Supporting Information

Controllable growth of WO_3@GDY heterointerface for efficient NH_3 synthesis

Determination of ammonia

Indophenol blue method was used for the detection of NH_3. Typically, 1 mL electrolyte (10-fold dilution of collected electrolyte) was mixed with 0.1 M NaOH, 125 μL color agent comprising 0.36 M salicylic acid, 0.36M NaOH, and 0.18M potassium sodium tartrate tetrahydrate, 12.5 μL 0.034M sodium nitroprusside and 12.5 μL NaClO/0.75 M NaOH solution. The UV-Vis measurements were performed after 1 h later and recorded with the range of 800 nm to 500 nm.

The ammonia concentration was determined by linear calibration curve of absorbance with serious known concentrations solution using the same indophenol blue method.

^{1}H NMR determination of ammonia

The synthesized ammonia was also determined by ^{1}H nuclear magnetic resonance (NMR, 400 MHz). Typically, 10 mg maleic acid was first dissolved into the 5 mL electrolytes, and the pH value was adjusted with 4 M H_2SO_4. Then 0.5 mL of the above solution was mixed with 0.05 mL DMSO-d_6 and tested by a 400 MHz SB Liquid Bruker Avance NMR spectrometer at room temperature.

Determination of nitrite

Griess reagent was used as the color-developing agent for the detection of NO_2^-. T Typically, the Griess reagent was composed of 0.8 g N-(1-Naphthyl) dihydrochloride, 0.04 g sulfanilamide, and 2 mL H_3PO_4 (85%) with 10 mL DI water. 2 mL electrolyte was mixed with 2 mL 0.1 M NaOH, after which mixed with the 40 μL Griess reagent and rested for 10 min at room temperature. UV-Vis spectrophotometer was used to record the absorption spectra in the range of 400-650 nm. And the nitrite concentration was determined by a linear calibration curve of absorbance with serious known concentrations solution using the same Griess test.

Calculation of FEs and Yield

The FE and yield of NH_3 were calculated as follows:

$$FE_{NH3} = \frac{8 \times F \times C_{NH4+} \times V}{Q} \qquad (Equation\ 1)$$

$$Y_{NH3} = \frac{C_{NH4+} \times V}{t \times S} \qquad (Equation\ 2)$$

where F is the Faradaic constant of 96485 C mol^{-1}, C_{NH4+} (μg mL^{-1}) is the concentration of ammonia, 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.

The FE and yield of NO_2^- were calculated as follows:

$$FE_{NO2-} = \frac{2 \times F \times C_{NO2-} \times V}{Q} \qquad (Equation\ 3)$$

$$Y_{NO2-} = \frac{C_{NO2-} \times V}{t \times S} \qquad (Equation\ 4)$$

where F is the Faradaic constant of 96485 C mol^{-1}, C_{NO2-} (μg 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.

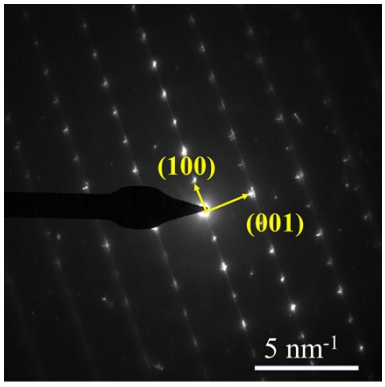

Figure S1. The SEAD pattern of WO_3@GDY.

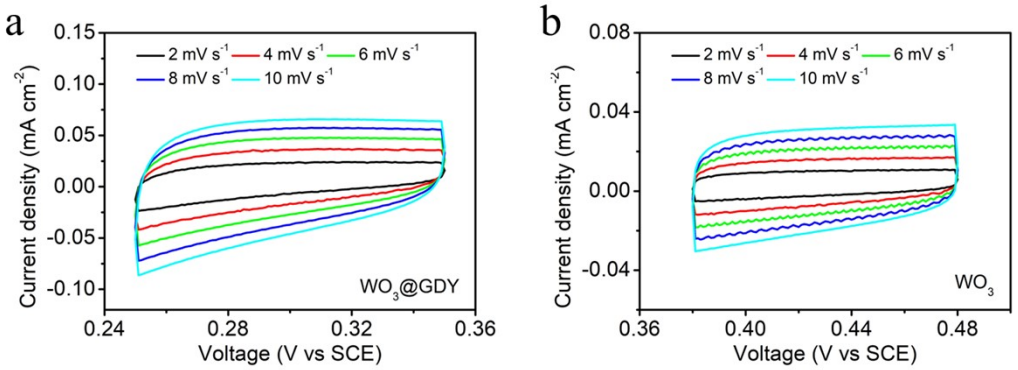

Figure S2 Cyclic voltammogram curves for a) WO_3@GDY, b) WO_3 catalysts at different scan rates.

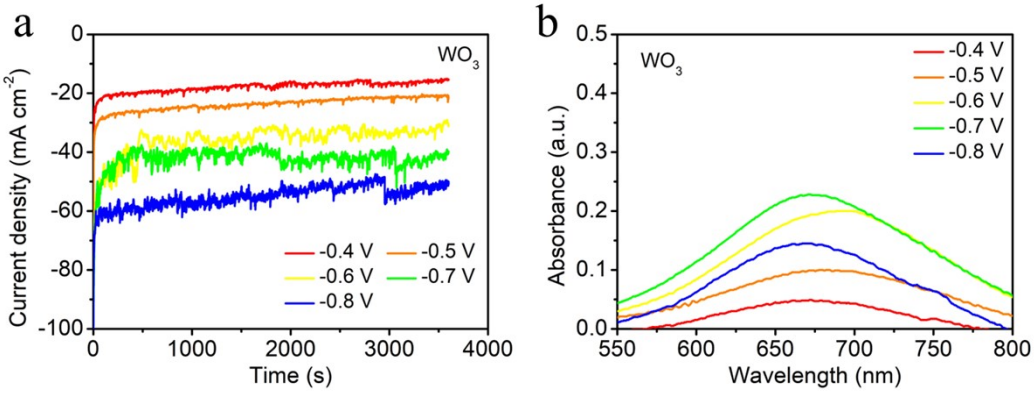

Figure S3. a) Chronoamperometry curves of WO_3 at different potentials. b) UV-Vis spectra of WO_3 with different voltages with diluted 10 times electrolyte.

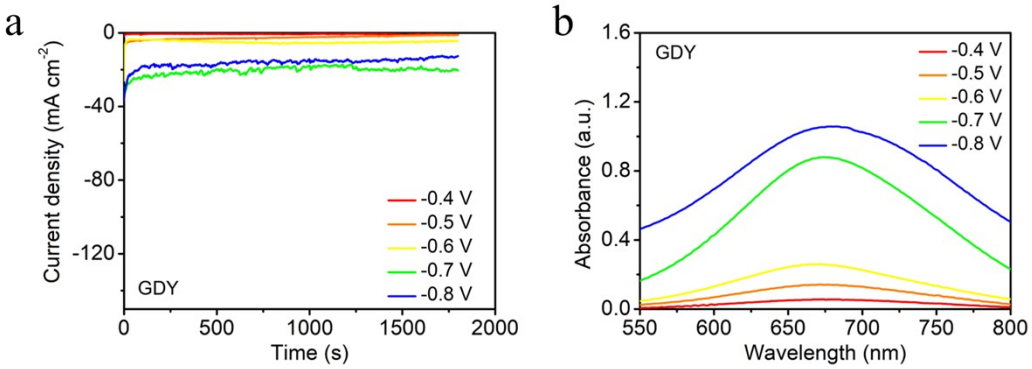

Figure S4. a) Chronoamperometry curves of GDY at different potentials. b) UV-Vis spectra of GDY with different voltages.

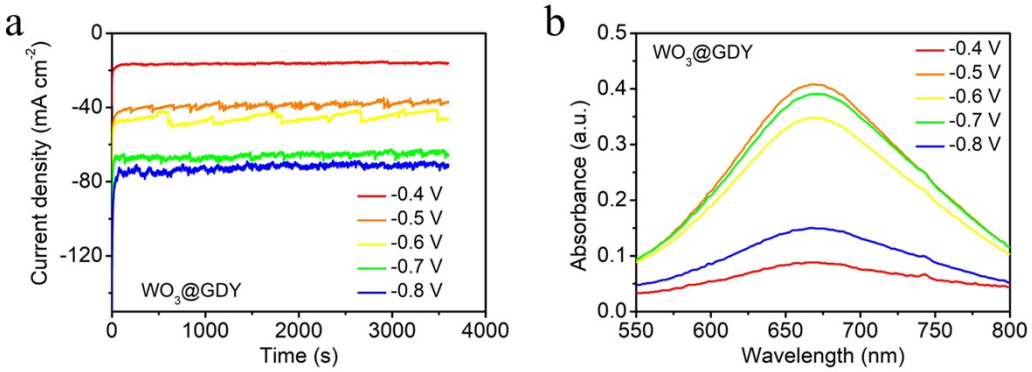

Figure S5. a) Chronoamperometry curves of WO_3@GDY at different potentials. b) UV-Vis spectra of WO_3@GDY with different voltages with diluted 10 times electrolyte.

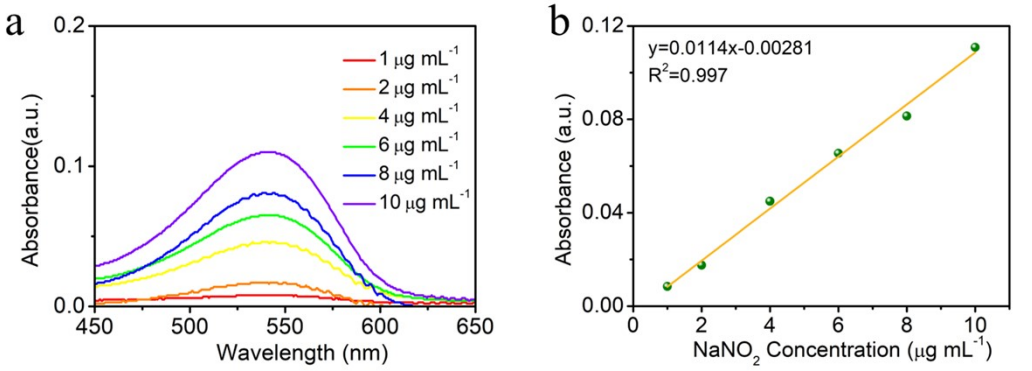

Figure S6. a) Absorption spectra of the solutions containing different known NO_2^- concentrations. b) The corresponding linear relationship between the absorbance at 540 nm and the NO_2^- concentration.

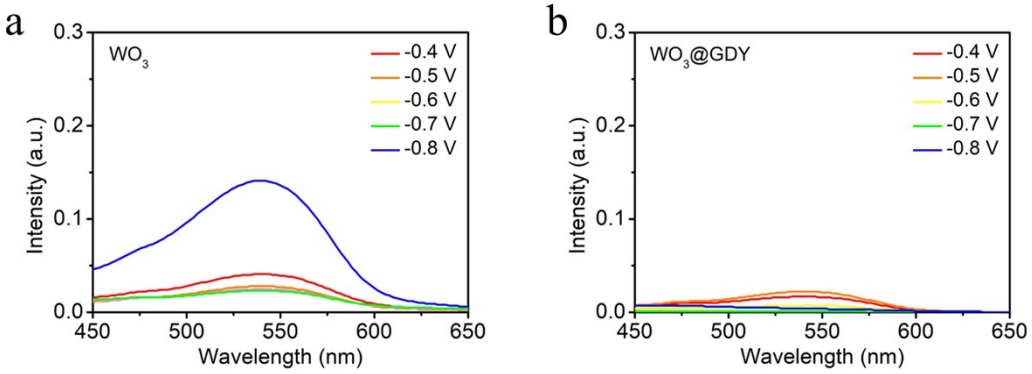

Figure S7. Absorption spectra of the electrolyte solutions at different potentials for detecting NO_2^- for a) WO_3 and b) WO_3@GDY.

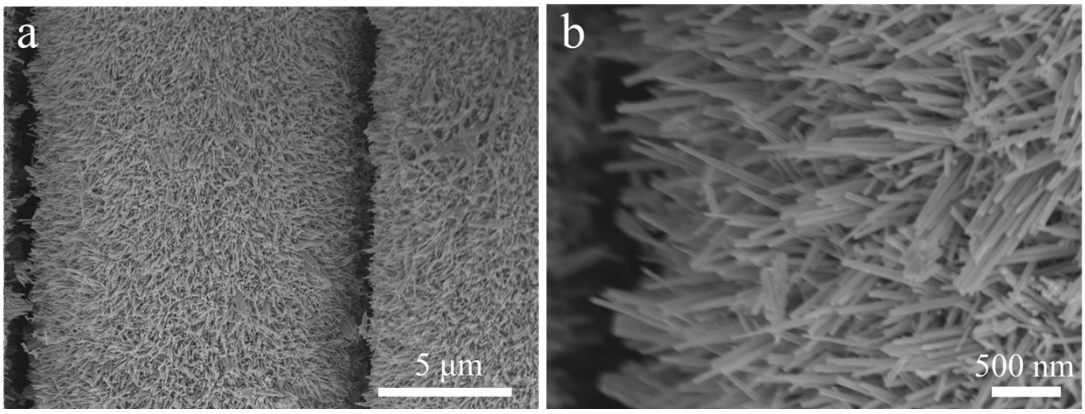

Figure S8. Low and high magnification SEM images of WO_3@GDY after continuous electrolysis for 20 hours.

Table S1. Comparison of the electrocatalytic NtRR performance under acidic conditions.

Catalyst	**$FE_{(NH3)}$**	**$Y_{(NH3)}$**	**Electrolyte**	**Ref.**
WO_3@GDY	85.4	2582.6 μg h^{-1} cm^{-2}	0.1 M HCl+ 0.1 M KNO_3	This work
CuO	80	162 μmol cm^{-2} h^{-1}	0.05 M KNO_3 + 0.05 M H_2SO_4	1
Ti	82	-	0.1 M KNO_3+0.3 M KNO_3	2

Ir NTs	84.7	921 μg h^{-1} mg_{cat}^{-1}	0.1 M $HClO_4$ + 1 M $NaNO_3$	3
Cu-PTCDA	8	485.7 μg h^{-1} mg^{-1}	0.001 M HCl + 0.5 g L^{-1} KNO_3	4
PA-RhCu	93.7	2.40 mg h^{-1} mg_{cat}^{-1}	0.1 M $HClO_4$ + 0.05 M KNO_3[1]	5

Reference

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