

Supporting Information

In-situ growth of GDY-MnO_x heterointerface for selective and efficient ammonia production

Experimental Section

Materials

KMnO₄ and tetrabutylammonium fluoride (TBAF) were purchased from Energy Chemical. The deionized water used in this experiment was purified with a Millipore system. The carbon cloth was pretreated with concentrated nitric acid, deionized water, acetone, ethanol, and deionized water before use. All the other reagents were used as received without any further purification.

Sample characterizations

Scanning electron microscopy (SEM) images were recorded using an S-4800 field emission scanning electron microscope. High-resolution TEM (HRTEM) images were conducted on the FEI Tecnai F20 electron microscope operated at 200 kV. X-ray photoelectron spectroscopy (XPS) was performed by a Thermo Scientific ESCA Lab 250Xi instrument with monochromatic Al K α X-ray radiation to determine the chemical composition and element states. The powder X-ray diffraction (XRD) experiments were carried out with a high-resolution X-ray diffraction system using Cu K α radiation ($\lambda = 0.15406$ nm). Raman spectra were collected by a Renishaw-2000 Raman spectrometer (473 nm excitation laser source). The ¹H NMR signal was collected by a Bruker 400 MHz system. (NMR, AVANCE III HD 400 MHz).

Synthesis of 3D GDY nanosheets on carbon cloth (CC)

The 3D GDY nanosheets were prepared through a typical coupling reaction. Briefly, several freshly washed Cu foils and CC was placed into a 45 mL glass bottle containing hexakis[(trimethylsilyl)ethynyl]benzene (HEB) pyridine-ethyl acetate-H₂O mixed solution under room temperature, and kept for 3 days. The as-prepared GDY was taken out and washed with N, N-dimethylformamide, and acetone several times to remove residual impurities, followed by washing with 1 M HCl solution to remove Cu species overnight. Finally, the freshly prepared GDY samples were used before being dried in

the vacuum oven at 60 °C for at least 12 h.

Preparation of MnO₂ and GDY-MnO_x

The MnO₂ and GDY-MnO_x samples were synthesized through a facile hydrothermal reaction. The MnO₂ and GDY-MnO_x samples were conducted by immersing the piece of pure carbon cloth or 3D GDY nanosheets into 40 ml of 0.1 M neutral KMnO₄ aqueous solution at 160 °C for 24 h. The obtained samples were labeled as MnO₂ and GDY-MnO_x respectively. The obtained nanocomposites were cleaned using distilled water several times to remove the remaining reactants and dried in a vacuum oven at 60 °C for 12 h.

Electrochemical measurements

Electrochemical measurements were performed on a CHI 660E electrochemical workstation (Shanghai CH. Instruments, China) with a customized H-type cell in a typical three-electrode system. The pretreated Nafion 117 membrane was used as the separator and the as-prepared catalyst was used as the working electrode directly in the H-type cell. The Nafion membranes were treated by boiling in water for 1 h, in H₂O₂ for 1 h and then in water for another 1 h, followed by being boiled in 0.5 M H₂SO₄ for 3 h and in water for 6 h before used. All the boiling steps were performed at 80°C. All the potentials reported in this work were converted into reversible hydrogen electrode (E vs. RHE) with the equation of $E_{\text{RHE}} = E_{\text{SCE}} + 0.059 \cdot \text{pH} + 0.242$.

The electrolyte solution with 0.1 M KOH and 0.1 M KNO₃ was saturated by Ar in the cathode and anode compartment for the nitrate reduction reaction. The electrolyte volume was 30 mL for one side. The LSV curves were performed at a rate of 2 mV s⁻¹. The potentiostatic test was conducted at various constant potentials for 1 h with a stirring rate of 200 rpm. For consecutive recycling tests, the electrolyte was collected after each 1 hour and the fresh electrolyte was added after washing the working electrode. The collected electrolyte of the cathode compartment was analyzed by UV-Vis spectrophotometry as mentioned below.

Quantification of ammonia

The produced ammonia was quantified by the indophenol blue method. The chromogenic reagent is composed of 0.36 M salicylic acid, 0.36 M NaOH and 0.18 M

potassium sodium tartrate tetrahydrate. The oxidizing reagent is 12.5 μL NaClO in 0.75 M NaOH solution. 2 mL electrolyte (50-fold dilution of collected electrolyte) was mixed with 250 μL color agent, 25 μL 0.034M sodium nitroprusside and 25 μL oxidizing reagent successively. The obtained mixture was stayed for 1 h to ensure the complete reaction without light. The UV-Vis measurements were conducted with a range of 800 nm to 500 nm. And the ammonia concentration was determined by a concentration-absorbance calibration curve with serious known concentrations solution using the same indophenol blue method.

The FE and yield of NH_3 were calculated as follows:

$$FE_{\text{NH}_3} = \frac{8 \times F \times C_{\text{NH}_4^+} \times V}{Q} \quad (\text{Equation 1})$$

$$Y_{\text{NH}_3} = \frac{C_{\text{NH}_4^+} \times V}{t \times S} \quad (\text{Equation 2})$$

where F is the Faradaic constant of 96485 C mol^{-1} , $C_{\text{NH}_4^+}$ (mmol mL^{-1}) is the concentration of ammonia which be calculated from the calibration curve, V is the volume of the cathodic electrolyte (mL), Q (C) is the total charge passing the electrode, t (h) is the electrolysis time, S (cm^2) is the area of the cathode.

¹H NMR determination of ammonia

To clarify the source of obtained ammonia, $^{15}\text{NO}_3^-$ and $^{14}\text{NO}_3^-$ was used as the nitrogen source to conduct the isotopic labeling nitrate reduction. After nitrate electroreduction reaction, 10 mL electrolyte was extracted and the pH value was adjusted with 4 M H_2SO_4 . 10 mg of maleic acid was added as the internal standard. Then, 0.5 mL of the mixed solution was added with 50 μL DMSO- d_6 for further quantification by ^1H NMR (400 MHz).

Quantification of nitrite

The obtained nitrite was quantified by the Griess test. Typically, the Griess chromogenic reagent was prepared by dissolving N-(1-Naphthyl) dihydrochloride (0.8 g), sulfanilamide (0.04 g) and H_3PO_4 (2 mL, 85%) into 10 mL of DI water. The diluted electrolyte (2 mL) was mixed with the Griess reagent (40 μL) and rested for 10 min at

room temperature. UV-Vis spectrophotometer was used to record the absorption spectra with the range of 400-650 nm. And the nitrite concentration was determined by calibration curve of absorbance with serious known concentrations solution using the same Griess test.

$$FE_{NO_2^-} = \frac{2 \times F \times C_{NO_2^-} \times V}{Q} \quad (\text{Equation 3})$$

$$Y_{NO_2^-} = \frac{C_{NO_2^-} \times V}{t \times S} \quad (\text{Equation 4})$$

where F is the Faradaic constant of 96485 C mol⁻¹, $C_{NO_2^-}$ (mmol mL⁻¹) is the concentration of ammonia which be calculated from the calibration curve, V is the volume of the cathodic electrolyte (mL), Q (C) is the total charge passing the electrode, t (h) is the electrolysis time, S (cm⁻²) is the area of the cathode.

Quantification of hydrazine

The N₂H₄ was quantified by the Watt and Chrisp method by UV-Vis spectroscopy. Typically, the color reagent is the mixed solution containing 5.99 g p-(dimethylamino)benzaldehyde, 30 mL concentrated HCl and 300 mL absolute ethanol. The mixed solution of 5 mL color reagent and 5 mL electrolyte stayed in the dark at room temperature for 10 minutes before testing. The absorbance at 460 nm of mixed solution was then measured by ultraviolet-visible spectroscopy.

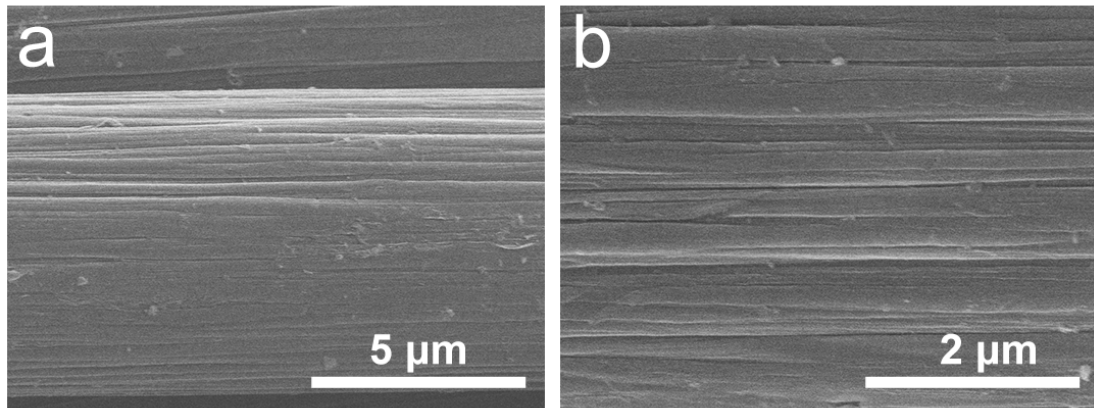


Figure S1. SEM images of pure carbon cloth.

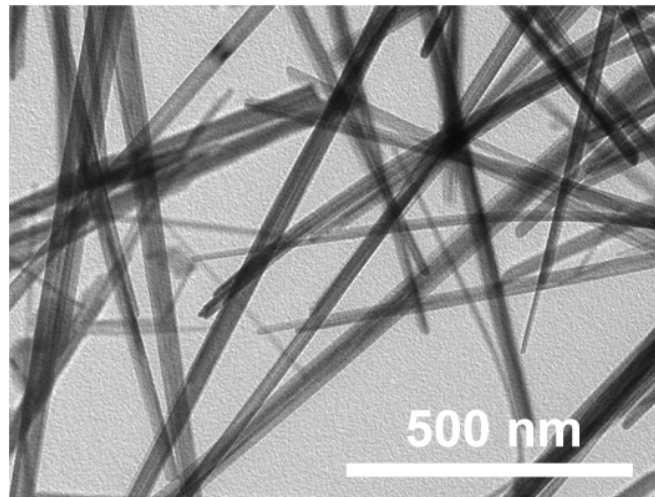


Figure S2. TEM images of GDY-MnO_x nanowires.

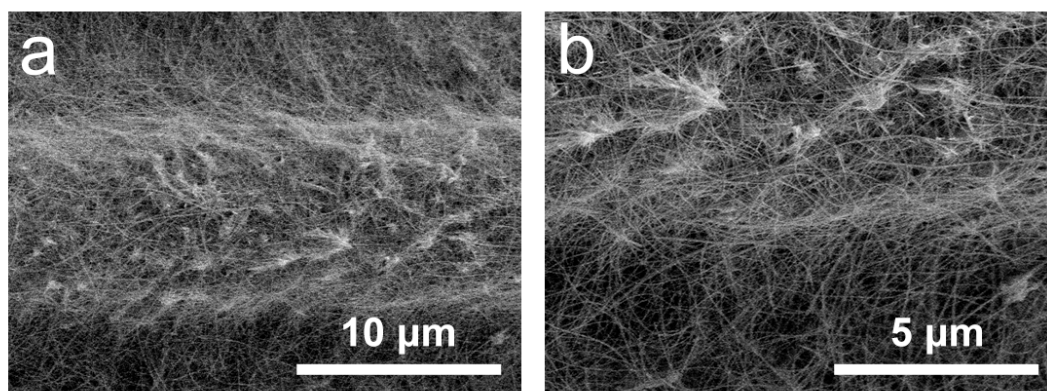


Figure S3. SEM images of MnO₂ nanowires.

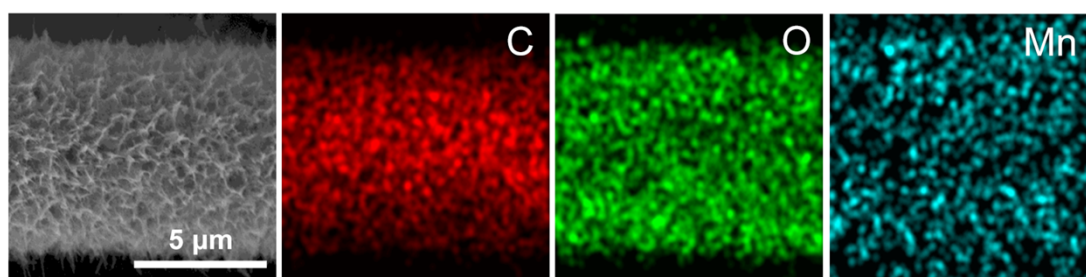


Figure S4. EDX mappings of C, O and Mn signals in MnO_x nanowire grown on GDY.

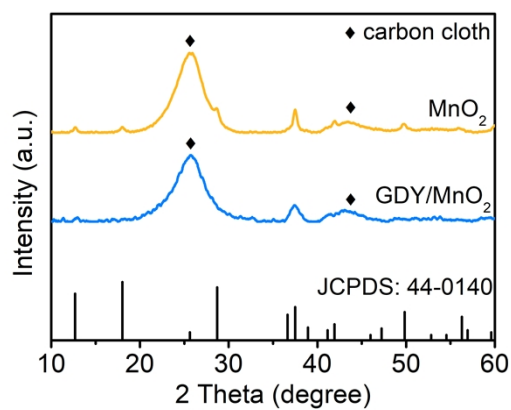


Figure S5. XRD patterns of MnO_2 and GDY-MnO_x .

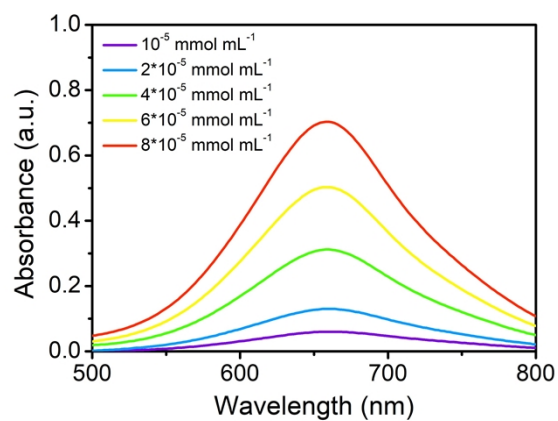


Figure S6. Absorption spectra of the solutions containing different known NH_4^+ concentrations.

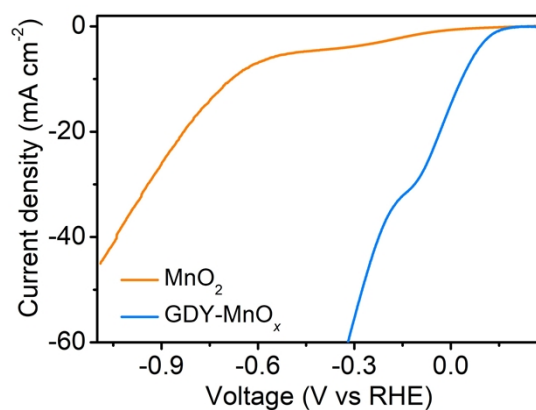


Figure S7. LSV curves of MnO₂ and GDY-MnO_x in 0.1 M KOH with 0.1 M NO₃⁻ electrolyte.

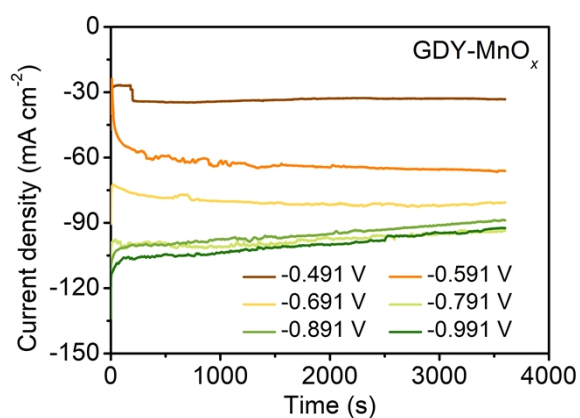


Figure S8. Chronoamperometry curves of GDY-MnO_x at different potentials.

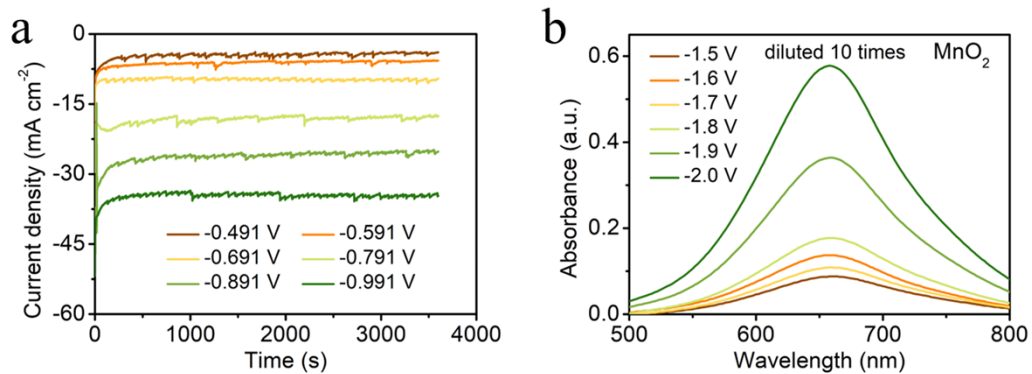


Figure S9. a) Chronoamperometry curves of MnO₂ at different potentials. b) UV-Vis spectra of MnO₂ with different voltages.

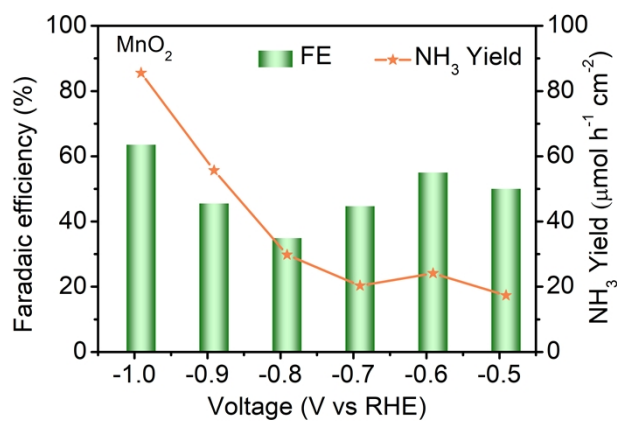


Figure S10. FEs and yields of NH₃ of MnO₂ at different potentials.

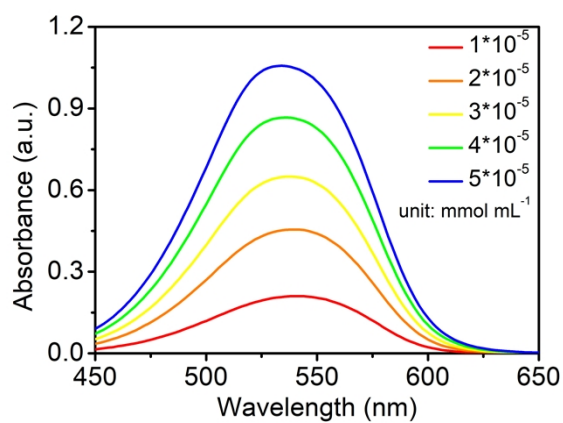


Figure S11. Absorption spectra of the solutions containing different known NO_2^- concentrations.

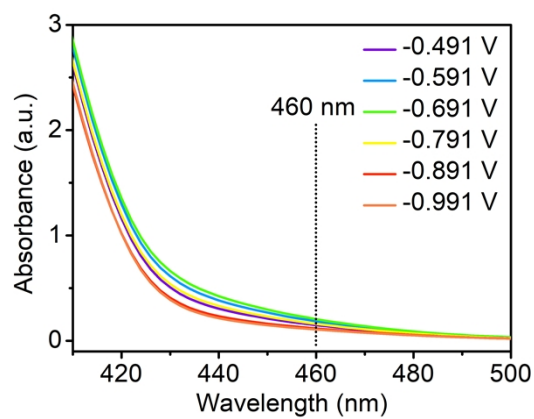


Figure S12. Absorption spectra of the electrolyte solutions at different potentials for detecting hydrazine for GDY- MnO_x .

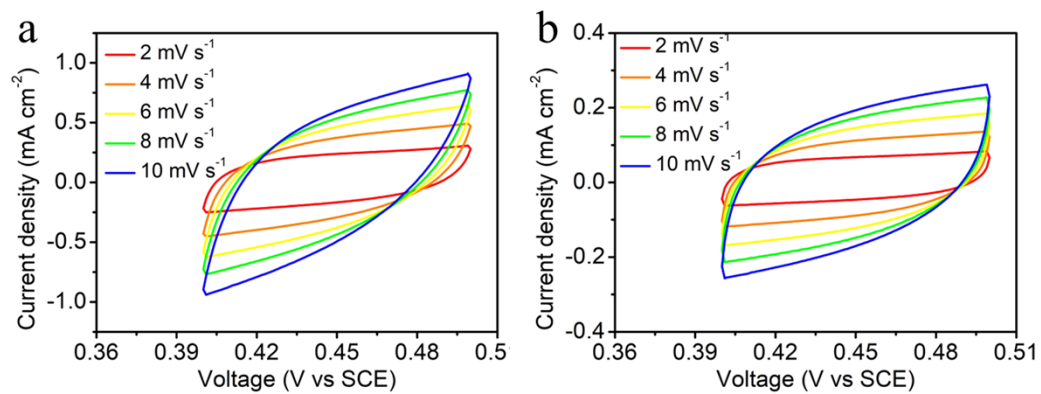


Figure S13. Cyclic voltammogram curves for a) GDY-MnO_x, b) MnO₂ catalysts at different scan rates.

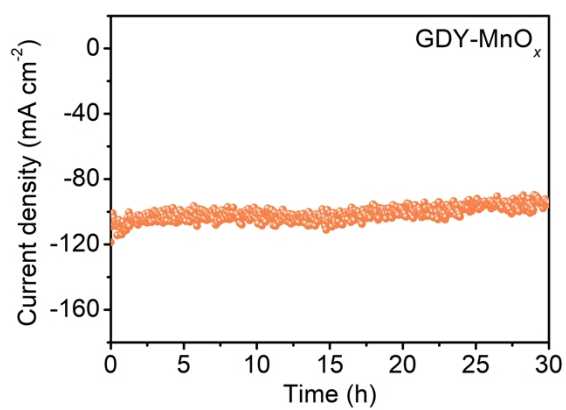


Figure S14. Stability experiment via chronoamperometry at -0.891 V vs RHE.

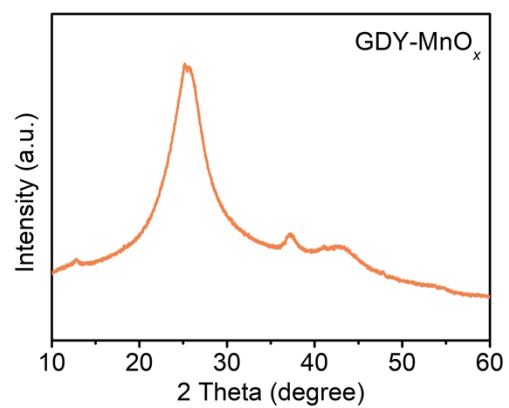


Figure S15. XRD pattern of GDY-MnO_x after electrolysis.

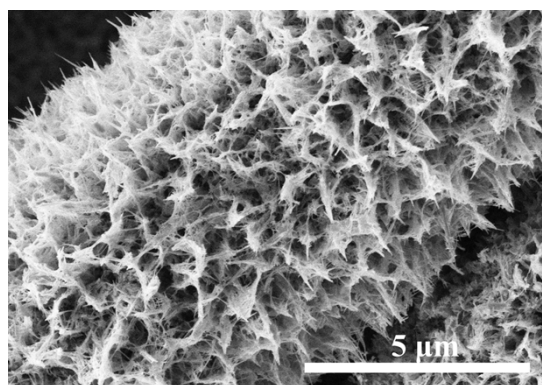


Figure S16. SEM image of GDY-MnO_x after electrolysis.

Table S1. The comparison of GDY-MnO_x with the reported catalysts for electrochemical NtRR.

Reference	Catalyst	Electrolyte	NH ₃ yield rate	Faradaic efficiency
1	CuO@PA NI/CF	0.5 M K ₂ SO ₄ + 200 ppm NO ₃ ⁻	0.213 mmol h ⁻¹ cm ⁻²	93.88%
2	Cu/MnO _x	0.1 M Na ₂ SO ₄ + 100 mM KNO ₃	29.3 mg h ⁻¹ mg _{cat.} ⁻¹	86.2%
3	Co ₃ O ₄ /Co	0.1 M Na ₂ SO ₄ + 1 mg mL ⁻¹ NO ₃ ⁻	4.43 mg h ⁻¹ cm ⁻²	88.7 %
4	Fe-TiO ₂	0.5 M K ₂ SO ₄ and 0.1 M KNO ₃	137.3 mg h ⁻¹ mg _{cat.} ⁻¹	92.3%
5	MoO ₂ -C NBF	1 M KOH + 0.1 M KNO ₃	109.28 μmol h ⁻¹ cm ⁻²	99.05 %
6	Fe-V ₂ O ₅	1 M KOH + 0.1 M KNO ₃	12.5 mg h ⁻¹ cm ⁻²	97.1%
7	Cu ₂ O- Cu/Ti	0.3 M KNO ₃ + 0.1 M HNO ₃	0.28 mmol·cm ⁻² ·h ⁻¹	92%
8	SmCoO ₃	0.1 M PBS + 0.1 M NaNO ₃	14.4 mg h ⁻¹ mg _{cat.} ⁻¹	81.3%
9	Fe1/NC- 900	0.1 M K ₂ SO ₄ + 0.5 M KNO ₃	18.8 mg h ⁻¹ mg _{cat.} ⁻¹	86%
10	CuO@M nO ₂ /CF	0.5 M K ₂ SO ₄ + 200 mg L ⁻¹ NO ₃ ⁻	0.240 mmol h ⁻¹ cm ⁻²	94.92%
11	FeOOH/C	0.1 M PBS + 0.1	2419 μg h ⁻¹ cm ⁻²	92%

	P	M NaNO ₃		
12	sm-LIG	1 M NaNO ₃	2456.8 μg h ⁻¹ cm ⁻²	83.7%
This work	GDY- MnO _x	0.1 M KOH+ 0.1 M NO ₃ ⁻	463.4 μmol h ⁻¹ cm ⁻²	95.4%

Reference

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