Electronic Supplementary Information

Experimental section

Materials: $FeCl_3\cdot6H_2O$ and Na_2SO_4 were purchased from Aladdin Ltd. in Shanghai. Ti mesh was provided by Hongshan District, Wuhan Instrument Surgical Instruments business, and was pretreated in HCl and then cleaned by sonication in water and ethanol for several times to remove surface impurities. The water used throughout all experiments was purified through a Millipore system.

Preparation of Fe_3O_4 on Ti mesh: $FeCl_3\cdot6H_2O$ (5.4 g) dissolved in 40 mL water under vigorous stirring for 30 min. Then the solution was transferred to a 50 mL Teflon-lined stainless-steel autoclave and in which a piece of Ti mesh because its flexibility and conductivity was immersed into the solution.[1] Then the autoclave was sealed and maintained at 120 °C for 12 h in an electric oven. After the autoclave cooled down at room temperature naturally. Then the product was annealed at 500 °C in air for 2.5 h. Finally, the Fe_3O_4 was produced by annealing at 420 °C for 2 h under a mixture of Ar/H_2 flow.

Characterization: XRD data were obtained from a LabX XRD-6100 X-ray diffractometer with Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm (SHIMADZU, Japan). XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. Scanning electron microscope (SEM) measurements were recorded on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. TEM images were obtained from a Zeiss Libra 200FE transmission electron microscope operated at 200 kV. The absorbance data of spectrophotometer were measured on SHIMADZU UV-1800 ultraviolet-visible (UV-Vis) spectrophotometer.

Electrochemical measurement: All the electrochemical measurements were conducted using a CHI660E potentiostat (CH Instruments, China) in a typical three-electrode setup with an electrolyte solution of 0.1 M Na_2SO_4, a graphite rod as the counter electrode and Ag/AgCl as the reference electrode. The potentials reported in this work were converted to RHE scale via calibration with the following equation: E (vs RHE)

=*E* (vs Ag/AgCl) + 0.197 + 0.059 × pH. For N_2 reduction experiments, the Na_2SO_4 electrolyte (0.1 M) was bubbled with N_2 for 30 min before the measurement.

Determination of NH_3: The produced ammonia was estimated by indophenol blue method by ultraviolet spectroscopy. In detail, 4 mL of post-tested solution was got from the electrochemical reaction vessel. Then, 50 uL of oxidation (contains 0.4 M sodium salicylate and 0.32 M sodium hydroxide), 500 uL of the colouring solution (sodium hypochlorite and 0.75 M sodium hydroxide) and 50 uL pf catalyst solution (0.1g sodium nitroferricyanide(III) dehydrate diluted to 10ml with deionized water) were added respectively to the sample solution. Absorbance measurments were performed after 2 h. The concentration of indophenol blue was determined using the absorbance at awavelength of 660 nm. The concentration-absorbance curve was calibrated using standard ammonia chloride solution with a serious of concentrations. The fitting curve ($Y = 0.718\ X + 0.0178$, $R^2 = 0.999$) shows good linear relation of absorbance value with NH_3 concentration by three times independent calibrations. The NH_3 concentration was calculated form the calibration curve, and the rate of NH_3 yield was calculated using the following equation:

NH_3 yield = $(c_{NH3} \times V) / (17 \times t \times A)$

where c_{NH3} is the measured NH_3 concentration, V is the volume of electrolyte, t is the reduction reaction time and A is the geometric area of the cathode (0.4 cm × 0.5 cm).

Determination of FE: Assuming three electrons were needed to produce one NH_3 molecule, the FE in 0.1 M Na_2SO_4 could be calculated as follows:

$FE = 3F \times c_{NH3} \times V / 17 \times Q$

Where F is the Faraday constant, Q is the quantity of applied electricity.

Determination of N_2H_4: The N_2H_4 presented in the electrolyte was estimated. A mixed solution of 5.99 g $C_9H_{11}NO$, 0.1 M Na_2SO_4 (30 mL) and 300 mL ethanol was used as a color reagent. Calibration curve was plotted as follow: first, preparing a series of reference solutions; second, adding 5 mL above prepared color reagent and stirring 20 min at room temperature; finally, the absorbance of the resulting solution was measured at 455 nm, and the yields of N_2H_4 were estimated from a standard curve using 5 mL residual electrolyte and 5 mL color reagent. Absolute calibration of this method was achieved using $N_2H_4 \cdot H_2O$ solutions of known concentration as standards, and the fitting curve shows good linear relation of absorbance with $N_2H_4 \cdot H_2O$ concentration ($y = 0.6009\ x + 0.047$, $R^2 = 0.999$) by three times independent calibrations.

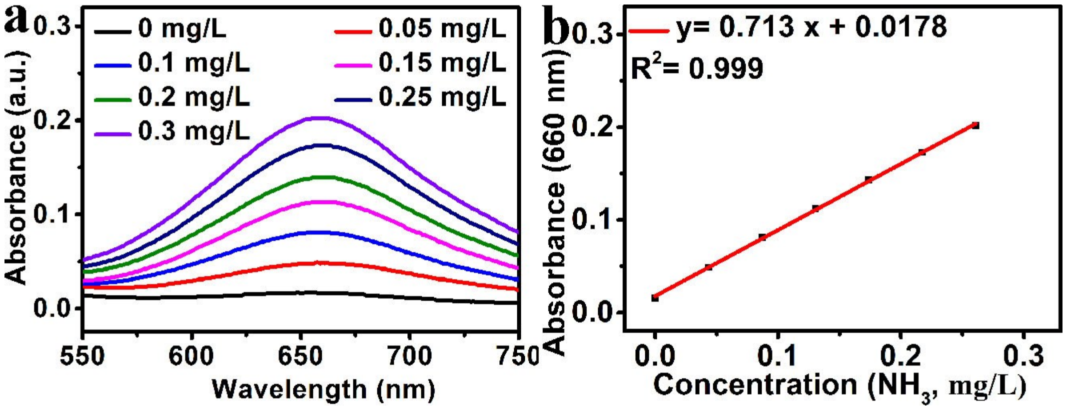

Fig. S1. (a) UV-Vis curves of indophenol assays with NH_4^+ ions after incubated for 2 h at room temperature. (b) Calibration curve used for calculation of NH_3 concentrations.

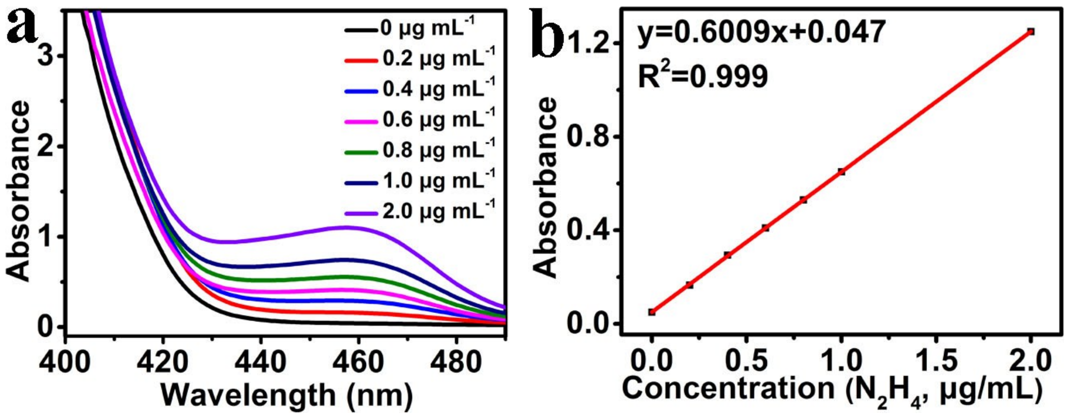

Fig. S2. UV-Vis absorption spectra of various $N_2H_4{\cdot}H_2O$ concentrations after incubated for 10 min at room temperature. (b) Calibration curve used for estimation of $N_2H_4{\cdot}H_2O$ concentration.

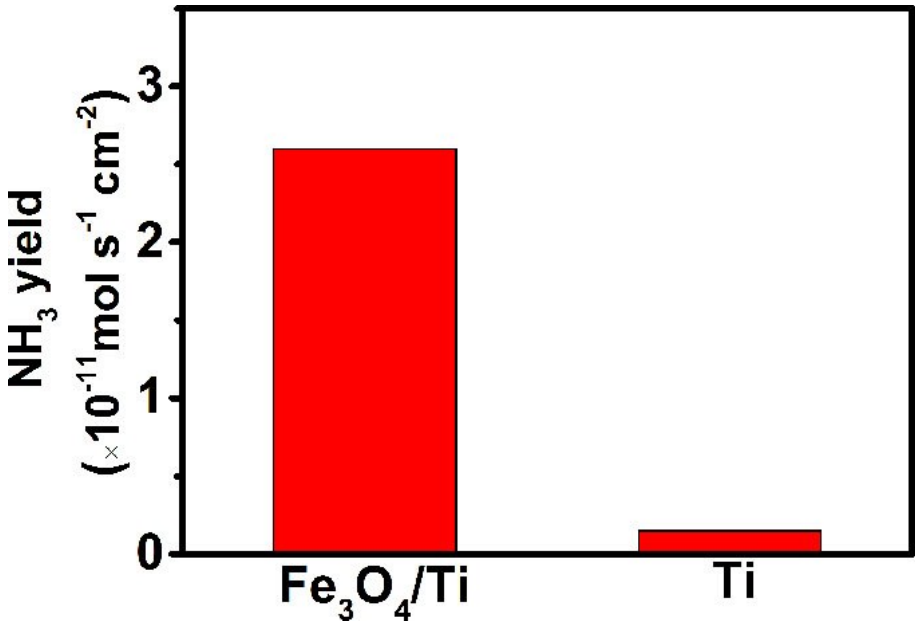

Fig. S3. NH_3 yields for Fe_3O_4/Ti and Ti.

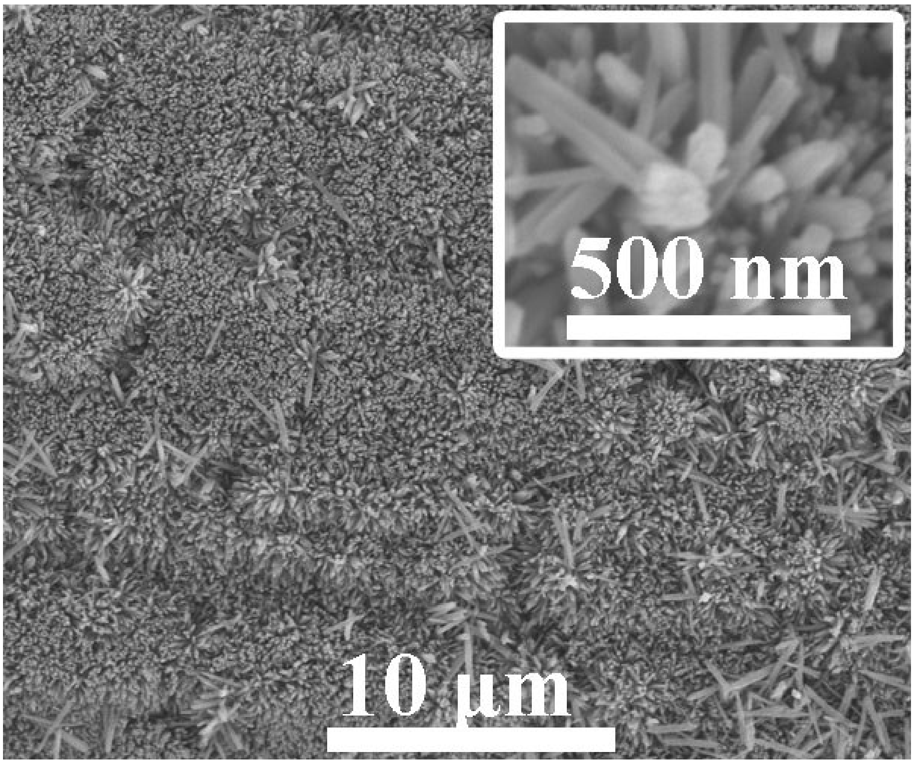

Fig. S4. SEM images for Fe_3O_4/Ti after stability test.

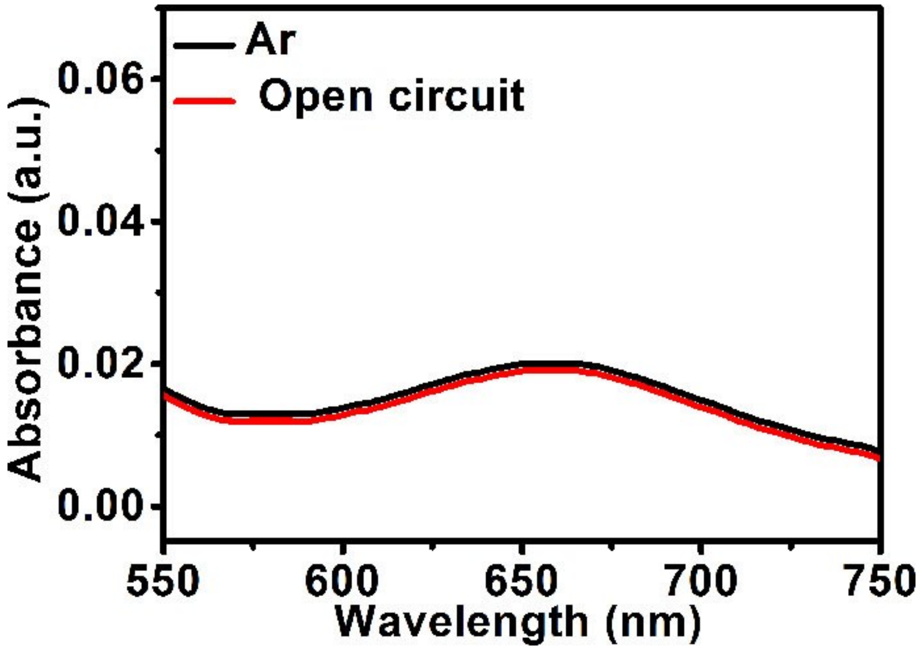

Fig. S5. UV-Vis absorption spectra of the electrolyte stained with indophenol indicator for 3 h electrolysis under different electrochemical conditions.

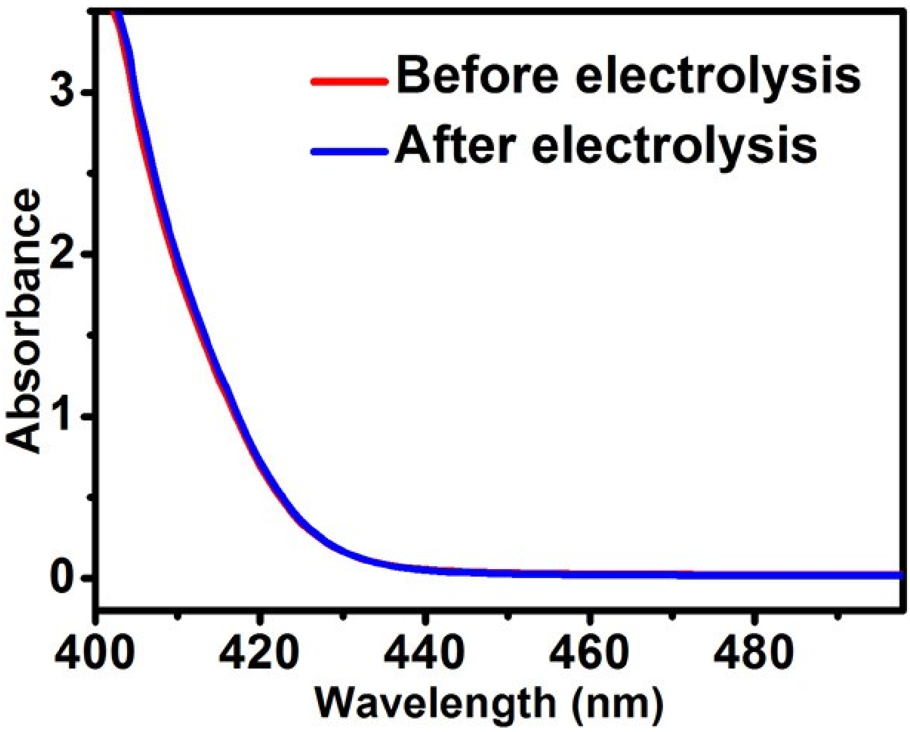

Fig. S6. UV-Vis absorption spectra of the electrolytes estimated by the method of Watt and Chrisp before and after 3-h electrolysis at room temperature.

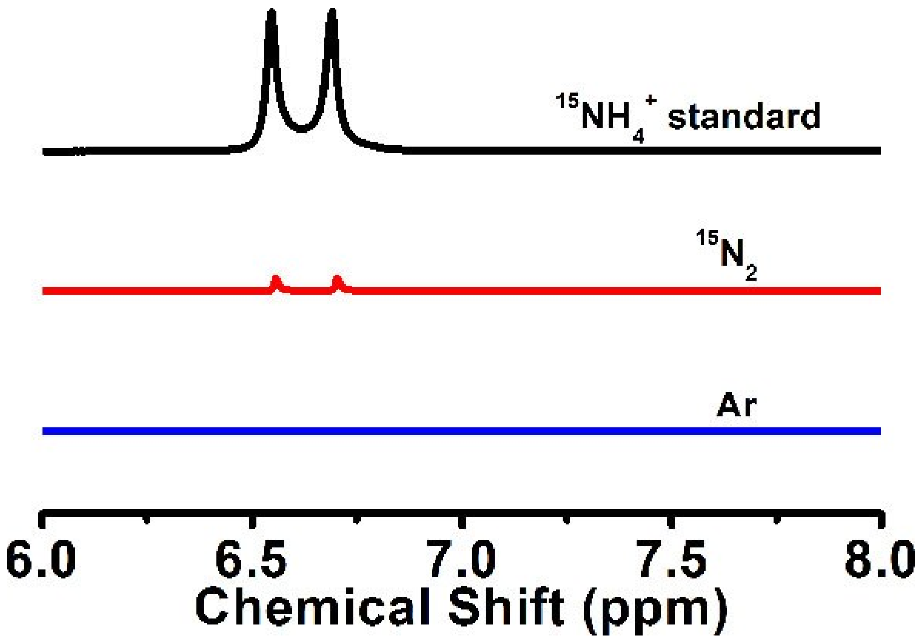

Fig. S7. ^1H nuclear magnetic resonance spectra for the post-electrolysis 0.1 M Na_2SO_4 electrolytes with $^{15}N_2$ and Ar. The spectrum for $^{15}NH_4^+$ standard sample is also shown.

Table S1. Comparison of the NH_3 electrosynthesis activity for Fe_3O_4/Ti with other NRR catalysts.

Catalyst	**Tempert ure (˚C)**	**Electrolyte**	**NH_3 yield (mol s^{-1} cm^{-2})**	**FE (%)**	**Ref.**
Fe_3O_4/Ti	25	0.1 M Na_2SO_4	5.60×10^{-11}	2.6	This work
Ru/C	20	2.0 M KOH	3.44×10^{-12}	0.28	2
Fe_2O_3-CNT	20	$KHCO_3$	3.58×10^{-12}	0.15	3
Mo nanofilm	25	0.01 M H_2SO_4	3.09×10^{-11}	0.72	4
PEBCD/C	25	0.5 M Li_2SO_4	2.58×10^{-11}	2.85	5
MoS_2/CC	25	0.1 M Na_2SO_4	8.08×10^{-11}	1.17	6
Ag	550	$BaZr_{0.8}Y_{0.2}O_{3-\delta}$ Electrolyte	2.94×10^{-14}	0.46	7
Pt/C	80	0.1 M Li_2SO_4	9.37×10^{-10}	0.83	8
Mo_2N	25	0.1 M HCl	4.6×10^{-10}	4.5	9
Porous Ni	25	H_2SO_4/Propanol	1.75×10^{-11}	0.9	10
MoO_3	25	0.1 M HCl	4.80×10^{-10}	1.9	11

References

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