Electronic Supplementary Information

Experimental Section

Materials: Boric acid (H_3BO_3), *p*-dimethylaminobenzaldehyde (*p*-$C_9H_{11}NO$), hydrazine hydrate ($N_2H_4 \cdot H_2O$), H_2O_2 (30 wt%), and Nafion (5 wt%) were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd.. Urea ($CO(NH_2)_2$), salicylate sodium ($Na_3C_6H_5O_7$), sodium hypochlorite (NaClO), and sodium nitroferricyanide ($Na_2[Fe(CN)_5NO]_2 \cdot H_2O$) were brought from Tianjin Fuyu Chemical Reagent Co. Ltd.. Sulfuric acid (H_2SO_4), hydrochloric acid (HCl) and ethanol (C_2H_5OH) were purchased from Chengdu Kelong Chemical Reagent Factory. Nafion 117 membrane (DuPont) was purchased from HESEN Co., Ltd.. The water used throughout all experiments was purified through a Millipore system. All reagents were used as received without further purification.

Preparation of MBN and BBN: In a typical synthesis,[1] $CO(NH_2)_2$ (9.00 g) and H_3BO_3 (1.85 g) were dissolved in deionized water (450 mL) at 65 °C, and water was then allowed to completely evaporate at that temperature. The intermediates were ground and loaded in an alumina boat crucible and then heated in a tubular furnace under N_2 atmosphere from room temperature to 1050 °C at a rate of 10 °C min^{-1}. This temperature was maintained for 3.5 h. The samples were allowed to cool to ambient temperature while maintaining the same nitrogen flow. At the end of the synthesis, a white powder (MBN) was obtained. The BBN was prepared by drying in the oven at 65 °C for 24 h before heated in a tubular furnace.

Preparation of MBN/CP electrode: The MBN ink was prepared by dispersing 5 mg of MBN catalyst dispersed into 1 mL ethanol containing 20 μL of 5 wt% Nafion and kept ultrasonic for 1 h. Then 40 μL of the MBN ink was loaded on the carbon paper (1 cm × 1 cm). The MBN/CP working electrode was prepared well.

Characterizations

XRD patterns were obtained from a Shimazu XRD-6100 diffractometer with Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm (Japan). SEM images were collected from the tungsten lamp-equipped SU3500 scanning electron microscope at an accelerating voltage of 20 kV (HITACHI, Japan). TEM images were obtained from a Zeiss Libra 200FE transmission electron microscope operated at 200 kV. XPS measurements were performed on an ESCALABMK II Xray photoelectron spectrometer using Mg as the exciting source. The absorbance data of spectrophotometer were measured on SHIMADZU UV-2700 ultraviolet-visible (UV-Vis) spectrophotometer.

Electrochemical measurements: Before NRR measures, Nafion 211 membrane was pre-treated by heating in 5% H_2O_2 solution and ultrapure water at 80 °C for 1 h, respectively. Electrochemical measurements were performed with a CHI 660D electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system using MBN/CP (1.0 cm × 1.0 cm) as the working electrode, a graphite rod as the counter electrode and an Ag/AgCl electrode as the reference electrode. Electrochemical characterization of the MBN/CP catalysts was carried out in 0.1 M Na_2SO_4 electrolytes. All experiments were carried out at room temperature (25 °C). For N_2 reduction experiments, the electrolyte was bubbled with N_2 for 30 min before the measurement. All potentials measured were calibrated to RHE using the following equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.059 \times pH + E^{\circ}_{Ag/AgCl} \qquad (E-1)$$

Determination of NH₃: The produced ammonia was estimated by indophenol blue method by ultraviolet spectroscopy.[2] In detail, 4 mL electrolyte was removed from the cathodic chamber and added into 50 μL oxidizing solution containing NaClO (ρCl = 4–4.9) and NaOH (0.75 M), followed by further adding 500 μL coloring solution

containing 0.4 M $C_7H_5O_3Na$ and 0.32 M NaOH, and 50 µL catalyst solution (0.1 g $Na_2[Fe(CN)_5NO] \cdot H_2O$ diluted to 10 mL with deionized water) in turn. After standing at 25 °C for 2 h, the UV-Vis absorption spectrum was measured. The concentration of indophenol blue was determined using the absorbance at a wavelength of 655 nm. The concentrationabsorbance curve was calibrated using standard ammonia chloride solution with a serious of concentrations. The fitting curve (y = 0.373x + 0.010, R^2 = 0.999) shows good linear relation of absorbance value with NH_4^+ concentration by three times independent calibrations.

Determination of N_2H_4: The N_2H_4 present in the electrolyte was determined by the method of Watt and Chrisp.[3] The p-$C_9H_{11}NO$ (5.99 g), HCI (30 mL), and C_2H_5OH (300 mL) were mixed and used as a color reagent. In detail, 5 mL electrolyte was removed from the electrochemical reaction vessel, and added into 5 mL prepared color reagent and stirred 15 min at 25 °C. The obtained calibration curve of N_2H_4 is y = 1.364x + 0.014, R^2 = 0.999.

Calculations of R_{NH3} and FE: R_{NH3} was calculated using the following equation:

$$R_{NH3} \ (\mu g \ h^{-1} \ mg_{cat.}^{-1}) = ([NH_3] \times V) / (17 \times t \times m_{cat.}) \qquad \text{(E-2)}$$

Where $[NH_3]$ ($\mu g \ mL^{-1}$) is the measured NH_3 concentration; V (mL) is the volume of electrolyte; t (h) is the reaction time; m (mg) is the mass loading of catalyst on CP.

FE was calculated according to following equation:

$$FE = 3 \times F \times [NH_3] \times V/(17 \times Q) \qquad \text{(E-3)}$$

Where F is the Faraday constant (96500 C mol^{-1}); and Q (C) is the quantity of applied electricity.
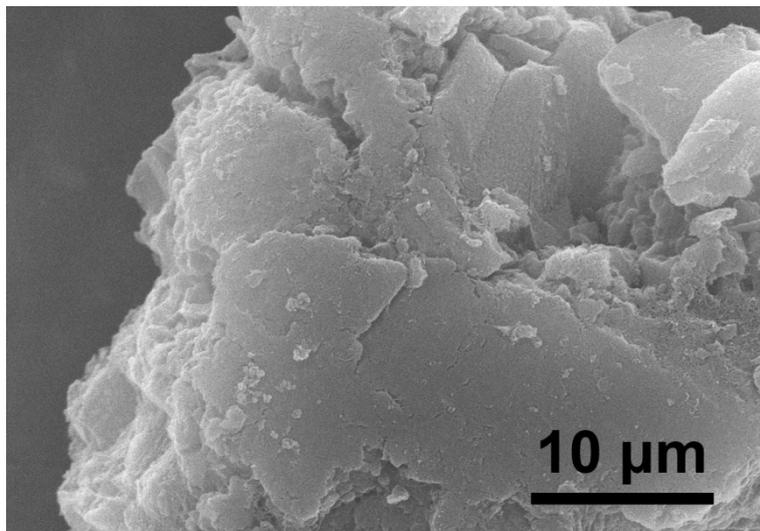
Fig. S1. SEM image of BBN.
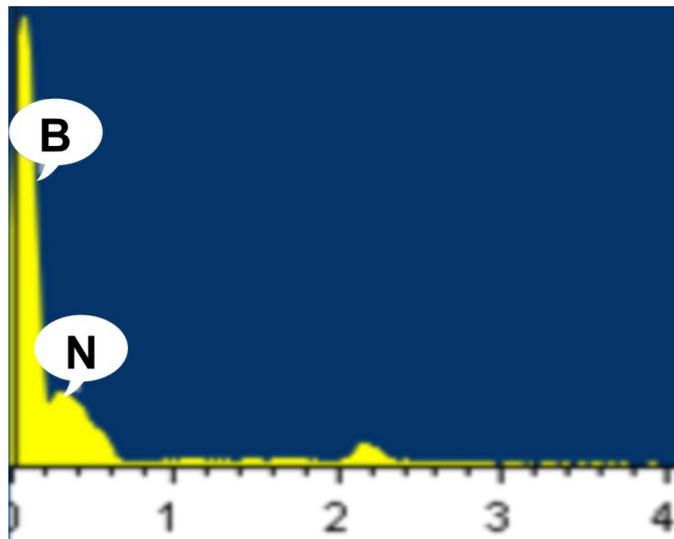
Fig. S2. EDX spectrum of MBN.
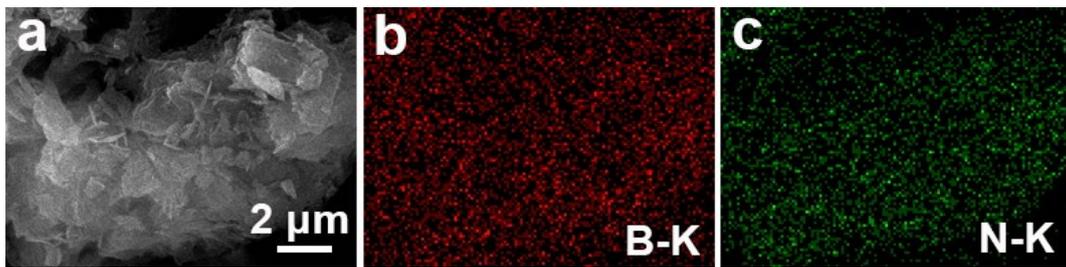
Fig. S3. (a) SEM and EDX elemental mapping images of (b) B and (c) N elements in MBN.
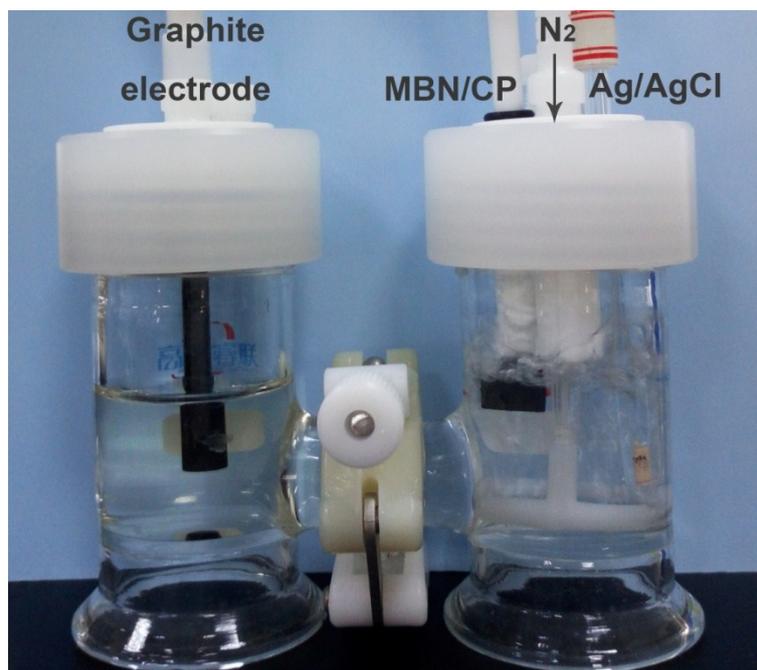
Fig. S4. Optical photograph of the reactor.
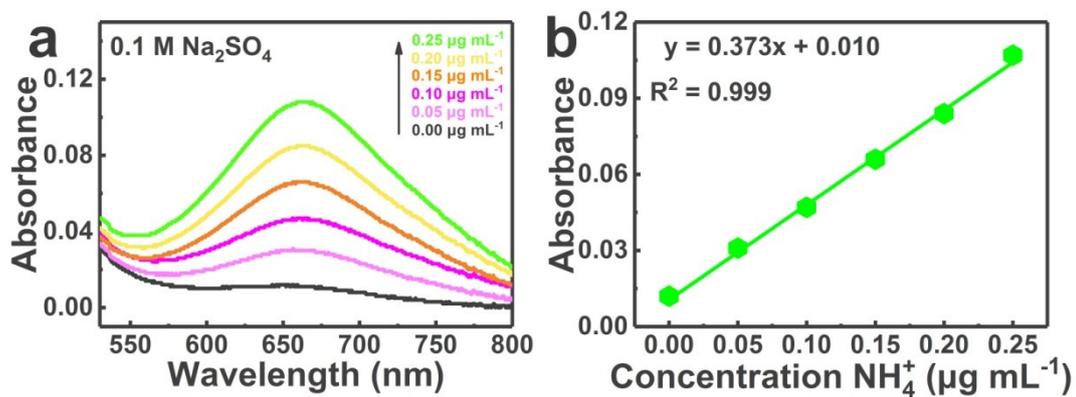
Fig. S5. (a) UV-Vis absorption spectra of indophenol assays with different NH_4^+ concentrations after incubated for 2 h at room temperature. (b) Calibration curve used for calculation of NH_4^+ concentrations.
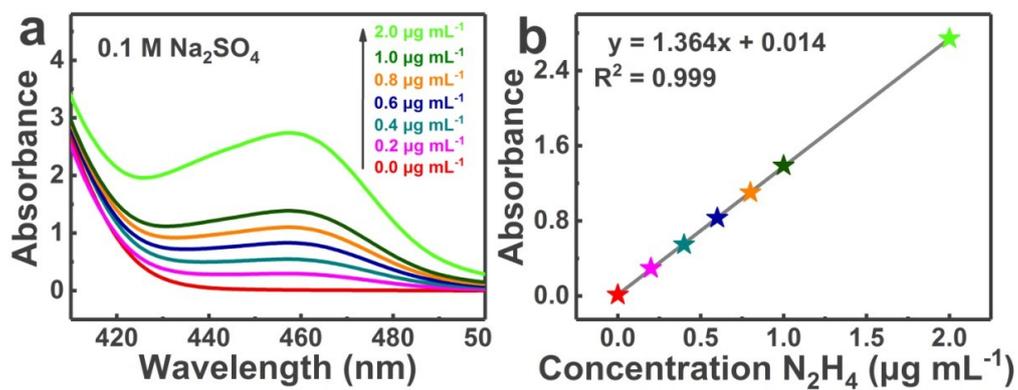
Fig. S6. UV-Vis absorption spectra of various N_2H_4 concentrations after incubated for 10 min at room temperature. (b) Calibration curve used for calculation of N_2H_4 concentrations.
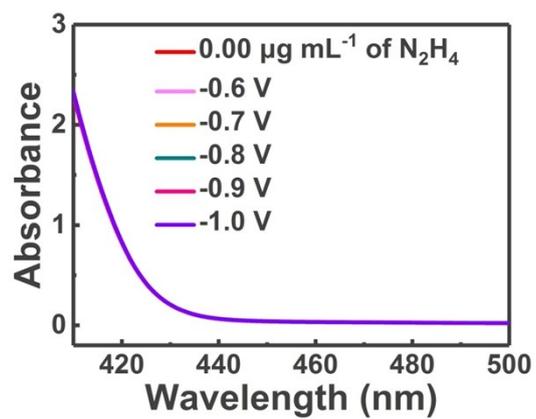
Fig. S7. UV-Vis absorption spectra of the electrolytes stained with *p*-C9H11NO indicator after NRR electrolysis at a series of potentials.
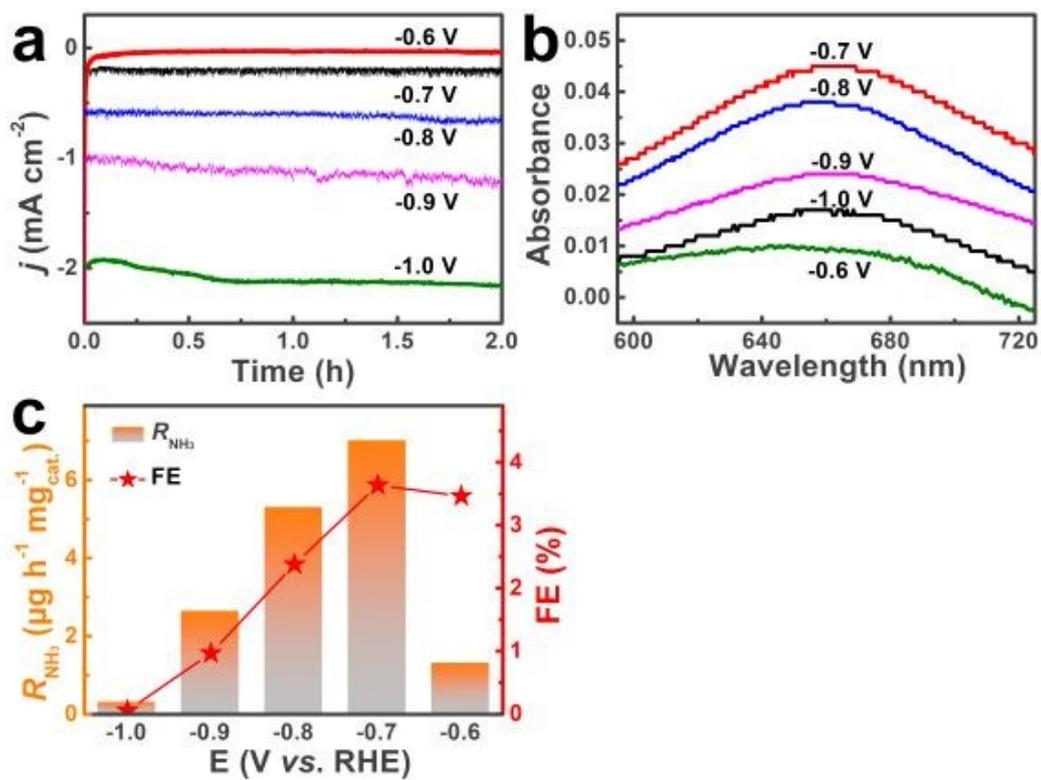
Fig. S8. (a) Chronoamperometry curves of BBN/CP in 0.1 M Na$_2$SO$_4$ solution at different potentials. (b) UV-Vis absorption spectra of the electrolytes stained with indophenol indicator after NRR electrolysis at different potentials for 2 h. (c) R_{NH_3} and corresponding FEs of BBN/CP for NRR at different potentials.
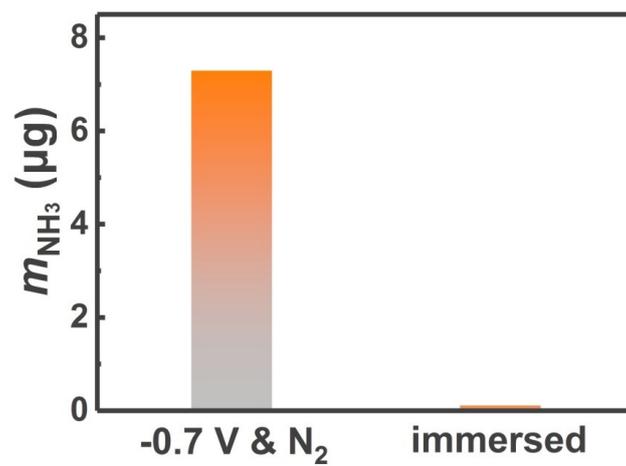
Fig. S9. m_{NH3} for MBN/CP at different test conditions.
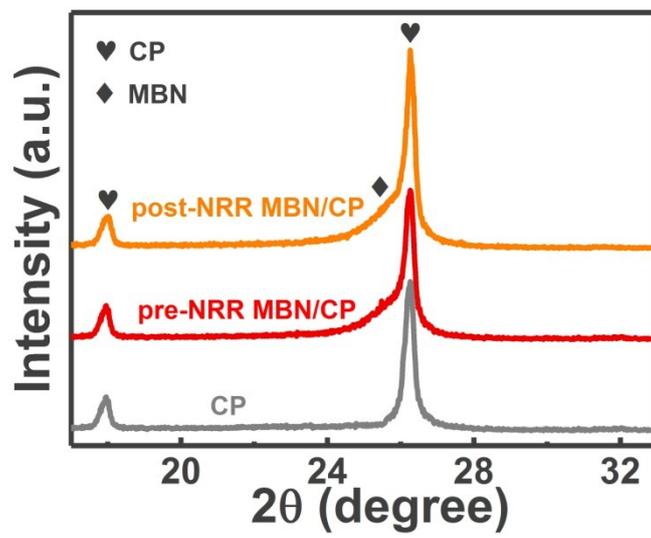
Fig. S10. XRD patterns of bare CP, MBN/CP and post-NRR MBN/CP.
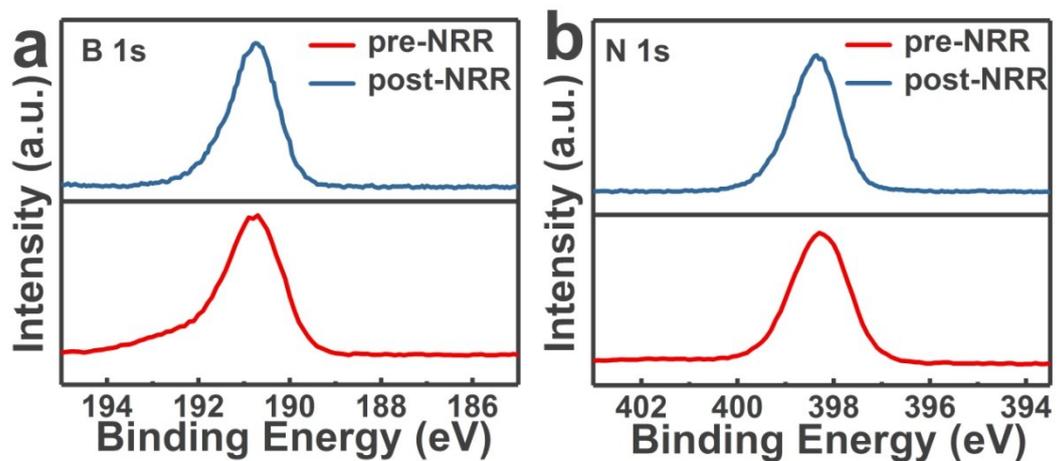
Fig. S11. XPS spectra of MBN in the (a) B 1s and (b) N 1s regions pre- and post-NRR.
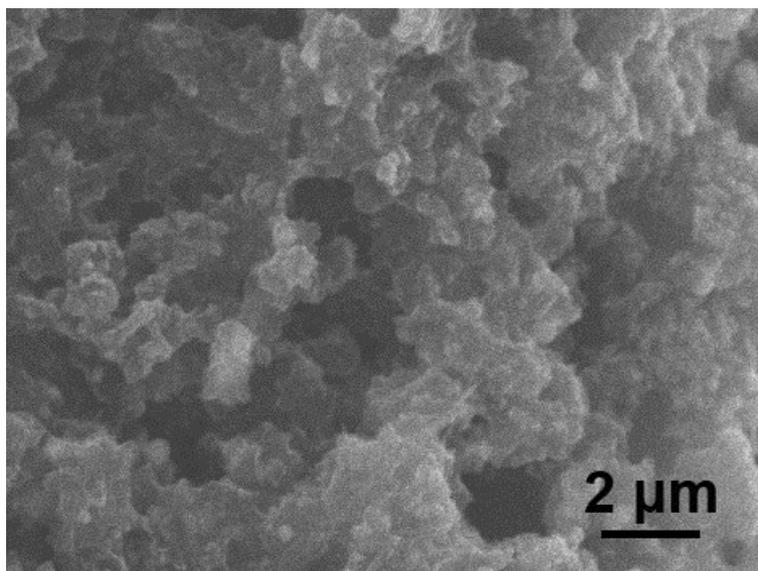
Fig. S12. SEM image of MBN post-NRR.

Table S1. Comparison of the NH_3 electrosynthesis activity for MBN/CP with other aqueous-based NRR electrocatalysts at ambient conditions.

Catalyst	Electrolyte	R_{NH_3}	FE (%)	Ref.
MBN/CP	**0.1 M Na_2SO_4**	**18.2 μg h^{-1} mg$_{cat.}^{-1}$**	**5.5**	**This work**
γ-Fe_2O_3	0.1 M KOH	0.212 μg h^{-1} mg$_{cat.}^{-1}$	1.9	4
Fe_2O_3-CNT	0.1 M $KHCO_3$	0.22 μg h^{-1} cm$_{cat.}^{-2}$	0.15	5
Fe_3O_4/Ti	0.1 M Na_2SO_4	3.43 μg h^{-1} cm$_{cat.}^{-2}$	2.60	6
Mo nanofilm	0.01 M H_2SO_4	1.89 μg h^{-1} cm$_{cat.}^{-2}$	0.72	7
MoO_3	0.1 M HCl	29.43 μg h^{-1} mg$_{cat.}^{-1}$	1.9	8
MoS_2/CC	0.1 M Na_2SO_4	4.94 μg h^{-1} cm$_{cat.}^{-2}$	1.17	9
Mo_2N	0.1 M HCl	78.4 μg h^{-1} mg$_{cat.}^{-1}$	4.5	10
MoN	0.1 M HCl	18.42 μg h^{-1} cm$_{cat.}^{-2}$	1.15	11
VN	0.1 M HCl	5.14 μg h^{-1} cm$_{cat.}^{-2}$	2.25	12
Au NRs	0.1 M KOH	1.64 μg h^{-1} cm$_{cat.}^{-2}$	3.88	13
a-Au/CeO$_x$-RGO	0.1 M HCl	8.3 μg h^{-1} mg$_{cat.}^{-1}$	10.1	14
TA-reduced Au/TiO_2	0.1 M HCl	21.4 μg h^{-1} mg$_{cat.}^{-1}$	8.11	15
Pd/C	0.1 M PBS	4.5 μg h^{-1} mg$_{cat.}^{-1}$	8.2	16
$Pd_{0.2}Cu_{0.8}$/rGO	0.1 M KOH	2.80 μg h^{-1} mg$_{cat.}^{-1}$	4.5	17
carbon nitride	0.1 M HCl	8.09 μg h^{-1} mg$_{cat.}^{-1}$	11.59	18
PCN	0.05 M H_2SO_4	27.2 μg h^{-1} mg$_{cat.}^{-1}$	1.42	19
N-doped porous carbon	0.1 M HCl	15.7 μg h^{-1} mg$_{cat.}^{-1}$	1.45	20
hollow Cr_2O_3 microspheres	0.1 M Na_2SO_4	25.3 μg h^{-1} mg$_{cat.}^{-1}$	6.78	21

TiO$_2$-rGO	0.1 M Na$_2$SO$_4$	15.13 μg h^{-1} mg$_{cat.}$$^{-1}$	3.3	22
Nb$_2$O$_5$ nanofiber	0.1 M HCl	43.6 μg h^{-1} mg$_{cat.}$$^{-1}$	9.26	23
defect-rich MoS$_2$ nanoflower	0.1 M Na$_2$SO$_4$	29.28 μg h^{-1} mg$_{cat.}$$^{-1}$	8.34	24
B$_4$C	0.1 M HCl	26.57 μg h^{-1} mg$_{cat.}$$^{-1}$	15.95	25
VO$_2$ hollow microsphere	0.1 M Na$_2$SO$_4$	14.85 μg h^{-1} mg$_{cat.}$$^{-1}$	3.97	26
Ti$_3$C$_2$T$_x$ nanosheet	0.1 M HCl	20.4 μg h^{-1} mg$_{cat.}$$^{-1}$	9.3	27
Mo$_2$C nanorod	0.1 M HCl	95.1 μg h^{-1} mg$_{cat.}$$^{-1}$	8.13	28
V$_2$O$_3$/C	0.1 M Na$_2$SO$_4$	12.3 μg h^{-1} mg$_{cat.}$$^{-1}$	7.28	29
oxygen-doped carbon nanosheet	0.1 M HCl	20.15 μg h^{-1} mg$_{cat.}$$^{-1}$	4.97	30

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