Electronic Supplementary Information

Experimental section

Materials: Sodium hydroxide (NaOH), ammonium chloride (NH_4Cl), salicylic acid ($C_7H_6O_3$), sodium citrate dehydrate ($C_6H_5Na_3O_7 \cdot 2H_2O$), *p*-dimethylaminobenzaldehyde ($C_9H_{11}NO$), sodium nitroferricyanide dihydrate ($C_5FeN_6Na_2O \cdot 2H_2O$), sodium nitrate ($NaNO_3$) and sodium hypochlorite (NaClO), were purchased from Aladdin Ltd. (Shanghai, China). Sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), hydrochloric acid (HCl), hydrazine monohydrate ($N_2H_4 \cdot H_2O$), phosphoric acid (H_3PO_4), N, N-dimethylformamide (DMF, C_3H_7NO), ethylalcohol (C_2H_5OH), and sopropyl alcohol (C_3H_7OH) were purchased from Beijing Chemical Corporation. (China). chemical Ltd. in Chengdu. Cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$), adenine ($C_5H_5N_5$), were purchased from Chengdu Kelong Chemical Regent Co. Ltd. Carbon paper (CP) was purchased from Qingyuan Metal Materials Co., Ltd (Xingtai, China). All reagents used in this work were analytical grade without further purification. The ultrapure water purified on a Millipore system was used in all experiments.

Preparation of Co-Adenine MOF: In a 250 mL round-bottom flask, 2.0 mmol adenine was added into 80 mL DMF and heated at 140 °C to form a transparent solution. Then, 1.0 mmol $Co(NO_3)_2 \cdot 6H_2O$ was ultrasonically dissolved in 20 mL DMF, and added to the above flask under vigorous stirring. The color of this mixture immediately turned to purple blue and gradually changed to brown. The reaction was allowed to proceed for 4 h, and the mixture was left to cool down to room temperature. Co-Adenine (identified as Co-Ade) MOF were collected by centrifugation, and then washed with water and ethanol for several times. The samples were finally dried at 160 °C overnight.

Preparation of Co@NC: the as-prepared Co-Ade MOF was heated to 700 °C at a heating rate of 5 °C min^{-1} and maintained for 1 h in Ar atmosphere.

Preparation of NC: As a control, the NC was prepared by the direct carbonization of adenine at the same conditions.

Characterizations: XRD dates were acquired by a LabX XRD-6100 X-ray diffraction instrument. SEM measurements were carried out on a Gemini Sigma 300/VP microscope. TEM images were collected on a HITACHI H-8100 electron microscopy. XPS spectra were recorded on an ESCALABMK II X-ray photoelectron spectrometer. UV-Vis absorption spectra were obtained on a SHIMADZU UV-2700 spectrophotometer. Gaseous products from nitrate reduction reaction were determined by GC with SHIMADZU GC-2014 gas chromatograph. A GC run was initiated per 1200 s. Argon (99.999%) was used as the carrier gas. A flame ionization detector with a thermal conductivity detector (TCD) was used to quantify H_2 and N_2. The electrolyzer outlet was introduced into a condenser before being vented directly into the gas sampling loop of the gas chromatograph. ^{1}H NMR spectra were acquired on a Brüker spectrometer operating at 400 MHz.

Electrochemical measurements: All electrochemical measurements were performed in a two-compartment cell separated by a treated Nafion 117 membrane using the CHI760E electrochemical workstation (Shanghai, Chenhua) with a standard three-electrode setup including catalyst coated on carbon paper as the working electrode, a Hg/HgO as the reference electrode, and a graphite rod as the counter electrode. Co@NC ink was obtained by mixing 10 mg of Co@NC catalyst, 960 μL of sopropyl alcohol, and 40 μL of Nafion (5 wt%) to achieve a catalyst concentration of 10 mg mL^{-1} via sonication for 60 min. Co@NC coated on carbon paper (identified by Co@NC/CP) was prepared by dropping 20 μL of the Co@NC ink onto carbon paper (mass loading: 0.2 mg) and drying in air. Electrolyte solution was Ar-saturated 0.1 M NaOH with additional 0.1 M $NaNO_3$. Before the long-term stability test, a thin tube was inserted into H-cell and fixed below the electrolyte level. At each sampling time, 0.5 mL of electrolyte was pipetted into the centrifugal tube for subsequent testing. All potentials reported in our work were converted to reversible hydrogen electrode (RHE) scale and the current density was normalized by the geometrical area of the electrode (0.25 cm^2).

Determination of NH_3: The NH_3 concentration was quantitatively determined by indophenol blue method.[1] Firstly, 2.0 mL of sample solution was mixed with 1.0 mL

of chromogenic reagent, 1.0 mL of oxidizing reagent, and 0.2 mL of catalysing reagent. The absorbance at 655 nm was then measured by a UV-Vis spectrophotometer after 2 h of dark incubation. The concentration-absorption spectra were calibrated using standard NH_4Cl solution with different concentration.

Determination of NO_2^-: The NO_2^- concentration was quantitatively determined by Griess method.[2] Firstly, 1.0 mL of deionized water, 1.0 mL of sample solution, and 2.0 mL of Griess reagent were sequentially added to a 10 mL of centrifuge tube. The absorbance at 540 nm was then measured by a UV-Vis spectrophotometer after 15 min of dark incubation. The concentration-absorption spectra were calibrated using standard $NaNO_2$ solution with different concentration.

Determination of N_2H_4: The N_2H_4 concentration was quantitatively determined by Watt and Chrisp method.[3] Firstly, 1.0 mL of sample solution was mixed with 1.0 mL of chromogenic reagent. The absorbance at 455 nm was then measured by a UV-Vis spectrophotometer after 15 min of dark incubation. The concentration-absorption spectra were calibrated using standard N_2H_4 solution with different concentration.

Determination of NH_3 yield and FE:

$$\mathrm{FE} = \frac{nCVF}{MQ}$$

$$\mathrm{NH_3\ yield} = \frac{CV}{17tA}$$

Where n is the number of electrons transferred during NO_3RR, C is the concentration of products, V is the volume of cathodic electrolyte (35 mL), F is the Faradaic constant (96500 C mol^{-1}), M is the molar mass of products, Q is the total quantity of applied electricity, t is the electrolysis time, and A is the geometric area of working electrode (0.5 × 0.5 cm^2).

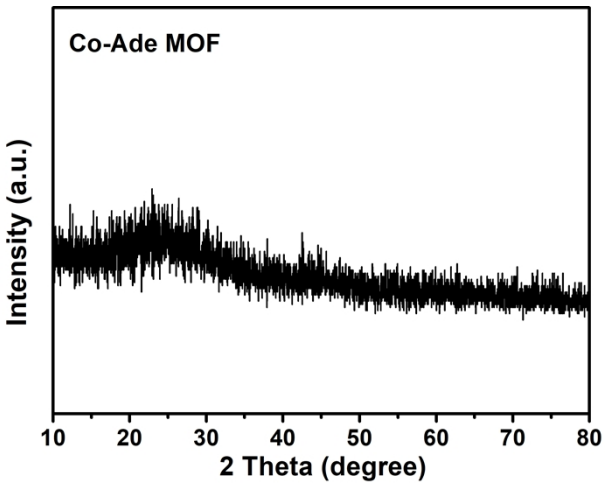

Fig. S1. XRD pattern of Co-Ade MOF.

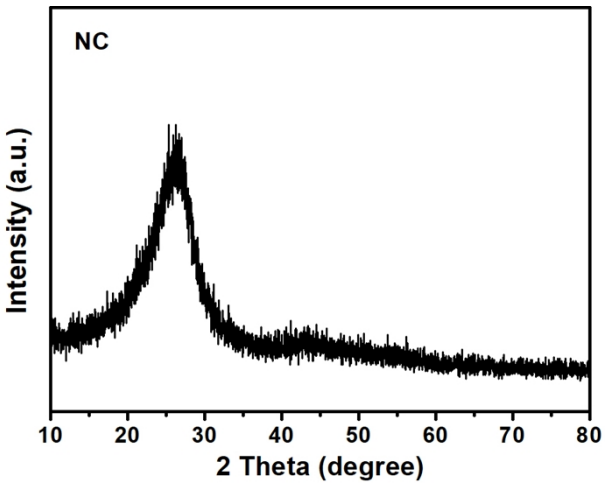

Fig. S2. XRD pattern of NC.

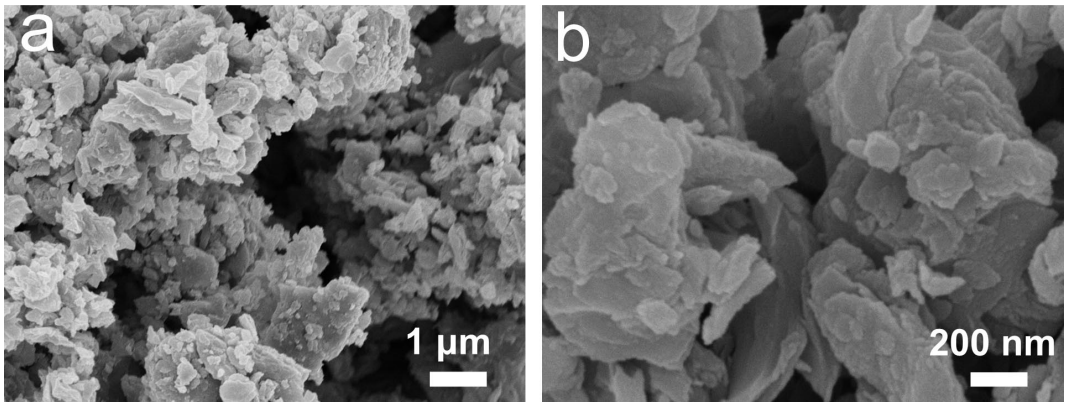

Fig. S3. (a) Low- and (b) high-magnification SEM images of NC.

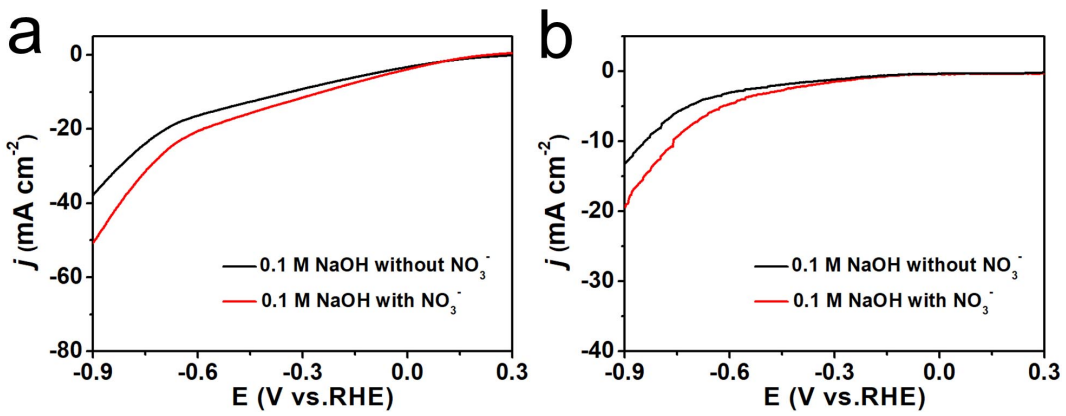

Fig. S4. LSV curves of (a) NC/CP and (b) bare CP in 0.1 M NaOH without and with 0.1 M NO_3^-.

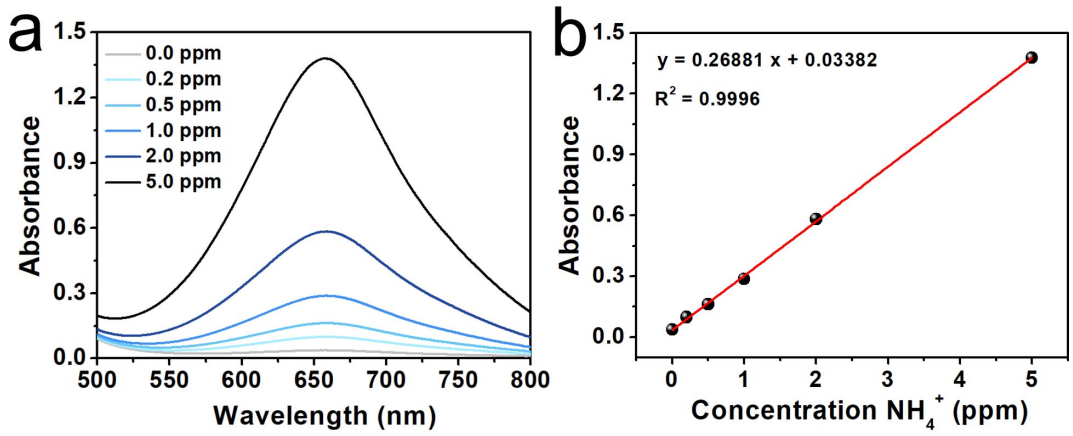

Fig. S5. (a) UV-Vis absorption spectra and (b) corresponding calibration curve used for calculation of NH_4^+ concentration.

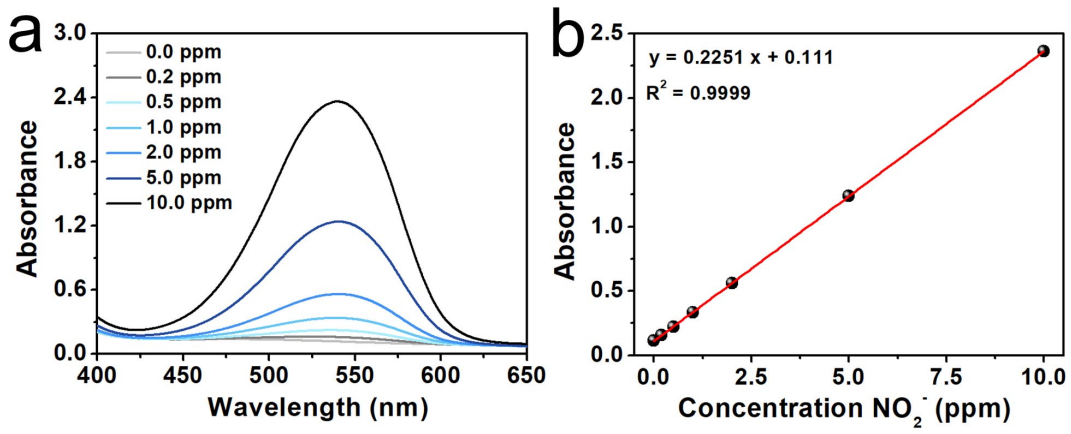

Fig. S6. (a) UV-Vis absorption spectra and (b) corresponding calibration curve used for calculation of NO_2^- concentration.

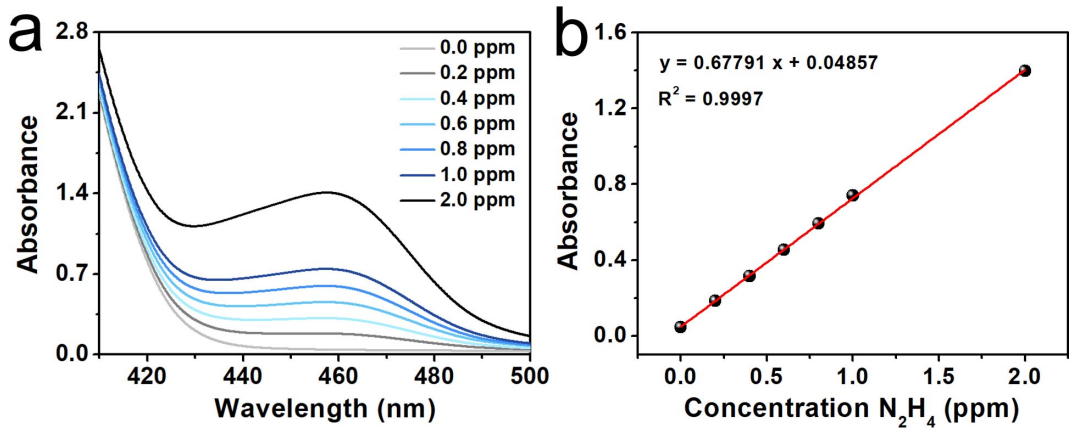

Fig. S7. (a) UV-Vis absorption spectra and (b) corresponding calibration curve used for calculation of N_2H_4 concentration.

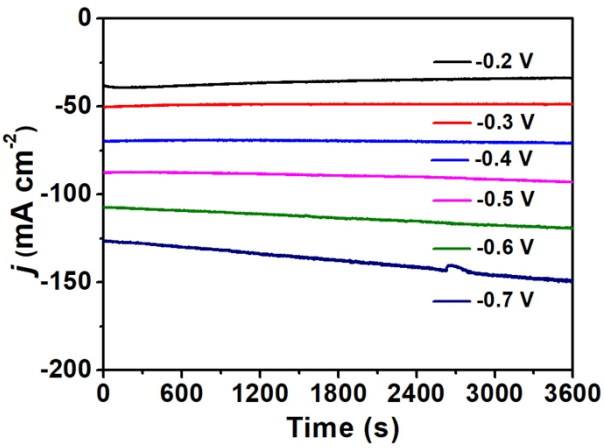

Fig. S8. CA curves for the NO_3RR process on Co@NC/CP at different applied potentials.

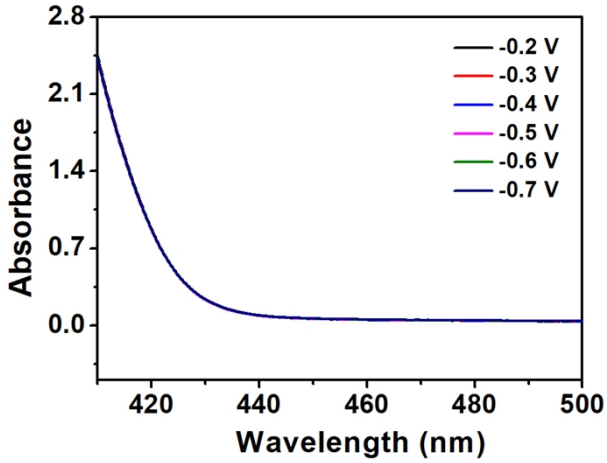

Fig. S9. UV-Vis absorption spectra of generated N_2H_4 for Co@NC/CP at different applied potentials.

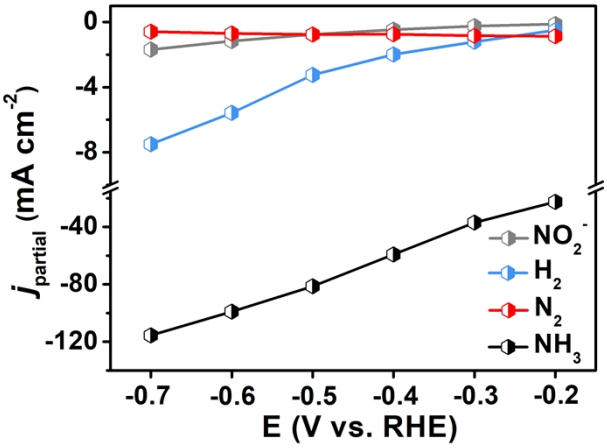

Fig. S10. Partial current densities of NO_2^-, H_2, N_2, and NH_3.

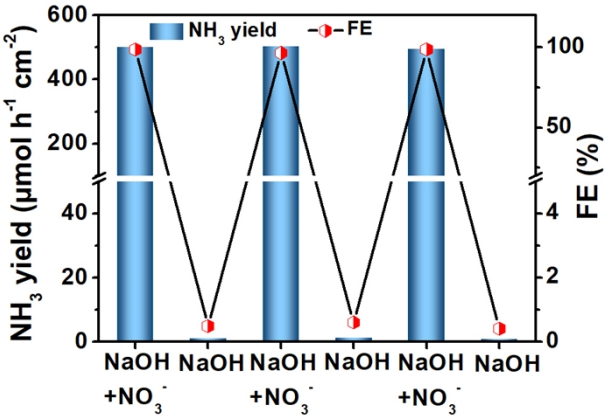

Fig. S11. NH_3 yields and FEs during the alternate cycle tests in NO_3^--containing and NO_3^--free 0.1 M NaOH at −0.5 V.

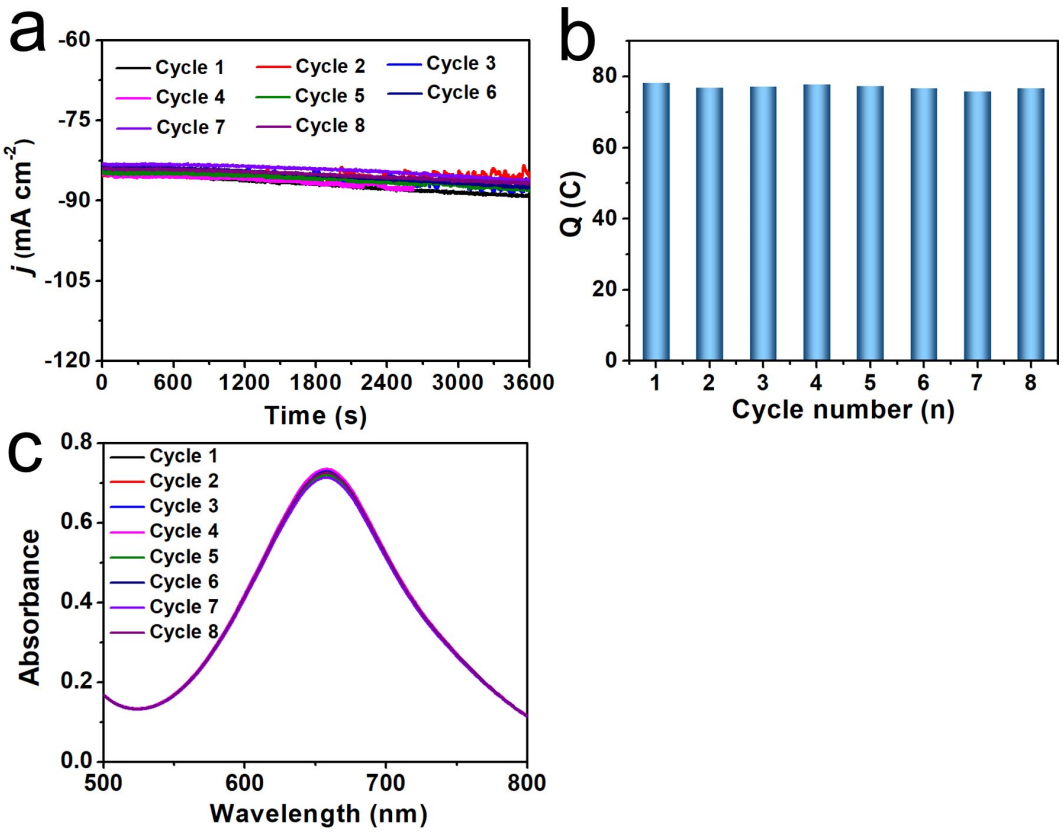

Fig. S12. (a) CA curves, (b) Q values, and (c) corresponding UV-Vis absorption spectra for generated NH_3 during recycling tests at –0.5 V.

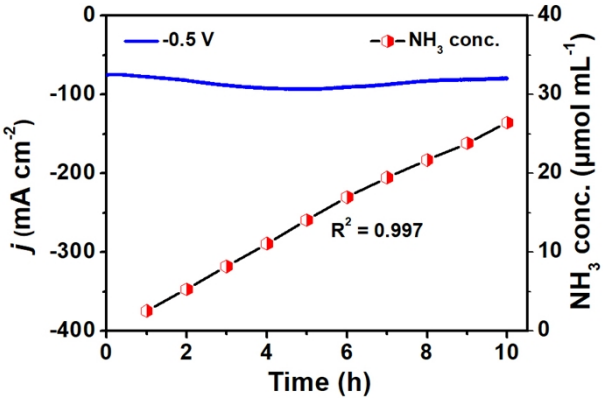

Fig. S13. Long-term stability test of Co@NC/CP at –0.5 V in 0.1 M NaOH with 0.1 M NO_3^- and corresponding NH_3 concentration for Co@NC/CP.

Table S1. Comparison of catalytic performance of Co@NC with other reported non-noble-metal NO_3RR electrocatalysts.

Catalyst	Electrolyte	FE (%)	NH_3 yield	Ref.
Co@NC	**0.1 M NaOH (0.1 M $NaNO_3$)**	**96.5**	**758.0 μmol h^{-1} $mg_{cat.}^{-1}$**	**This work**
Co-NCNT	0.1 M NaOH (0.1 M $NaNO_3$)	92.0	580.3 μmol h^{-1} cm^{-2}	4
Co/CoO NSA	0.1 M Na_2SO_4 (3.23 mM $NaNO_3$)	93.8	194.5 μmol h^{-1} cm^{-2}	5
Co_3O_4@NiO	0.5 M Na_2SO_4 (3.23 mM $NaNO_3$)	55.0	6.9 μmol h^{-1} $mg_{cat.}^{-1}$	6
Co-P/TP	0.2 M Na_2SO_4 (3.23 mM $NaNO_3$)	93.6	24.5 μmol h^{-1} cm^{-2}	7
CoO@NCNT	0.1 M NaOH (0.1 M $NaNO_3$)	93.8	531.8 μmol h^{-1} cm^{-2}	8
Fe SAC	0.1 M K_2SO_4 (0.5 M KNO_3)	75.0	1176.5 μmol h^{-1} $mg_{cat.}^{-1}$	9
Fe-PPy SACs	0.1 M KOH (0.1 M KNO_3)	100	30.0 μmol h^{-1} $mg_{cat.}^{-1}$	10
Fe_3O_4/SS	0.1 M NaOH (0.1 M $NaNO_3$)	91.6	721.4 μmol h^{-1} cm^{-2}	11
Cu_3P NA/CF	0.1 M PBS (0.1 M $NaNO_3$)	62.9	49.9 μmol h^{-1} cm^{-2}	12
Cu/Cu_2O NWAs	0.5 M Na_2SO_4 (3.23 mM $NaNO_3$)	95.8	244.9 μmol h^{-1} cm^{-2}	13
$Cu_{50}Ni_{50}$	1 M KOH (0.01 M KNO_3)	93.0	/	14
In-S-G	0.1 M KOH (0.1 M KNO_3)	75.0	220.0 μmol h^{-1} $mg_{cat.}^{-1}$	15
Pd/TiO_2	0.5 M NaOH (0.25 M $NaNO_3$)	92.1	66.0 μmol h^{-1} cm^{-2}	16
TiO_{2-x}	0.5 M Na_2SO_4 (0.81 mM $NaNO_3$)	85.0	45.0 μmol h^{-1} cm^{-2}	17
Ni_3N/N-C-800	0.5 M Na_2SO_4 (0.05 M $NaNO_3$)	85.0	688.8 μmol h^{-1} $mg_{cat.}^{-1}$	18
BCN@Ni	0.1 M KOH (0.1 M KNO_3)	90.0	1706 μmol h^{-1} $mg_{cat.}^{-1}$	19
Ni_3B@$NiB_{2.74}$	0.1 M KOH (0.1 M KNO_3)	98.7	198.3 μmol h^{-1} cm^{-2}	20

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