Electronic Supplementary Information

Single-atom metal-N_4 sites molecular electrocatalysts for ambient nitrogen reduction

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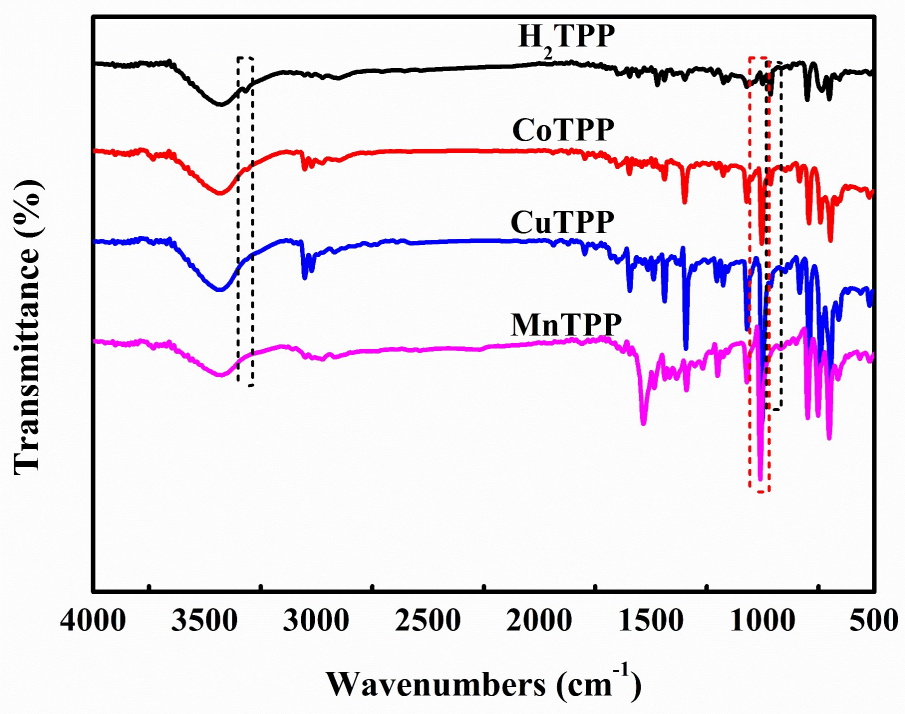

Fig. S1. FT-IR spectra of H_2TPP, CoTPP, CuTPP and MnTPP, respectively.

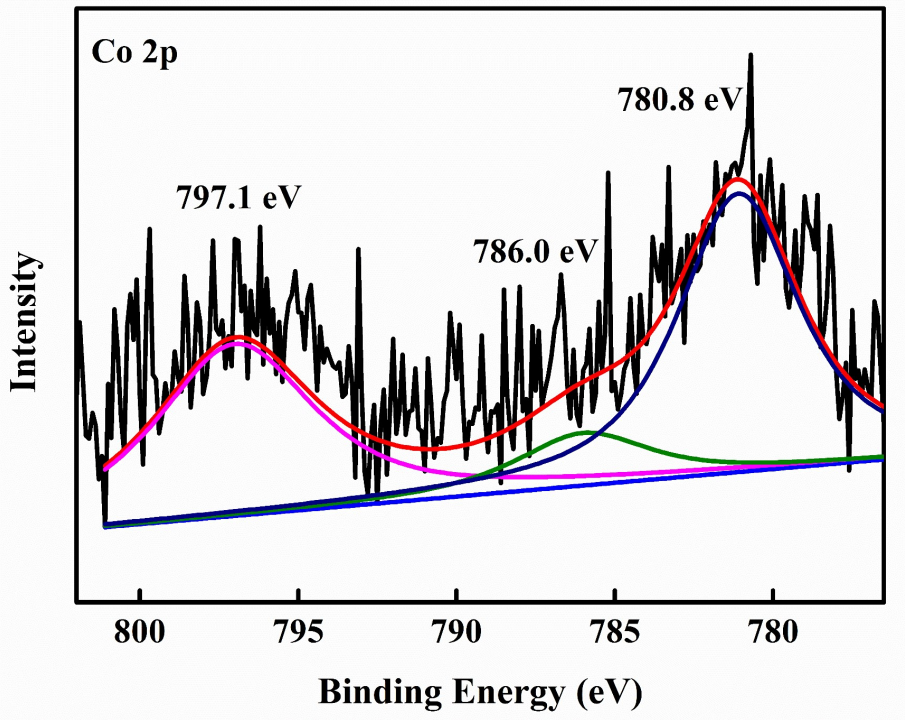

Fig. S2 XPS of CoTPP in the Co 2p regions.

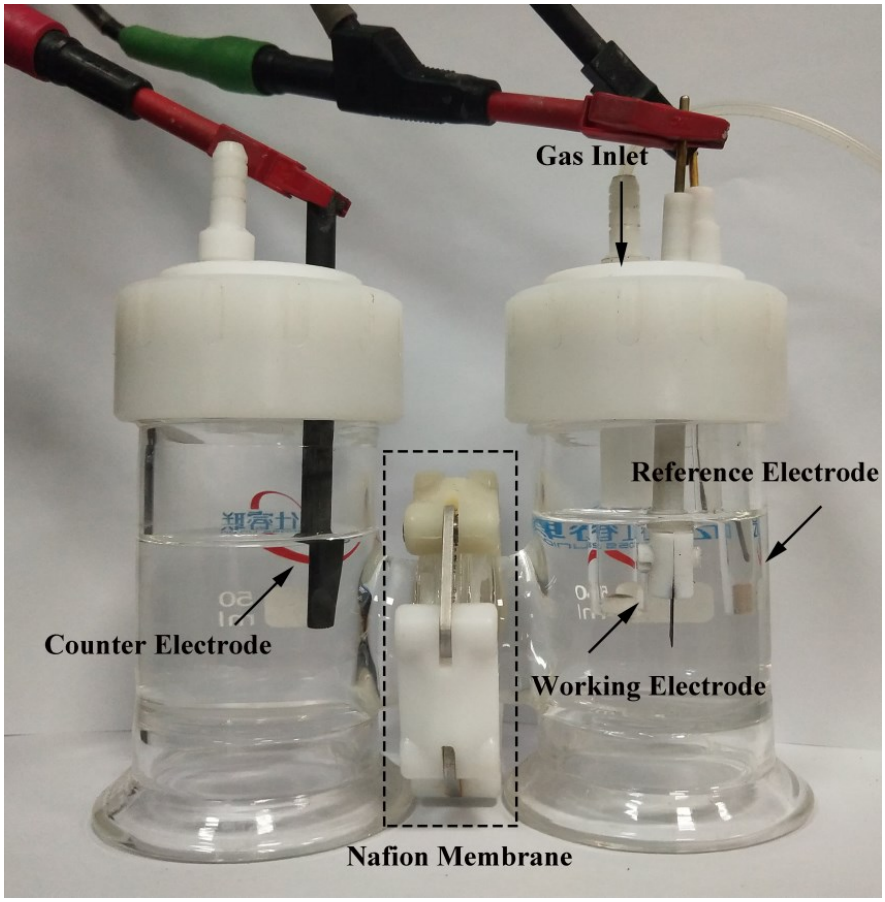

Fig. S3. The H-shape electrolytic cell for nitrogen reduction reaction.

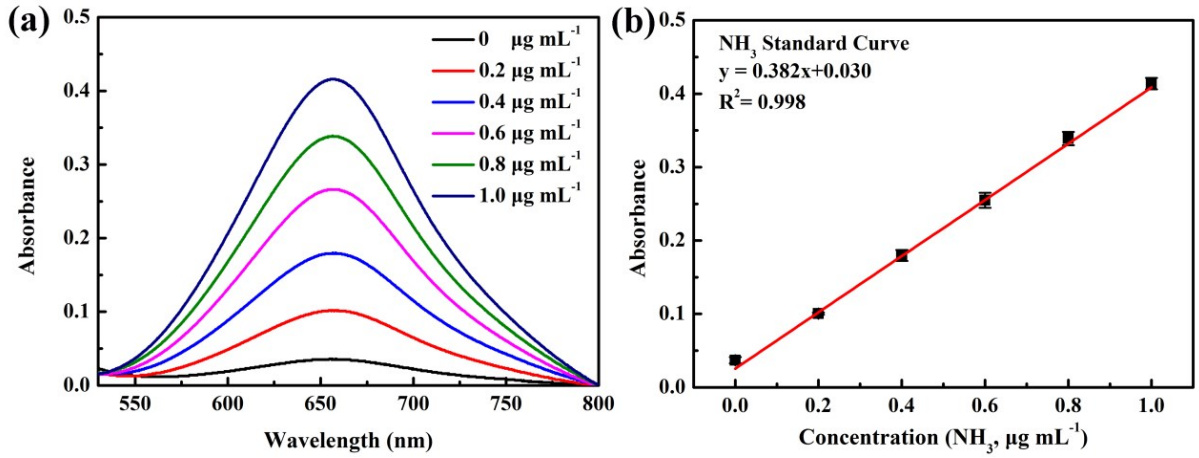

Fig. S4. Calibration curve in 0.1 M HCl using NH_4Cl solution of known concentration as standards for three times. (a) UV-Vis absorption spectra of of various NH_4^+ concentrations after incubated for 2 h at room temperature. (b) Calibration curve used for estimation NH_3 concentration.

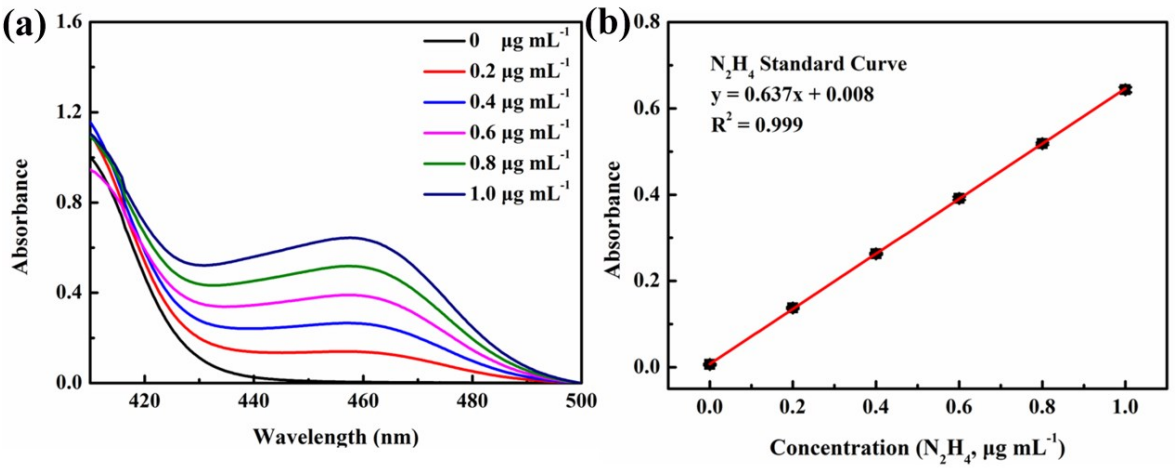

Fig. S5. Calibration curve in 0.1 M HCl using hydrazine solution of known concentration as standards for three times. (a) UV-Vis absorption spectra of various N_2H_4 concentrations after incubated for 20 min at room temperature. (b) Calibration curve used for estimation of N_2H_4 concentrations.

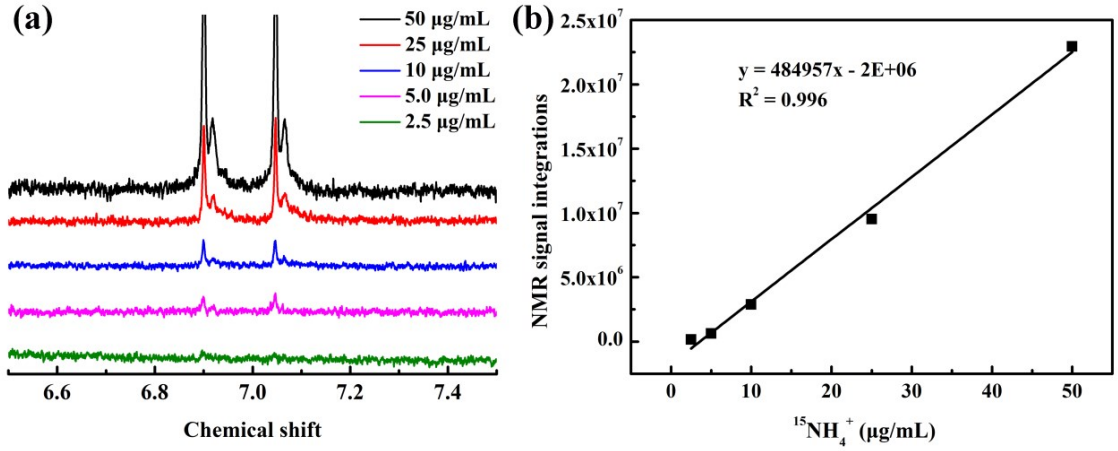

Fig. S6. (a) ^1H NMR spectra for standard $^{15}NH_4^+$ solution with concentrations of 2.5, 5.0, 10, 25 and 50 μg mL^{-1} in 0.1 M HCl. (b) Calibration curve of ^1H NMR signal for standard NH_4^+ solutions with various concentrations of 2.5, 5.0, 10, 25 and 50 μg mL^{-1} in 0.1 M HCl. The black line is the linear fitting of NMR signal integration value with a R^2 value of 0.996.

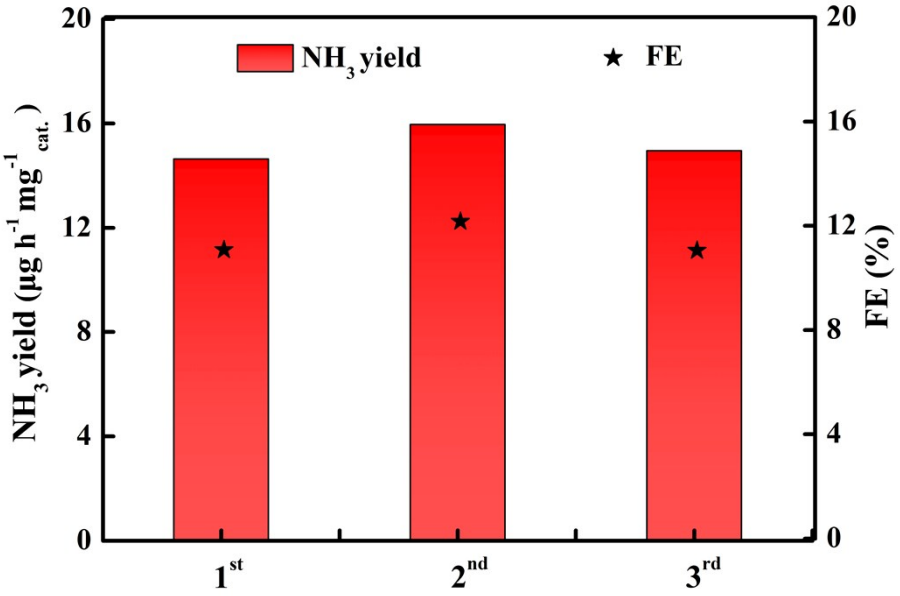

Fig. S7. NH_3 yields and FEs of CoTPP measured for three times at –0.3 V *vs.* RHE in 0.1 M HCl.

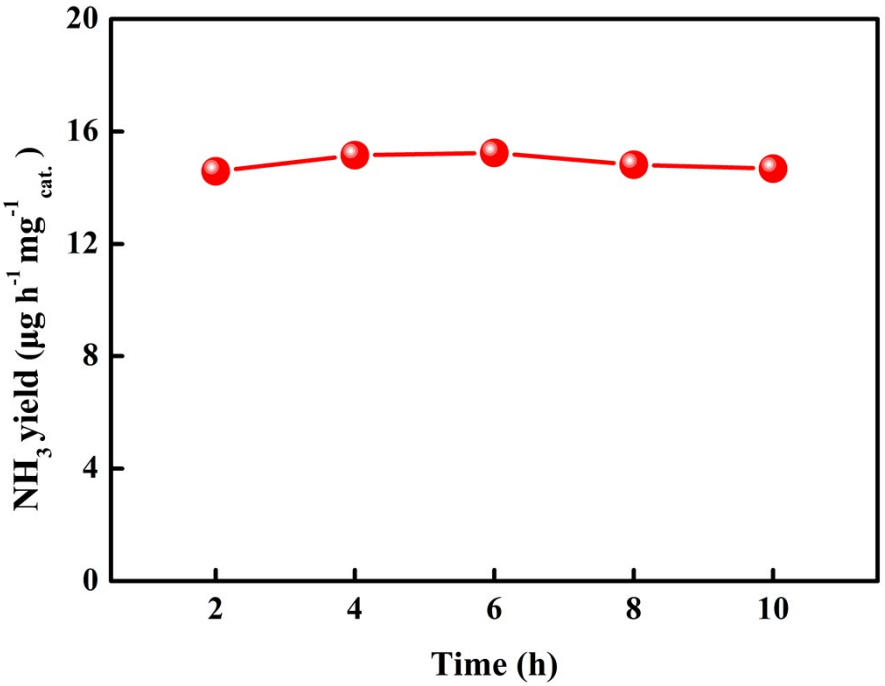

Fig. S8. The ammonia yields of CoTPP electrocatalyst during 10 h electrolysis.

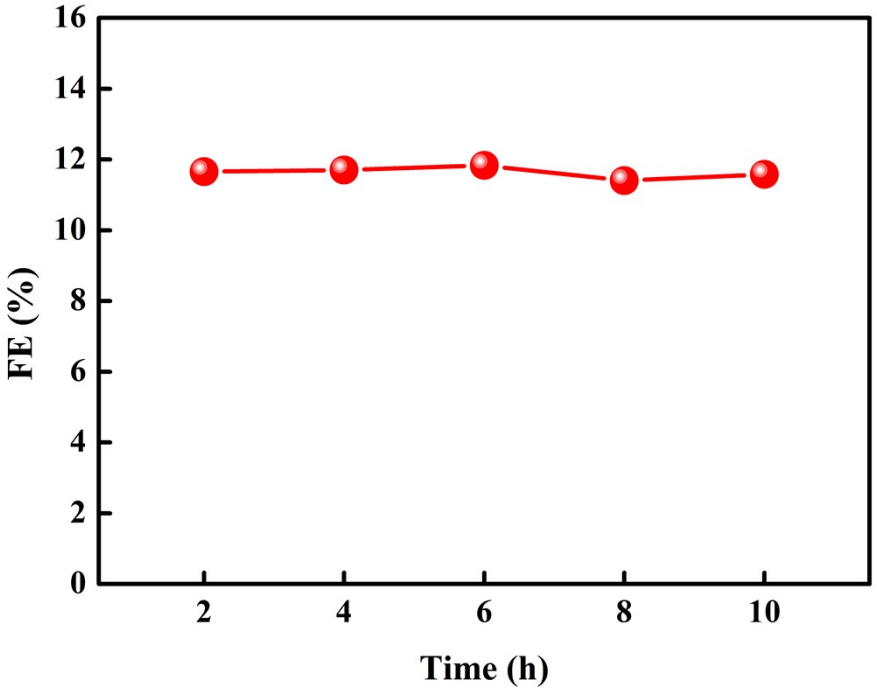

Fig. S9. The FEs of CoTPP electrocatalyst during 10 h electrolysis.

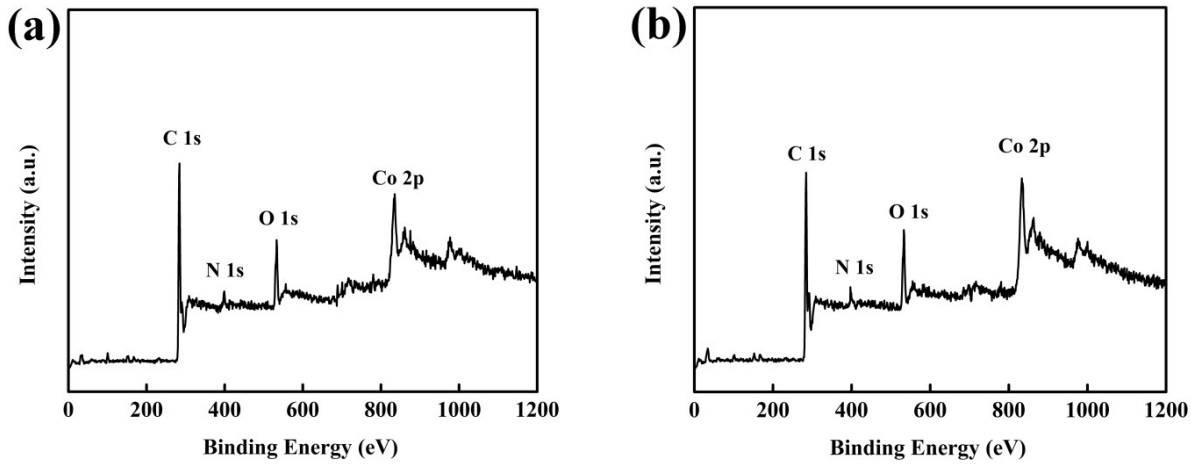

Fig. S10. XPS spectra for CoTPP before (a) and after (b) 2 h electrolysis.

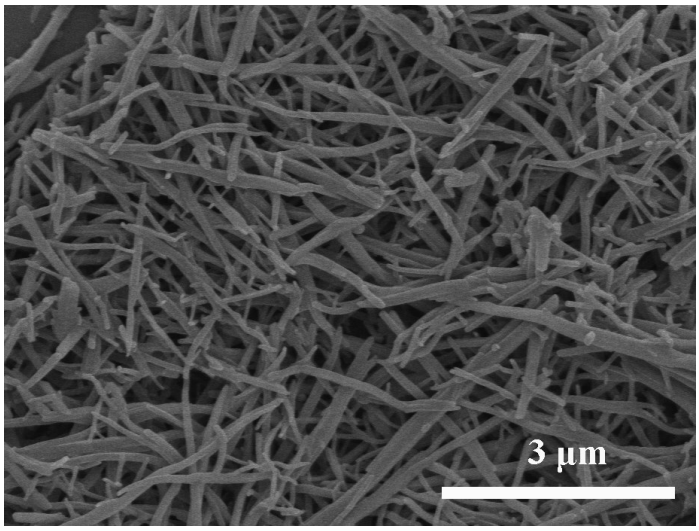

Fig. S11. SEM images of CoTPP after 2 h electrolysis.

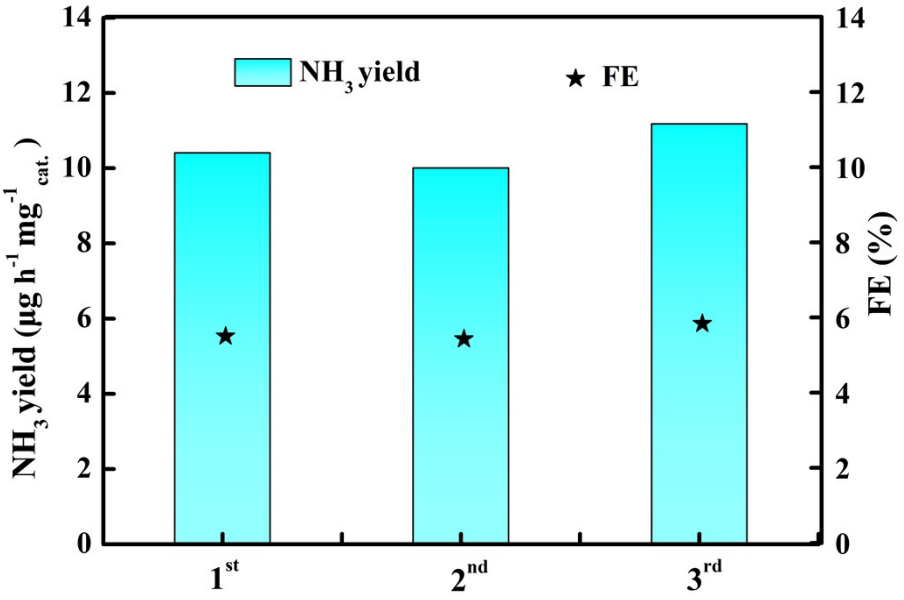

Fig. S12. NH_3 yields and FEs of CuTPP measured for three times at –0.3 V *vs.* RHE in 0.1 M HCl.

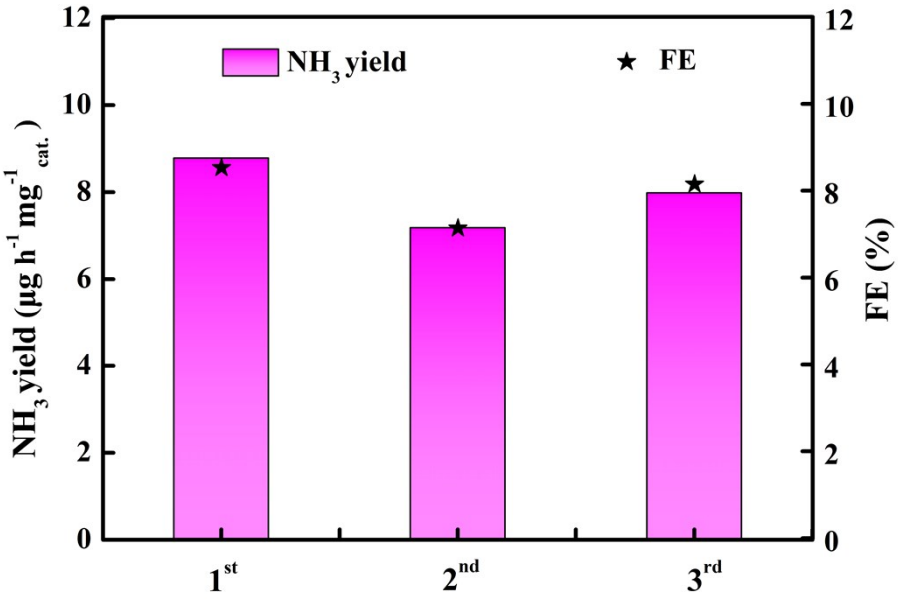

Fig. S13. NH_3 yields and FEs of MnTPP measured for three times at –0.4 V *vs.* RHE in 0.1 M HCl.

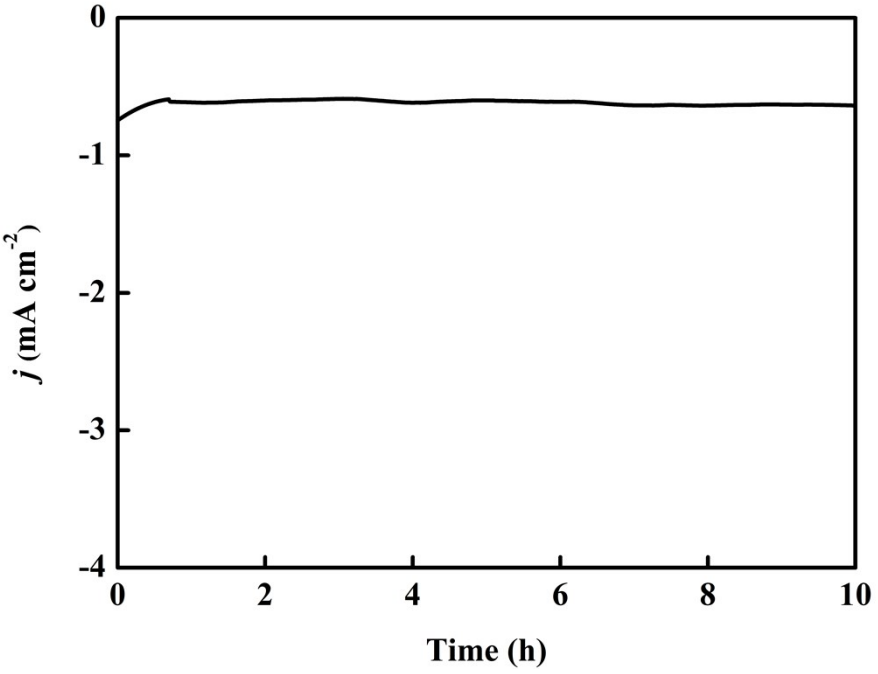

Fig. S14. Time-dependent current density curve of CuTPP for 10 h at the electrolysis of –0.3 V *vs.* RHE.

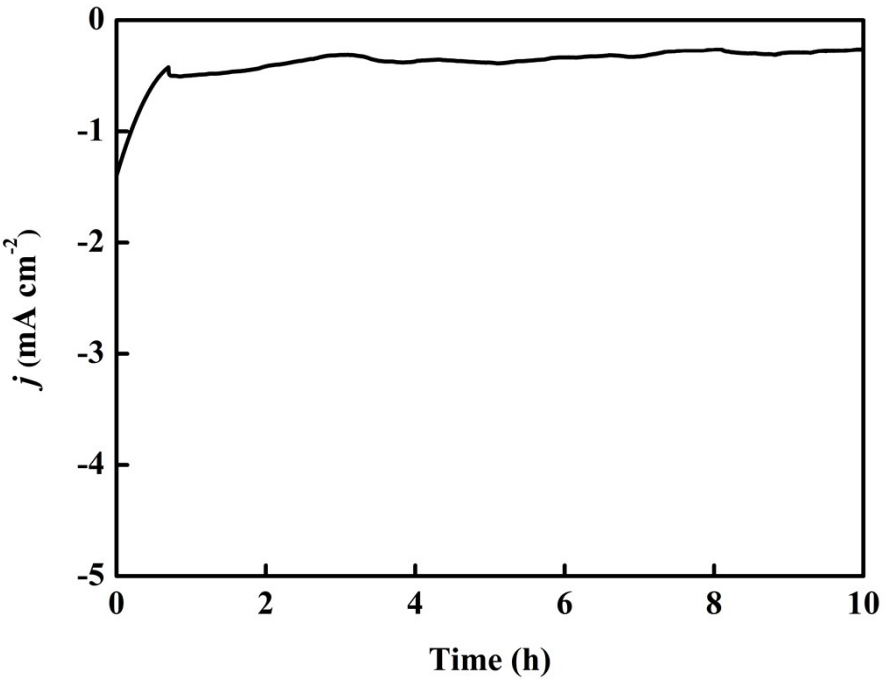

Fig. S15. Time-dependent current density curve of MnTPP for 10 h at the electrolysis of –0.4 V *vs.* RHE.

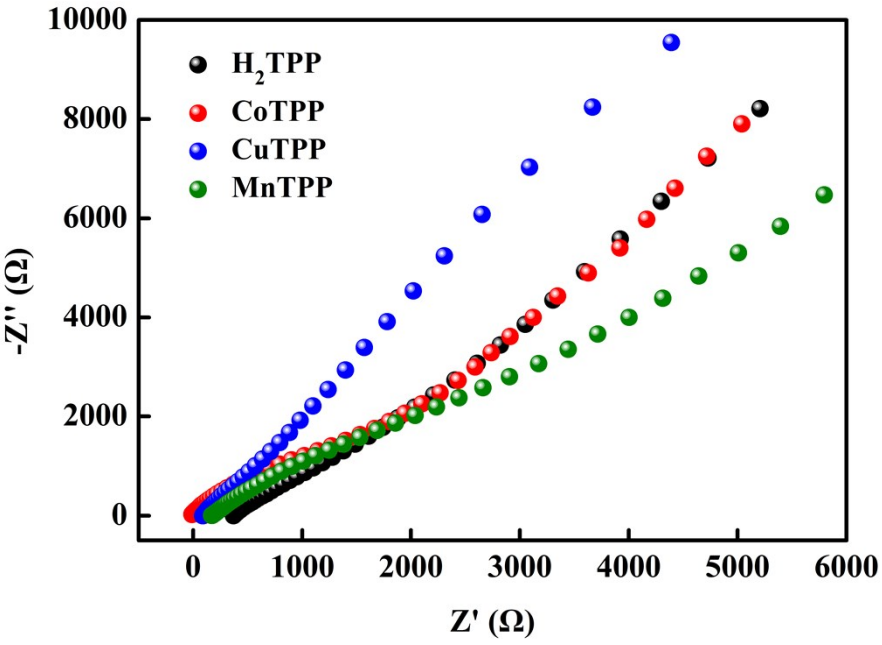

Fig. S16. Nyquist plots of H_2TPP and MTPP.

Table S1. Comparison of electrocatalytic NRR performance for CoTPP with noble-metal-free electrocatalysts under ambient conditions.

Catalyst	Electrolyte	NH_3 Yield rate ($\mu g\ h^{-1}\ mg^{-1}_{cat.}$)	FE (%)	Potential (V)	Reference
CoTPP	**0.1 M HCl**	**15.18**	**11.43**	**-0.3**	**This work**
FePc/C	0.1 M Na_2SO_4	10.25	10.5	-0.3	ACS Catal. 2019, **9** 7311-7317
CoP	1 M KOH	10.78	7.36	-0.4	Small Methods, 2018, **2**, 1800204
V_2O_3/C	0.1 M Na_2SO_4	12.3	7.28	-0.6	Inorg. Chem. Front., 2019, **6**, 391-395
Nb_2O_5/CC	0.1 M Na_2SO_4	17.63	2.26	-0.6	Inorg. Chem. Front., 2019, **6**, 423-427
CoS_2/NS-G	0.05 M H_2SO_4	25.0	25.9	-0.2	Proc. Natl. Acad. Sci., 2019, **116**, 6635-6640
MoN	0.1 M HCl	18.42	1.15	-0.3	ACS Sustainable Chem. Eng., 2018, **6**, 9550-9554
WO_3	0.1 M HCl	4.2	12.8	-0.12	Nano Energy, 2019, **62**, 869-875
γ-Fe_2O_3	0.1 M KOH	0.212	1.9	0.0	ACS Sustainable Chem. Eng., 2017, **5**, 10986-10995
TiO_2	0.1 M HCl	3.0	6.5	-0.12	Appl. Catal. B: Environ., 2019, **257**, 117896
Bi nanoplates	0.2 M Na_2SO_4	5.453	11.68	-0.6	Angew. Chem. Int. Ed., 2019, **58**, 9464-9469
Mo_3Fe_3C	0.1 M Li_2SO_4	1.23	27	-0.05	Nano Energy, 2020, **68** 104374
Mo_2C/C	0.5 M Li_2SO_4	11.3	7.8	-0.3	Adv. Mater., 2018, **30**, 1803694
MoO_3 nanosheets	0.1 M HCl	29.43	1.9	-0.5	J. Mater. Chem. A, 2018, **6**, 12974-12977