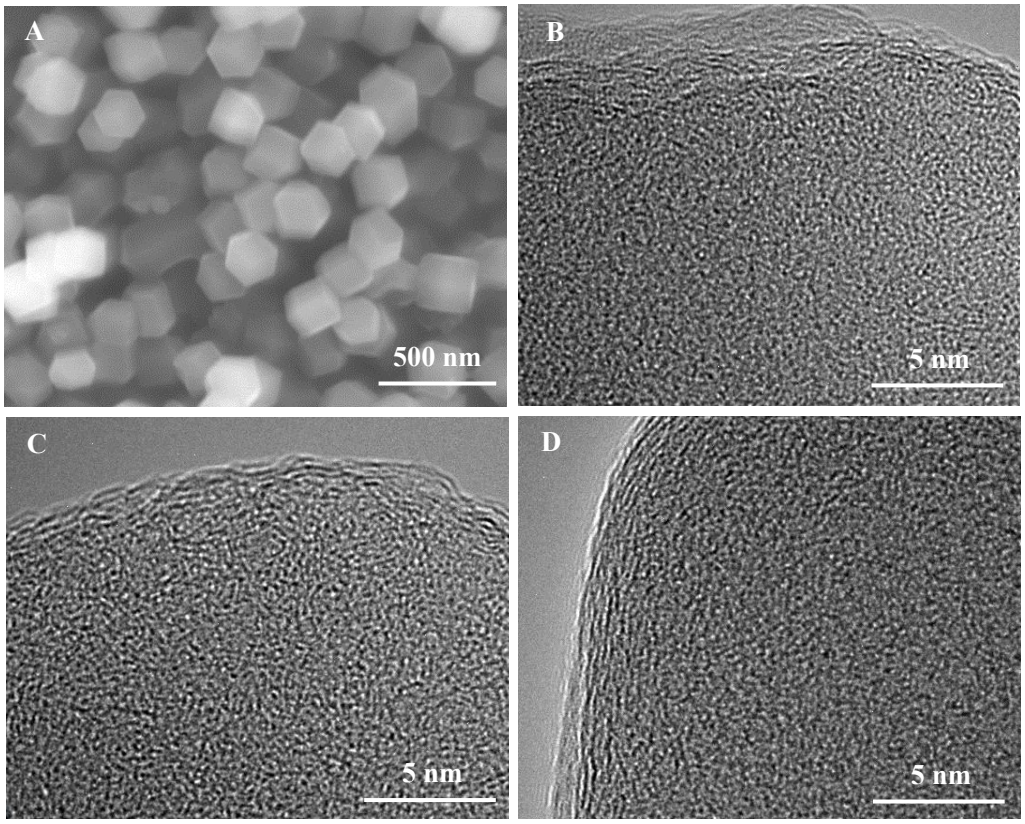

Fig. S1 (A) SEM image of Zn/Co bimetallic ZIF precursor, TEM images of (B) CSA/NPC-750, (C) CSA/NPC-850 and (D) CSA/NPC-950.

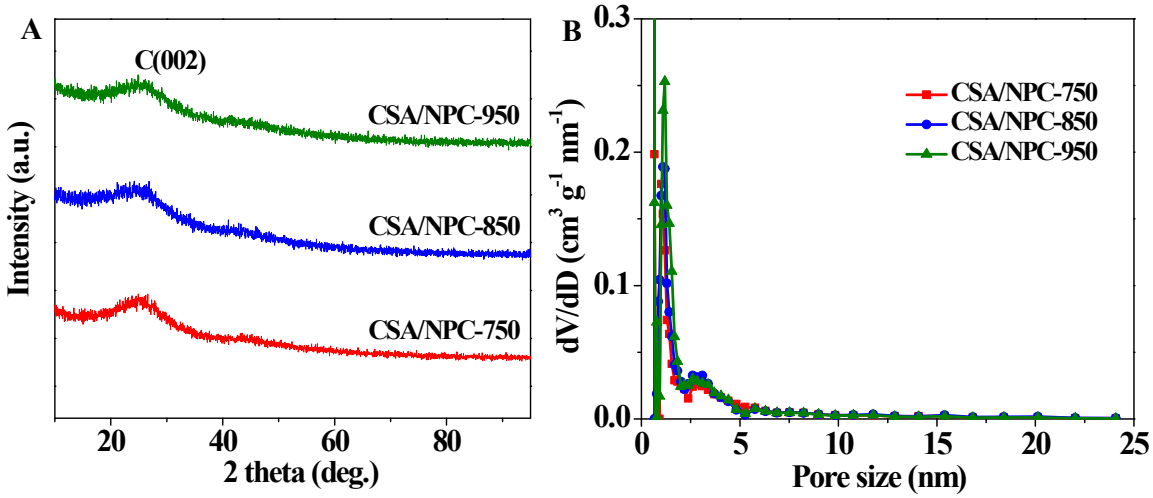

Fig. S2 (A) X-ray diffraction spectra and (B) pore size distribution of CSA/NPC-750, CSA/NPC-850 and CSA/NPC-950 (DFT method).

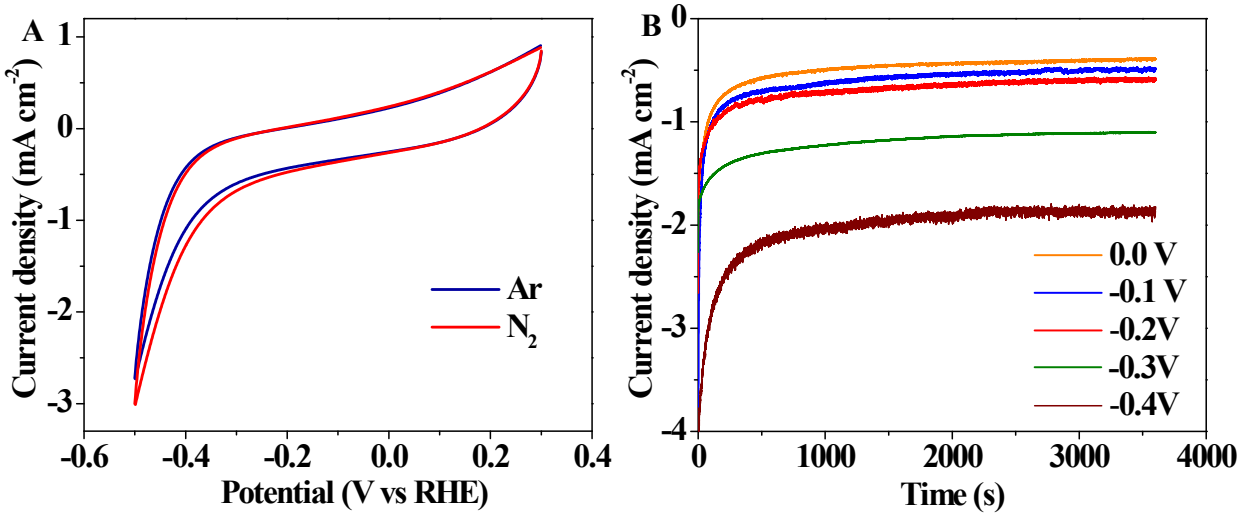

Fig. S3 (A) Cyclic voltammograms of CSA/NPC-750 on glassy carbon in N_2 or Ar saturated 0.05 M Na_2SO_4 with scan rate of 20 mV s^{-1}, (B) Chronoamperometric curves for electrochemical reduction of N_2 on CSA/NPC-750 at 0.0~-0.4 V (vs RHE).

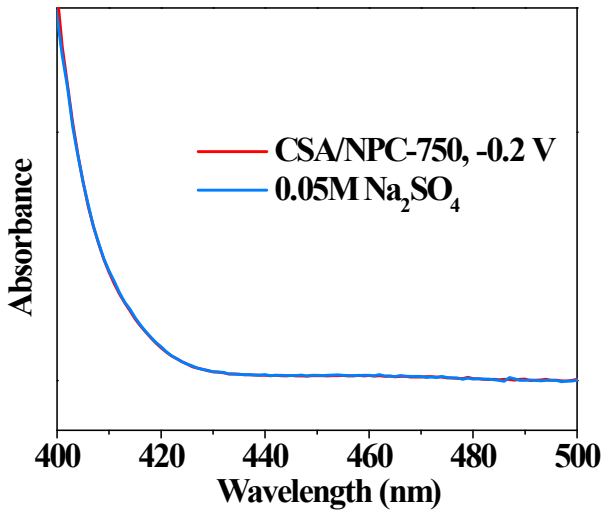

Fig. S4. UV-Vis curves of 0.05 M Na_2SO_4 and the sample for N_2 reduction on CSA/NPC-750 (1 h, -0.2 V, 0.05 M Na_2SO_4) measured by p-dimethylaminobenzaldehyde method.

To find out whether hydrazine can be produced, electrochemical reduction of N_2 was conducted on CSA/NPC-750 at -0.2 V in 0.05 M Na_2SO_4 for 1 h and hydrazine concentration of the solution was measured by p-dimethylaminobenzaldehyde spectrophotometric method. Details as follows: 2.0 g p-dimethylaminobenzaldehyde, 100 mL ethanol and 10 mL HCl (12.0 mol/L) were mixed and used as color reagent. 0.8 mL color reagent was added into a mixture of 2.0 mL solution (taken from electrochemical cell

after N_2 reduction for 1 h) and 2.0 mL HCl (0.24 mol/L). After mixing thoroughly, the resulting solution sat for 20 min. Its absorbance was measured at 458 nm. The absorbance of 0.05 M Na_2SO_4 was used as reference. As shown in Fig. S4, the absorbance of the sample obtained from N_2 reduction on CSA/NPC-750 at -0.2 V is 0.0211, which is similar to that of 0.05 M Na_2SO_4 (0.0209). Therefore, hydrazine is not produced during N_2 reduction on CSA/NPC-750.

To confirm ammonia is produced from N_2 reduction, $^{15}N_2$ reduction has been performed on CSA/NPC-750 at 0.05 M Na_2SO_4. Details as follows: Ar purge was undertaken for 30 min to remove $^{14}N_2$ in the cell and electrolyte, followed by $^{15}N_2$ purge for 20 min. Electrochemical reduction of $^{15}N_2$ was conducted on CSA/NPC-750 at -0.2 V with $^{15}N_2$ flow. After $^{15}N_2$ reduction for 1 h, the sample was collected and adjusted to pH 2 with HCl for ammonia quantification by H-NMR on Bruker 700 MHz spectrometer with DMSO as internal standards. The sample was mixed with 0.2 mM DMSO (D_2O was used as solvent) with ratio of 9:1. H-NMR measurement was performed for 2500 scans with water suppression. As reference, electrolysis was also conducted under Ar on CSA/NPC-750 (-0.2 V, 1 h) and the solution was collected for ^{1}H-NMR measurement with the same method mentioned above. As reference, the ^{1}H-NMR spectrum of 0.5 mM $^{14}NH_4Cl$ (pH 2) was measured by the same method with 250 scans. Calibration curve for $^{15}NH_4^+$ was tested using $^{15}NH_4Cl$ with concentrations of 0-300 uM. As shown in Fig. S5A, doublet at 6.93 ppm and 7.08 ppm can be observed on the ^{1}H-NMR spectrum for $^{15}N_2$ reduction sample, while triplet around 6.91-7.09 ppm appear on the ^{1}H-NMR spectrum for $^{14}NH_4^+$ standard sample and no discernable peak can be observed for electrolysis under Ar. The doublet (6.93 ppm and 7.08 ppm) for $^{15}N_2$ reduction sample can be attributed to the signal of $^{15}NH_4^+$,[1] and the triplet (6.91-7.09 ppm) arises from $^{14}NH_4^+$. The ^{15}N labelling and Ar electrolysis experiments indicate the detected ammonia in this work is produced from N_2 reduction. To confirm it, the $^{15}NH_4^+$ produced from $^{15}N_2$ reduction is quantified with the calibration curve in Fig. S5B, which shows the peak area ratio of $^{15}NH_4^+$/DMSO versus $^{15}NH_4^+$ concentration. The obtained $^{15}NH_4^+$ production rate is 0.82 μmol cm^{-2} h^{-1}, consistent with result of 0.86 μmol cm^{-2} h^{-1} from $^{14}N_2$ reduction. These results confirm the ammonia detected in this work is produced from N_2 reduction.

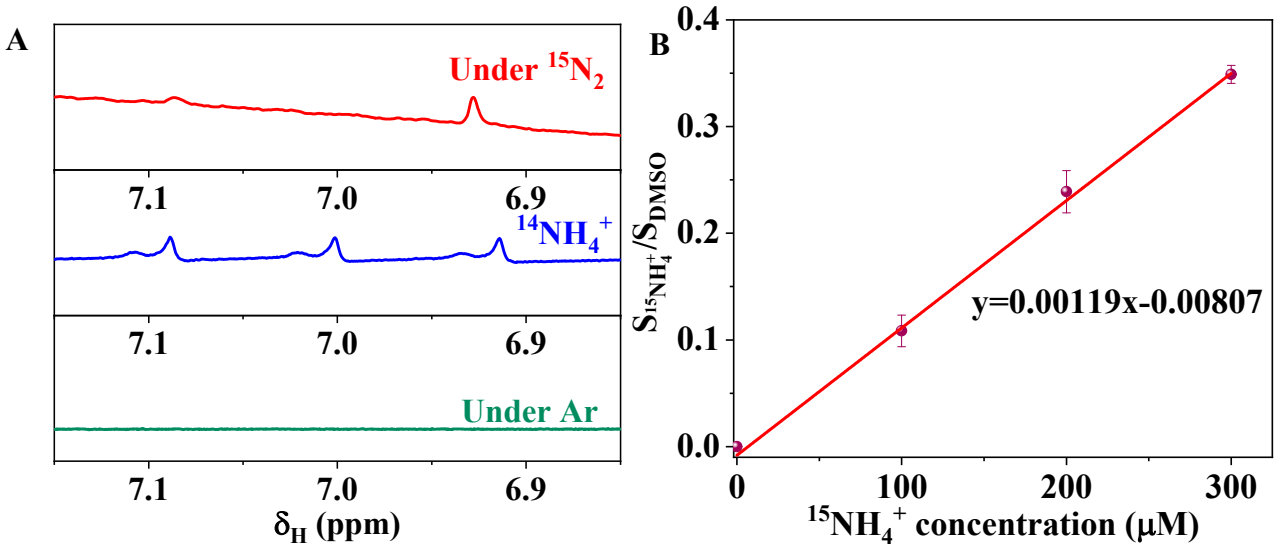

Fig. S5 ^{1}H-NMR spectra for (A) 0.5 mM NH_4^+ standard (250 scans), $^{15}N_2$ reduction and Ar electrolysis on CSA/NPC-750 at -0.2 V (2500 scans), (B) calibration curve for $^{15}NH_4^+$: the peak area ratio of $^{15}NH_4^+$/DMSO versus $^{15}NH_4^+$ concentration.

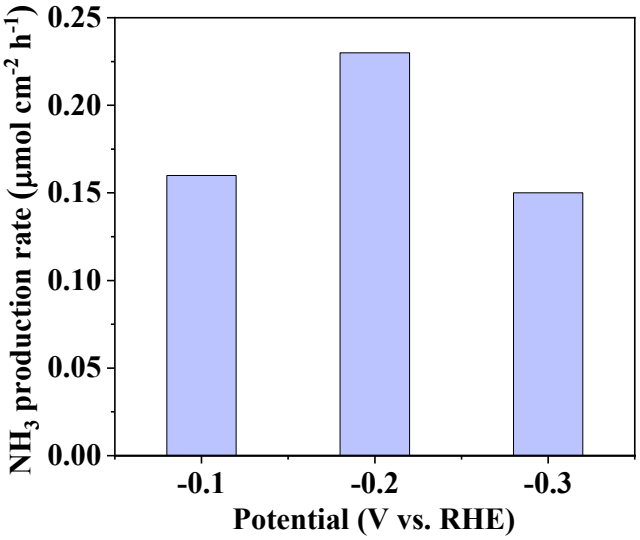

Fig. S6 The NH_3 production rates of CSA/NPC-700 for electrochemical reduction of N_2 at -0.1~-0.3 V (vs RHE) and 0.05 M Na_2SO_4.

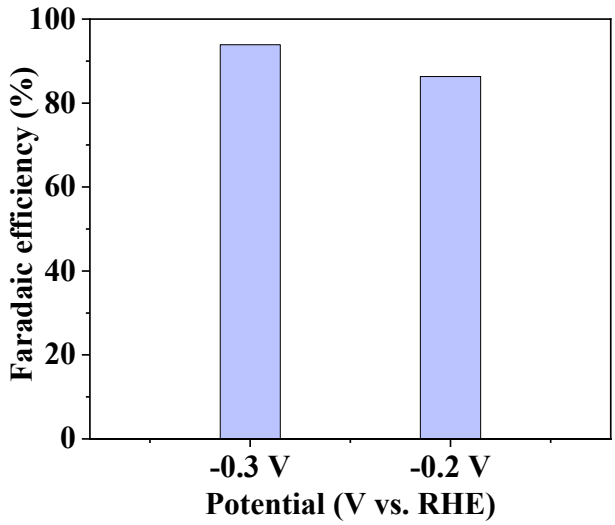

Fig. S7 The H_2 production efficiencies during electrochemical reduction of N_2 on CSA/NPC-750 at -0.2 V and -0.3 V.

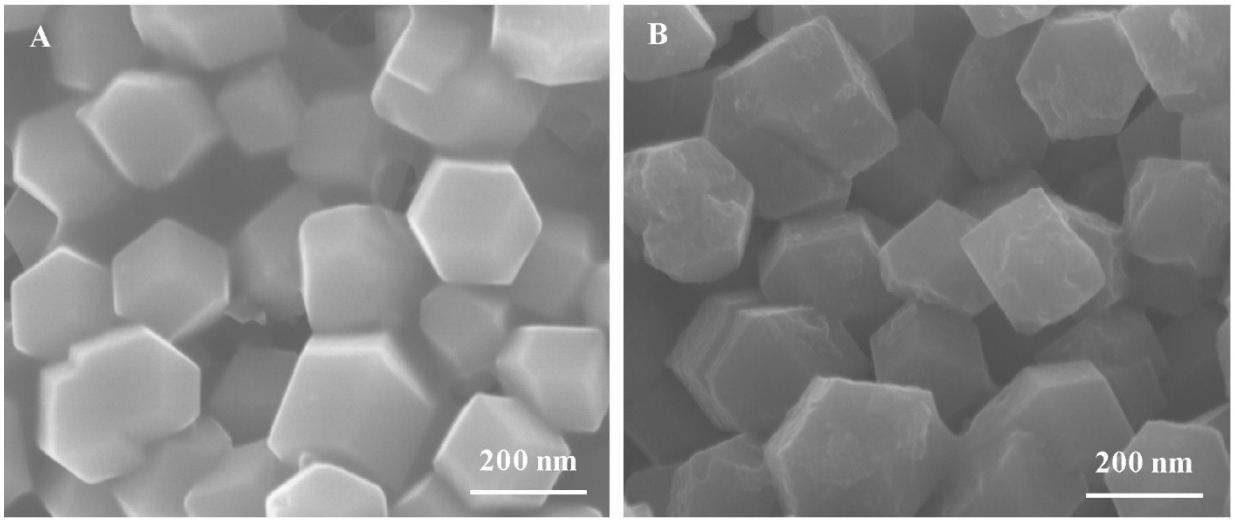

Fig. S8 SEM images of CSA/NPC-750 electrode (A) before and (B) after electrochemical reduction of N_2 at -0.2 V.

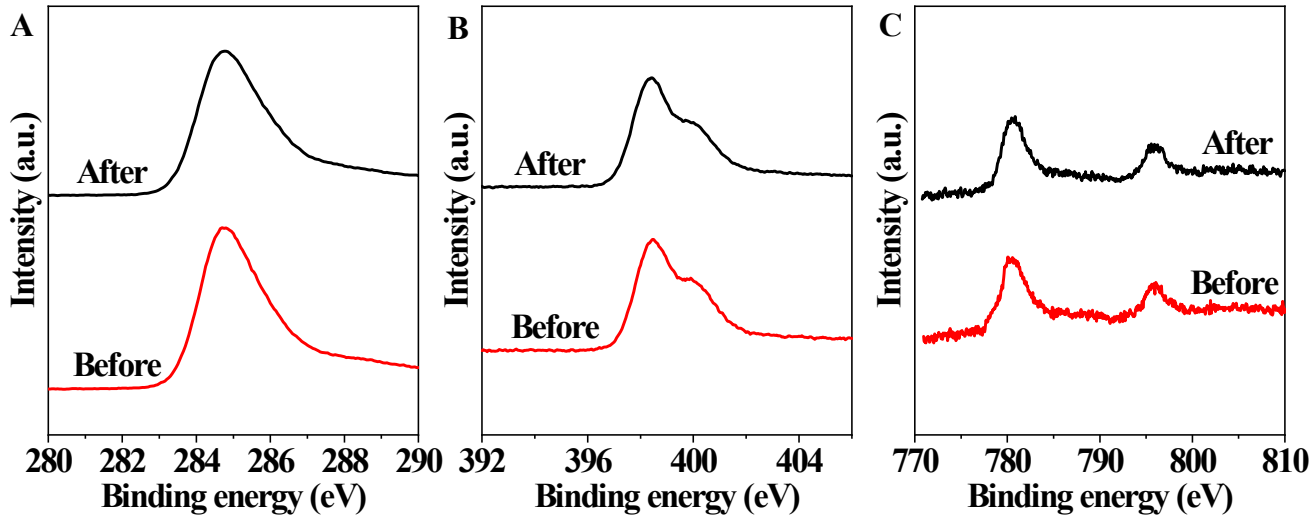

Fig. S9 (A) C 1s, (B) N 1s and (C) Co 2p XPS spectra of CSA/NPC-750 before and after electrochemical reduction of N_2 at -0.2 V.

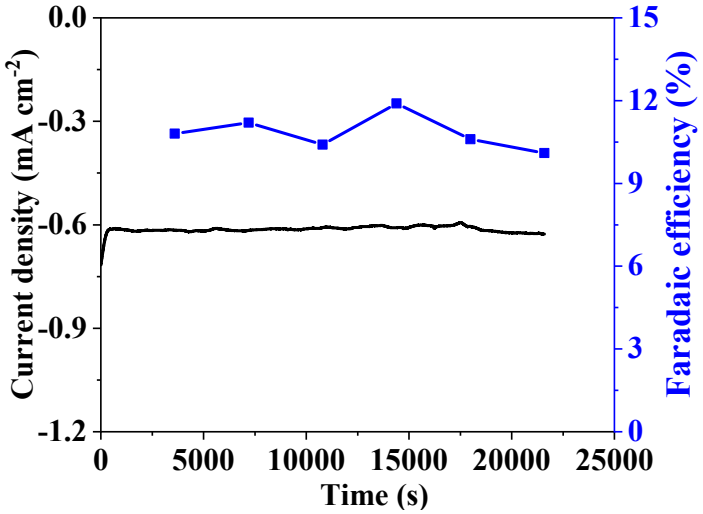

Fig. S10 Chronoamperometric curve and NH_3 production efficiency during electrochemical reduction of N_2 on CSA/NPC-750 at -0.2 V.

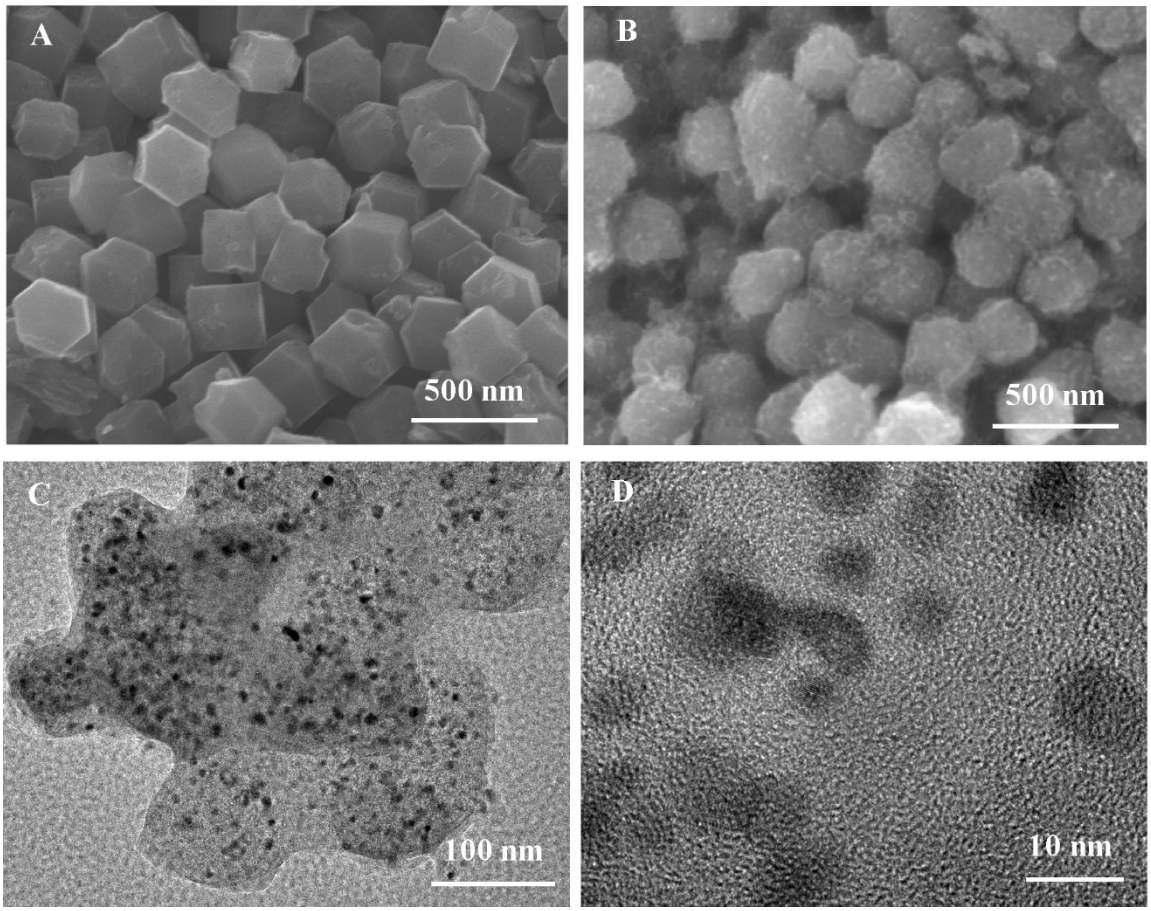

Fig. S11 SEM images of (A) NPC-750 and (B) Co/NPC-750, (C) low and (D) high resolution TEM images of Co/NPC-750.

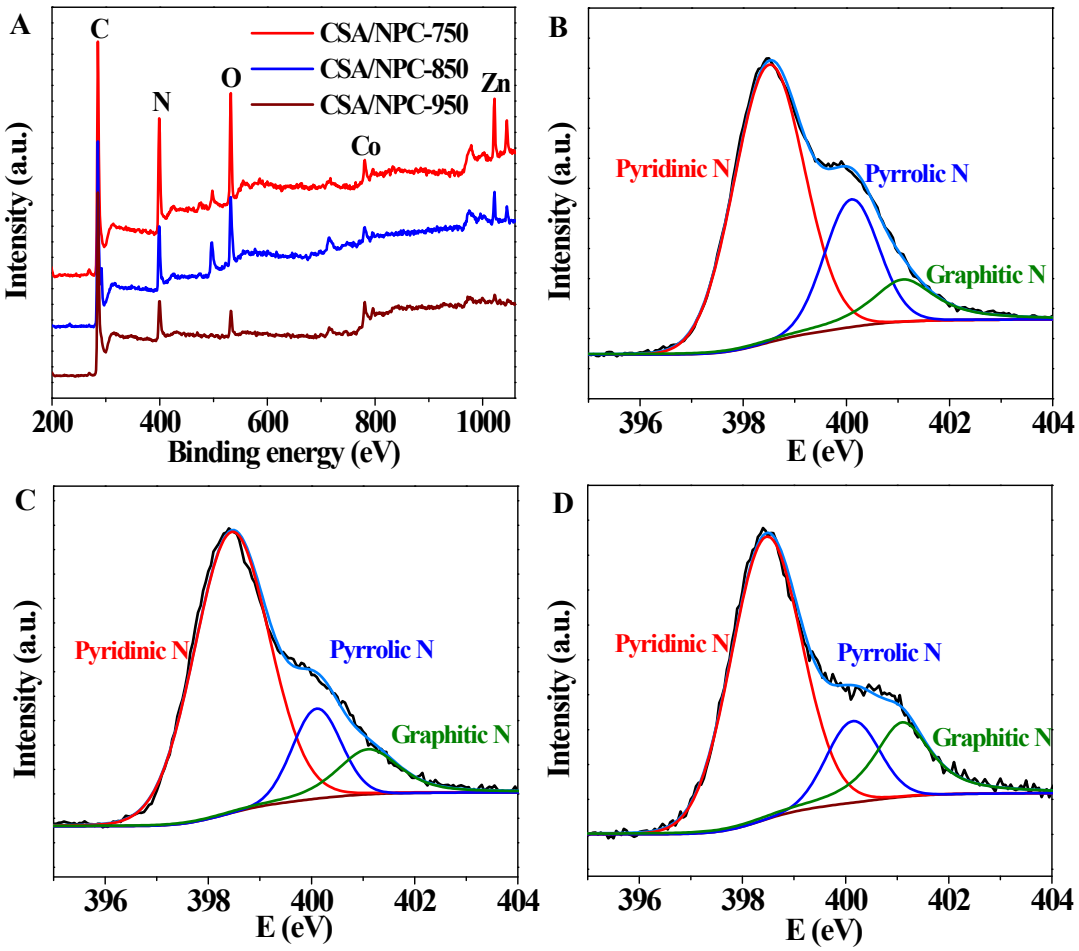

Fig. S12 (A) XPS survey scan spectra of CSA/NPCs, N 1s XPS spectra of (B) CSA/NPC-750, (C) CSA/NPC-850 and (D) CSA/NPC-950.

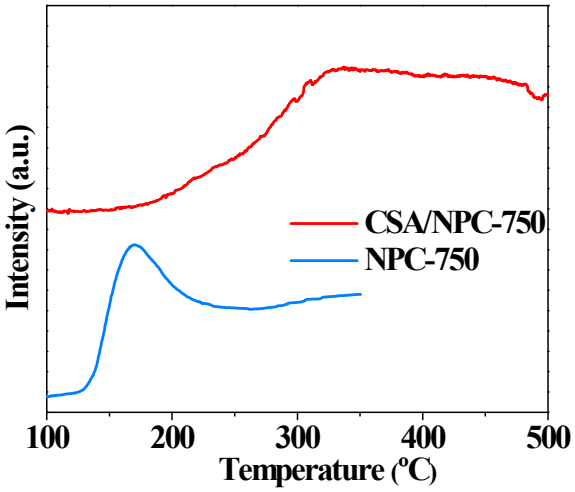

Fig. S13 N_2-TPD curves of CSA/NPC-750 and NPC-750.

DFT calculation was conducted on Vienna Ab-initio Simulation Package (VASP) with the projector augmented wave (PAW) potentials, the generalized gradient approximation (GGA) parameterized by Perdew, Burke and Ernzerhof (PBE) for texchange correlation functional.[2,3] The Co single atoms embedded N-doped carbon (CSA/NPC) with a 7×7 unit cell was used as model (Fig. S14). Both Co atoms coordinated with four N atoms (Co-N4) and pyridinic N were considered in this model. The kinetic energy cutoff was set to 400 eV for the plane-wave basis. To eliminate the interaction of periodic images of the system, vacuum layer above the CSA/NPC plane was selected to be 20 Å. The model structures are optimized by using thresholds for the total energy of 10^{-4} eV and force of 0.01 eV/Å. The free energy of possible reaction pathways for NH_3 synthesis was calculated[4-6] as follows: $\Delta G = \Delta E_{DFT} + \Delta E_{ZPE} - T\Delta S$, where ΔE_{DFT} is the DFT total energy, ΔE_{ZPE} is the zero-point energy, and $T\Delta S$ is the entropy difference between the initial adsorbed state and final state. During the DFT calculation, the H, N_2H_x and NH_x adsorbed on CSA/NPC are optimized by searching all the possible structures and find the lowest energy ones.

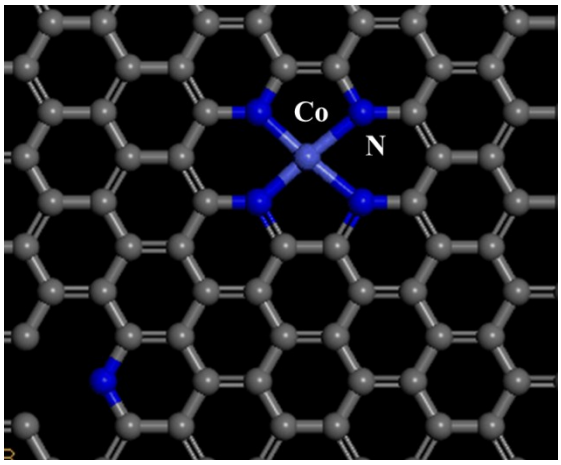

Fig. S14 The model of CSA/NPC used for DFT calculation.

2. Supplementary tables

Table S1. The EXAFS fitting results of CSA/NPC-750.

Electrocatalysts	Bond type	N	R	σ^2	ΔE_0 (eV)
CSA/NPC-750	Co-N	4.0	1.89	0.0034	-6.7

N is the coordination number, R is the distance between absorber and backscatter atoms, σ^2 is the Debye-Waller factor value, ΔE_0 is edge-energy shift

Table S2. Comparison of NH_3 synthesis performance between CSA/NPC-750 and electrocatalysts reported recently

Electrocatalysts	Production rate ($\mu mol\ h^{-1}\ cm^{-2}$)	Efficiency (%)	Conditions	References
Au/CeO_x-RGO	0.098	10.1%	-0.2 V, pH 2	Adv. Mater. 2017, 29, 1700001
Au nanorod	0.097	8.11%	-0.2 V, pH 13	Adv. Mater. 2017, 29, 1604799
Fe_2O_3/CNT	0.013	0.18%	-1.4 V, pH 7	Angew. Chem. Int. Ed. 2017, 56, 2699
MoS_2	0.29	1.17%	-0.5 V, pH 7	Adv. Mater. 2018, 30, 1800191
Carbon nitride	0.95	11.59%	-0.2 V, pH 1	Angew. Chem. Int. Ed. 2018, 57, 10246
CSA/NPC	0.86	10.5%	-0.2 V, pH 7	This work

Table S3. The N/C and Co/C ratios obtained from XPS for CSA/NPC-750 before and after electrochemical reduction of N_2 at -0.2 V.

	N/C ratio	Co/N ratio
Before use	0.319	0.0152
After use	0.335	0.0146

XPS is used to quantify CSA/NPC-750 before and after electrochemical reduction of N_2 at -0.2 V. As shown in Figure S11 and Table S3, the atom ratios of N/C and Co/C are 0.319 and 0.0152 before use. After electrochemical reduction of N_2 for six cycles (1 h for each cycle), the N/C ratio is 0.335. The slightly increased N content could be caused by measurement error and/or adsorbed ammonia. The Co/C ratio is 0.0146 after use, which can be considered as the same before reaction.

Table S4. The metal and N contents of CSA/NPCs, NPC-750 and Co/NPC-750

Electrocatalysts	Co content	Zn content	N content
CSA/NPC-750	1.4 wt%	4.3 wt%	20.6 at.%
CSA/NPC-850	1.5 wt%	1.8 wt%	15.3 at.%
CSA/NPC-950	1.8 wt%	0.03 wt%	13.0 at.%
NPC-750	0	4.2 wt%	20.7 at.%
Co/NPC-750	8.2 wt%	4.1 wt%	21.8 at.%

Metal content is measured by inductively coupled plasma atomic emission spectroscopy, N content is measured by XPS.

3. References

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