

## Supporting Information

### **Self-supported electrocatalyst V doped NiO achieving high ammonia yield of 30.55 $\mu\text{g}/\text{h}/\text{cm}^2$ under ambient conditions**

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## **1.Experimental Section**

### **1.1 Chemicals and Materials.**

Potassium hydroxide (GR 95%), salicylic acid (AR 99.5%), sodium citrate dihydrate (AR 99%), Nickel nitrate hexahydrate (AR 99.5%), ammonium chloride (AR 99.5%), N<sub>2</sub>H<sub>4</sub> solution (100ug/ml 5% HCl), Vanadium(III) chloride, Sodium hypochlorite solution(available chlorine≥5%) and sodium nitro ferricyanide dihydrate were purchased from Aladdin. Deionized water (Millipore, 18.2 MΩ·cm) was used as the solvent. N<sub>2</sub> gas (99.99%), Ar gas (99.99%). Nafion 211 membrane (Dupont).

### **1.2 Preparation of Catalysts.**

#### **Synthesis of V/NiO**

V/NiO was successfully prepared in situ by using a simple hydrothermal process on Ni foam. Typically, 10 mmol of vanadium chloride, 10 mmol of nickel nitrate, 100 mmol of urea and 3.2g glucose were mixed together in a solution containing 40 mL of ethanol and 40 mL of water. After vigorous stirring for 60 min, the above homogeneous mixture was then transferred into a 100 mL Teflon-lined stainless reactor. A piece of 2×3cm nickel foam was ultrasonically treated with 3 M hydrochloric acid, acetone, and water for 30min, respectively. Pretreated nickel foam was then transferred into Teflon-lined stainless reactor and heated at 180°C for 7h (5°C/min). After fully cooled to room temperature, nickel foam was taken out and washed three

times using water and acetone then dried at 60°C. Afterwards, the nickel foam with V-Ni precursor was calcination at 500°C by 3 °C heating ramp/min and then holding for 2 h to form V/NiO. NiO was prepared without the introduction of vanadium chloride and 3.2g glucose.

### **1.3 Characterizations.**

The microtopography of the prepared samples was characterized by transmission electron microscopy (TEM, JEOL 2100 plus + ARM 200 F). Energy dispersive X-ray spectroscopy attached to the transmission electron microscope was used to obtain elemental composition. The crystalline phases were performed by X-ray diffraction (XRD) using an Rigaku D/MAX-2500 powder diffractometer. The chemical states of the prepared sample were conducted using a Thermo Scientific ESCALAB 250Xi photoelectron spectrometer. The absorbance data of spectrophotometer were collected on a SHIMADZU UV-2550 ultravioletvisible (UV-vis) spectrophotometer.

### **1.4 Electrochemical measurements.**

All electrochemical measurements were carried out in a three-electrode H-cell electrochemical system. The anode and cathode components were separated by a Nafion 117 membrane (DuPont). Nafion 117 membrane was pretreated by three steps. First, the membrane was boiling in ultrapure water for 1h. Secondly, the membrane was treating in H<sub>2</sub>O<sub>2</sub>(5%) aqueous solution at 80 °C for 1h. Finally, the membrane was treated in 0.5M H<sub>2</sub>SO<sub>4</sub> for 2h. After this steps , the membrane was dip in 30 ml ultrapure water until the electrochemical measurements started. Working electrode is directly

using V/NiO which slice into 0.8cm\*1cm. (working area: 0.64 cm<sup>2</sup>)

All electrochemical measurements were carried out on an electrochemical workstation (CHI660E, CH Instrumental Corporation, Shanghai, China). Working electrodes and reference electrode (Hg/HgO electrode) were placed directly in the cathodic chamber, counter electrode (Pt electrode) was placed in the anodic chamber. All potentials were converted to reversible hydrogen electrode (RHE) scale via calibration with the equation:

$$E (\text{vs. RHE}) = E (\text{vs. Hg/HgO}) + 0.098 + 0.059 \times \text{pH}$$

Before NRR process started, 0.1M KOH was saturated by N<sub>2</sub>(99%) for 30 min. During the NRR process, continuous N<sub>2</sub> was supplied into the electrolyte.

#### **1.4.1 Quantification of ammonia.**

When tested in 0.1M KOH solution, we used spectrophotometry method to detect the quantification of ammonia.<sup>1</sup> Briefly, after 1h electrocatalysis, 2ml electrolyte was removed from cathode, and following 2mL of 1M NaOH solution containing 5% salicylic acid and 5% sodium citrate was added into the solution. Subsequently, 1 mL of 0.05M NaClO and 0.2 mL of 1% C<sub>3</sub>FeN<sub>6</sub>Na<sub>2</sub>O·2H<sub>2</sub>O were added into the above solution. Then the solution was incubated under dark conditions at for 2h before UV-vis absorption spectrum was measured at a wavelength of 655 nm (Shimadzu, UV-2550).

NH<sub>4</sub><sup>+</sup> calibration curve was calculated by using a series of different concentrations standard NH<sub>3</sub> solution (0μg/mL, 0.25μg/mL, 0.5μg/mL, 0.75μg/mL, 1μg/mL). NH<sub>4</sub>Cl was dried in oven before used. Calibration curve showed good linear relationship

( $y=0.316x+0.035$   $R^2=0.999$ ).

#### 1.4.2 Quantification of hydrazine.

The quantification of hydrazine was detected by the method of Watt and Chrisp.<sup>2</sup> In detail, 5.99g  $C_9H_{11}NO$ , 30 mL HCl, and 300 mL ethanol were mixed and used as the color reagent. After NRR process, 5ml electrolyte was taken from cathode, 5ml color reagent was then added into the electrolyte, the solution was incubated under dark conditions at 25 °C for 20min. Then the solution was measured at 455nm. As for  $N_2H_4$  standard solution, the absorbance at the wavelength of 455 nm was plotted against  $N_2H_4$  concentration gradient (0 $\mu$ g, 0.25 $\mu$ g, 0.5 $\mu$ g, 0.75 $\mu$ g, 1 $\mu$ g) The calibration curve showed good linear relationship ( $y=1.294x+0.018$   $R^2=1$ ).

#### 1.4.3 Quantification of nitrate

Firstly, 1.0 mL electrolyte was taken out from the electrolytic cell and diluted to 5 mL to detection range. Then, 0.1 mL 1 M HCl were added into the solution. After shaking and standing for 15 minutes, the absorbance was detected by UV-Vis spectrophotometry at a wavelength of 220 nm and 275 nm. The final absorbance of nitrate-N was calculated based on the following equation:  $A=A_{220nm} - 2A_{275nm}$ . The calibration curve can be obtained through different concentrations of  $KNO_3$  solutions and the corresponding absorbance. It showed an excellent linear relationship between the absorbance value and the  $KNO_3$  concentration from the fitting curve ( $y = 0.0603x + 0.031$ ,  $R^2 = 0.9988$ ).

#### 1.4.4 Quantification of nitrite

The color developer was configured as follows: 20 g of p-

aminobenzenesulfonamide was added to a mixed solution of 250 ml of water and 50 ml of phosphoric acid, and then 1 g of N-(1-naphthyl)-ethylenediamine dihydrochloride was dissolved in the above solution. Finally, the above solution was transferred to a 500 mL volumetric flask and diluted to the mark. 1.0 mL electrolyte was taken out from the electrolytic cell and diluted to 5 mL to detection range. Next, 0.1 mL color reagent was added into the aforementioned 5 mL solution. After shaking and standing for 20 minutes, the absorbance was tested by UV-Vis spectrophotometry at a wavelength of 540 nm. The calibration curve can be obtained through different concentrations of NaNO<sub>2</sub> solutions and the corresponding absorbance. It showed an excellent linear relationship between the absorbance value and the NaNO<sub>2</sub> concentration from the fitting curve ( $y = 0.847x + 0.02$   $R^2 = 0.9998$ ).

#### **1.4.5 Calculation of the Faradaic efficiency and yield.**

The Faradaic efficiency of NRR was calculated as follows

$$FE = 3F \times c \times V / (17 \times Q)$$

where F is the Faraday constant, c is the measured NH<sub>3</sub> concentration, V is the volume of the electrolyte, and Q is the quantity of electric charge for one electron of NRR testing.

The NH<sub>3</sub> formation rate was determined using the following equation:

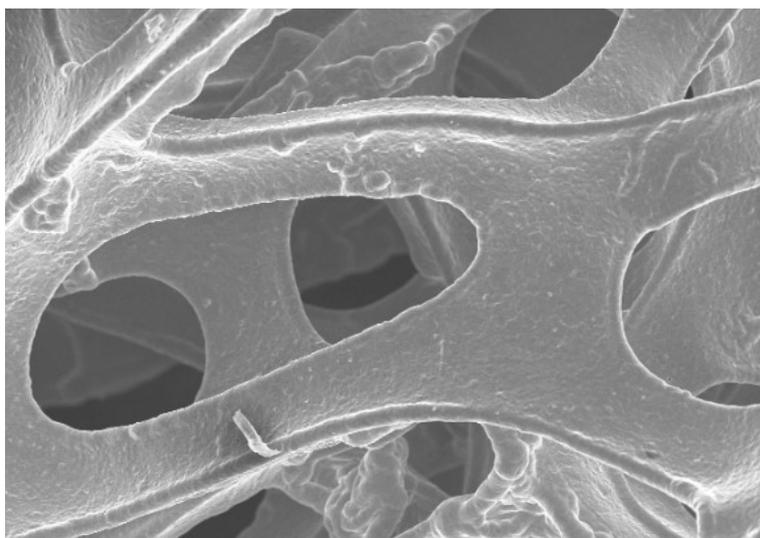
$$r(\text{NH}_3) = (c \times V)/(t \times m)$$

where c is the measured NH<sub>3</sub> concentration, V is the volume of the electrolyte, t is the

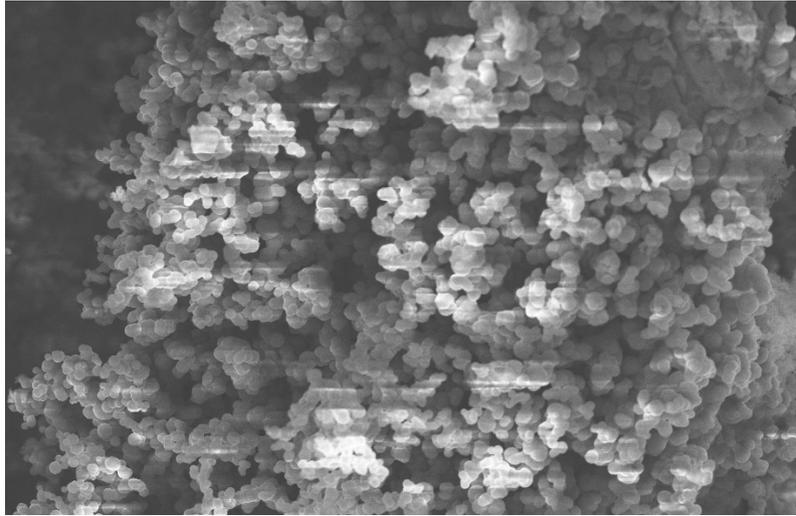
reduction reaction time, and  $m$  is the loading mass of sample (loading mass: 0.25mg).

#### 1.4.6 $^{15}\text{N}_2$ isotope labelling experiments

$^{15}\text{N}$  isotopic labeling experiment was conducted using  $^{15}\text{N}_2$  as the feeding gas (99%, supplied by Shanghai Shoucheng Biotechnology Co.Ltd.) with identical experimental procedure as that of  $^{14}\text{N}_2$  experiment. The yielded  $^{15}\text{NH}_3$  was detected using  $^1\text{H}$  NMR (Bruker Avance-600 MHz). The reference  $^{15}\text{NH}_4\text{Cl}$  sample was dissolved in 0.1 M KOH solution for the measurement, and 10ml electrolyte obtained from  $^{15}\text{N}_2$ -saturated 0.1 M KOH solution with a reaction time of 1 h and a concentration time of 12 h at  $80^\circ\text{C}$  to concentrate electrolyte to 1ml. At last, 0.5ml Dimethyl sulfoxide- $d_6$ (DMSO- $d_6$ ) was added into 1ml concentrated KOH, and 1-3 drops of 0.5M  $\text{H}_2\text{SO}_4$  was added to adjust pH to 1-3 for the  $^1\text{H}$  NMR measurement.<sup>3</sup>



**Fig. S1. SEM image of bare Ni.**



**Fig. S2. SEM image of V/Ni precursor.**

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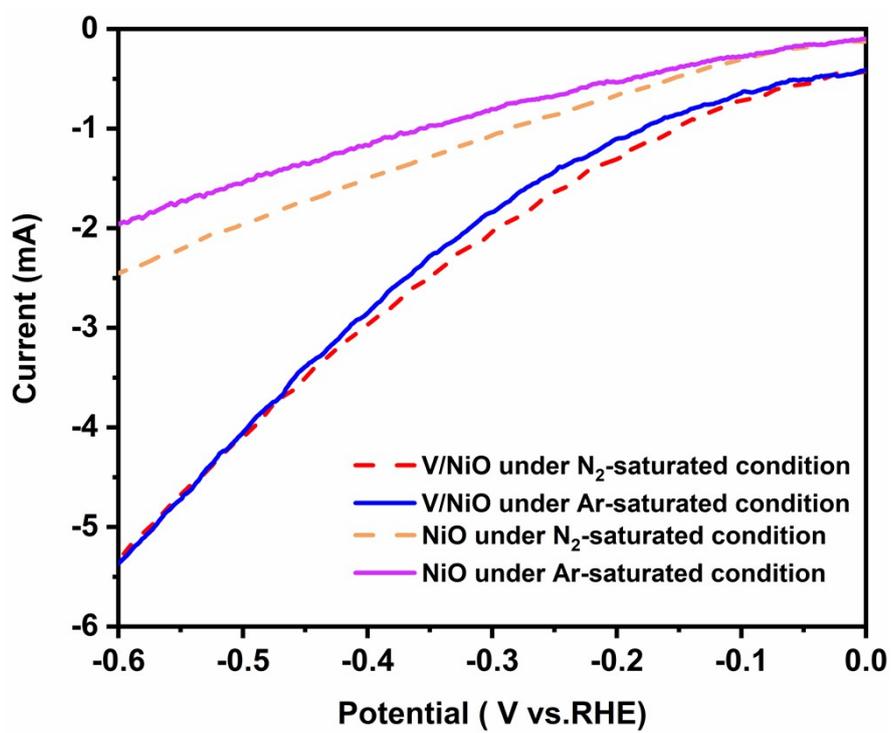
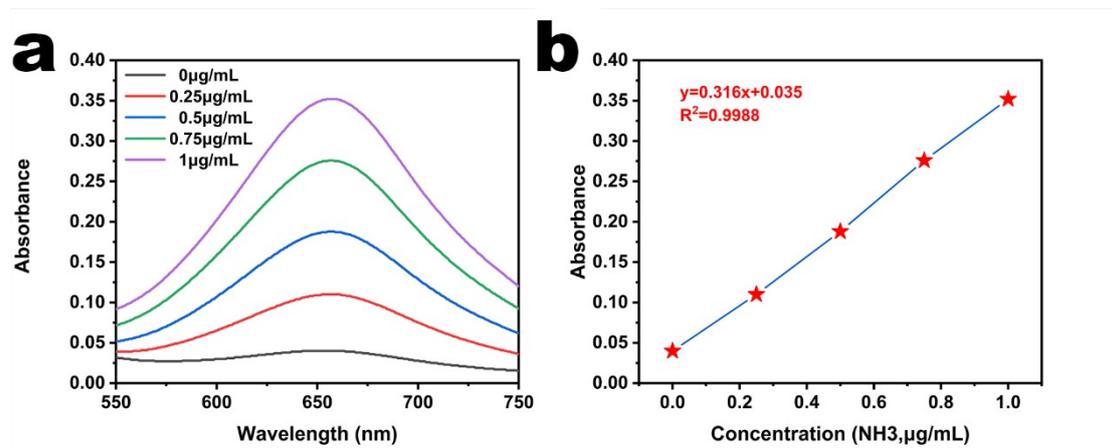


Figure.S3. LSV curves of V/NiO and NiO in Ar- and N<sub>2</sub>-saturated 0.1M KOH.



**Fig. S4. (a) UV-Vis spectra of various  $\text{NH}_3$  concentrations (mother solution: 0.1M KOH) after incubated for 1 h at room temperature. (b) Calibration curve used for calculation of  $\text{NH}_3$  concentrations.**

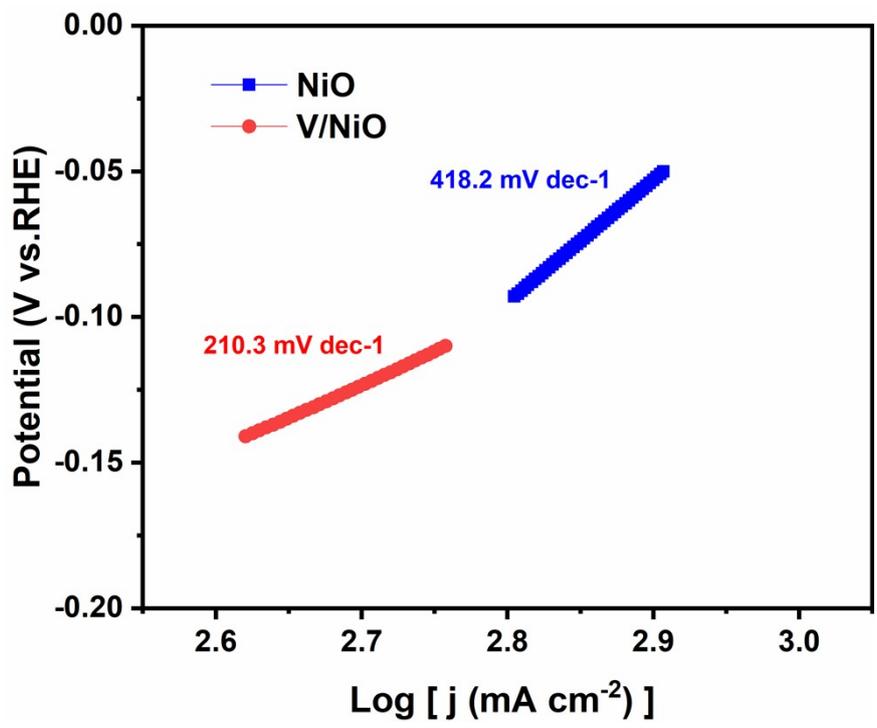


Figure.S5. Tafel plots of V/NiO and NiO

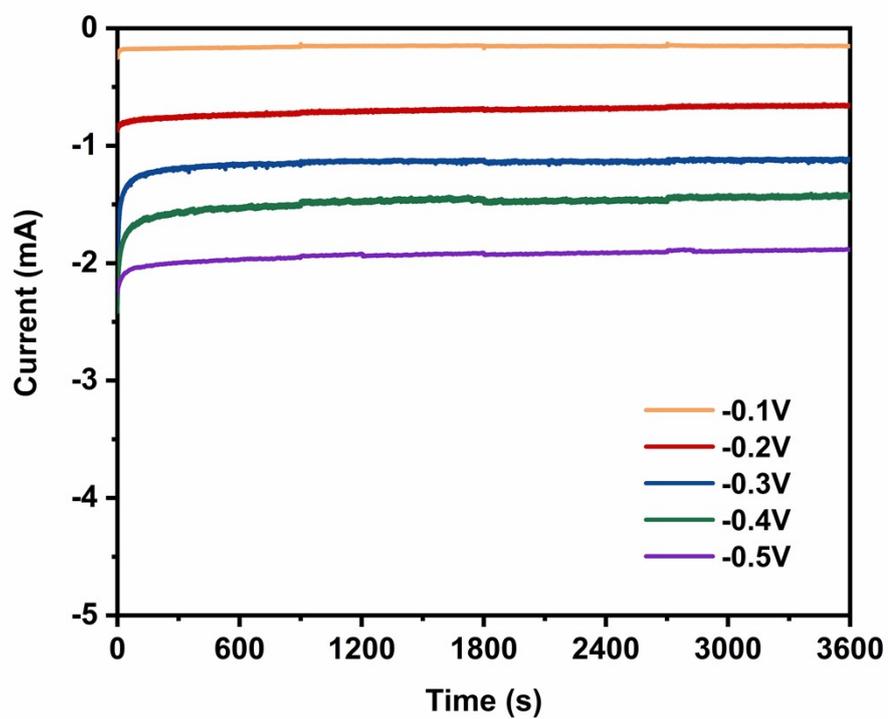


Figure.S6. Chronoamperometry curves of NiO at different potentials.

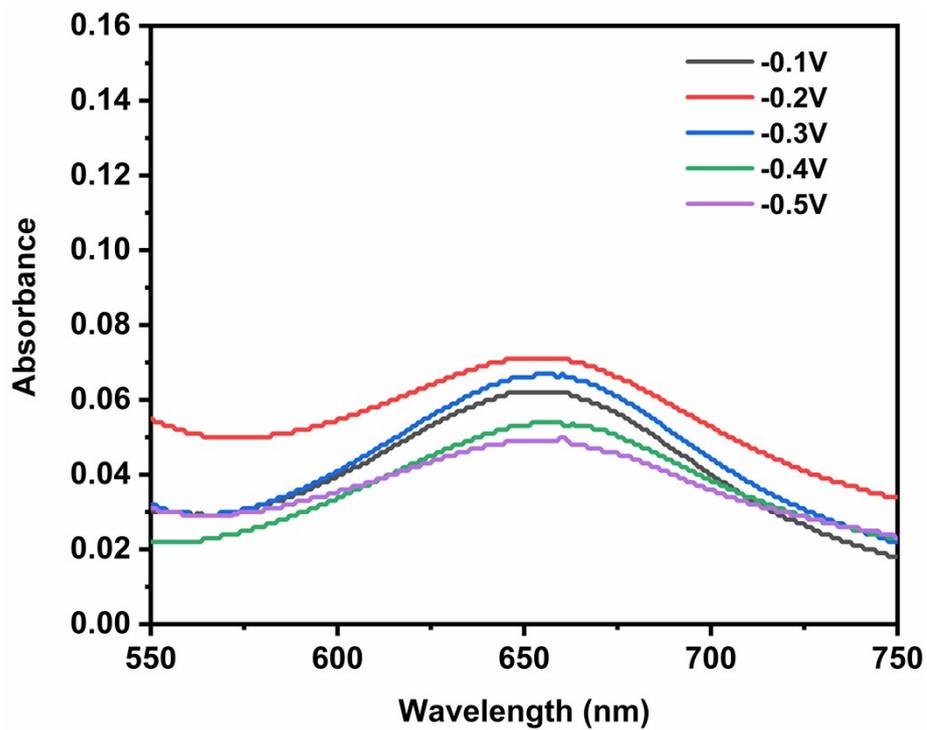


Figure.S7. UV-vis absorption spectra of NiO after NRR process at different potentials.

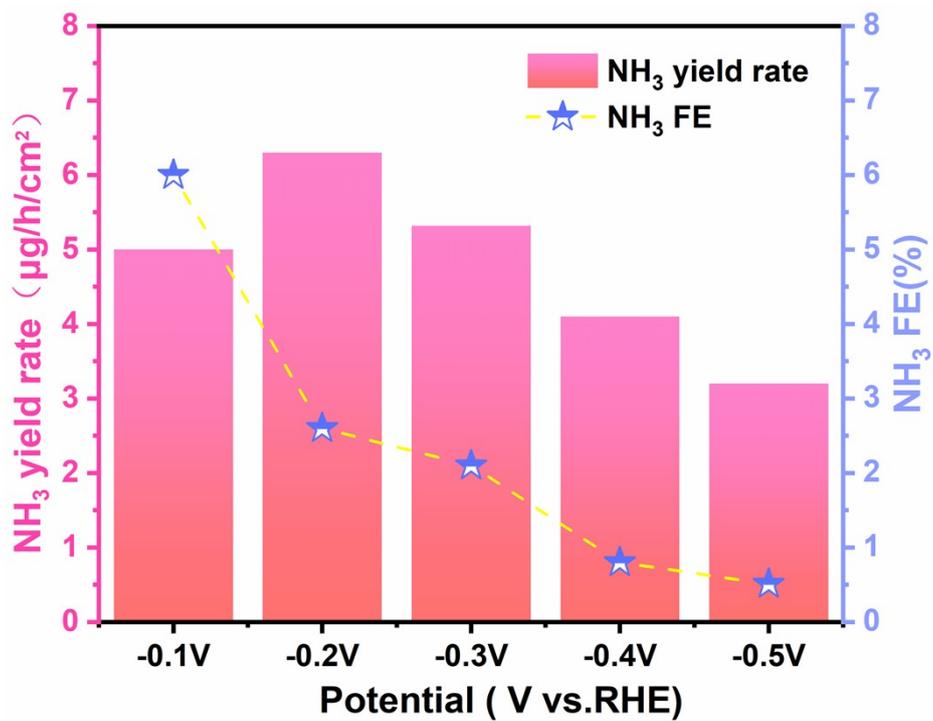
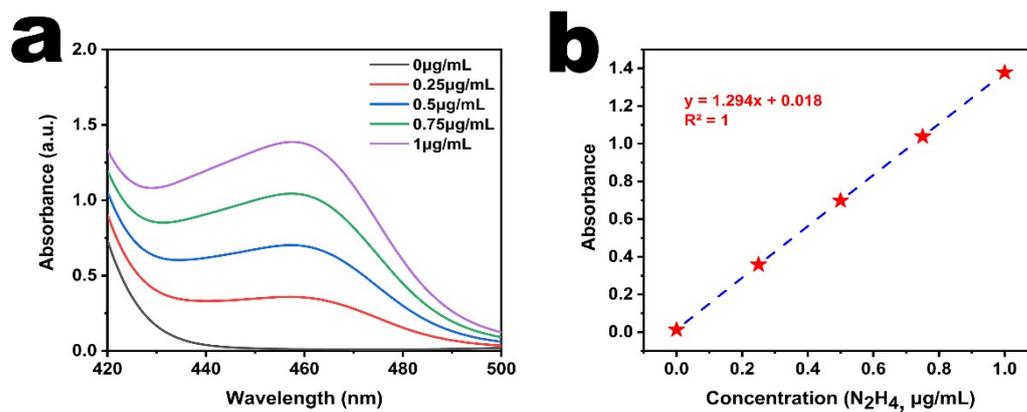
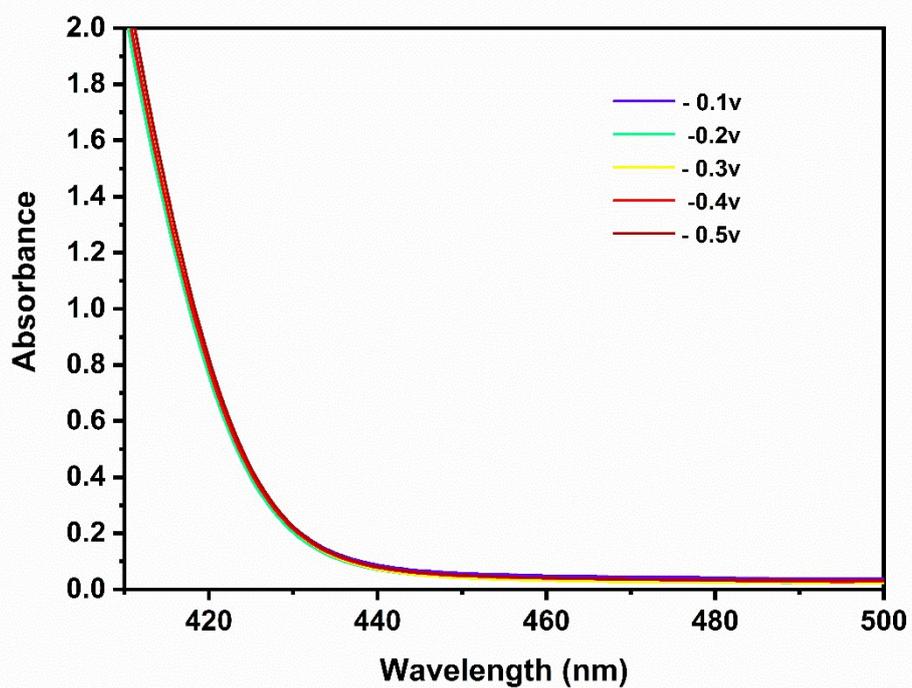


Figure.S8. NH<sub>3</sub> yield rates and NH<sub>3</sub> FEs of NiO at five potentials.



**Fig. S9. (a) UV-Vis spectra of various  $N_2H_4$  concentrations (mother solution: 0.1M KOH) after incubated for 20min at room temperature. (b) Calibration curve used for calculation of  $N_2H_4$  concentrations.**



**Fig. S10.** UV-Vis spectra of the electrolyte estimated by the method of Watt and Chrisp (incubated for 20 min) after 1 h electrolysis at a series of potentials under ambient conditions.

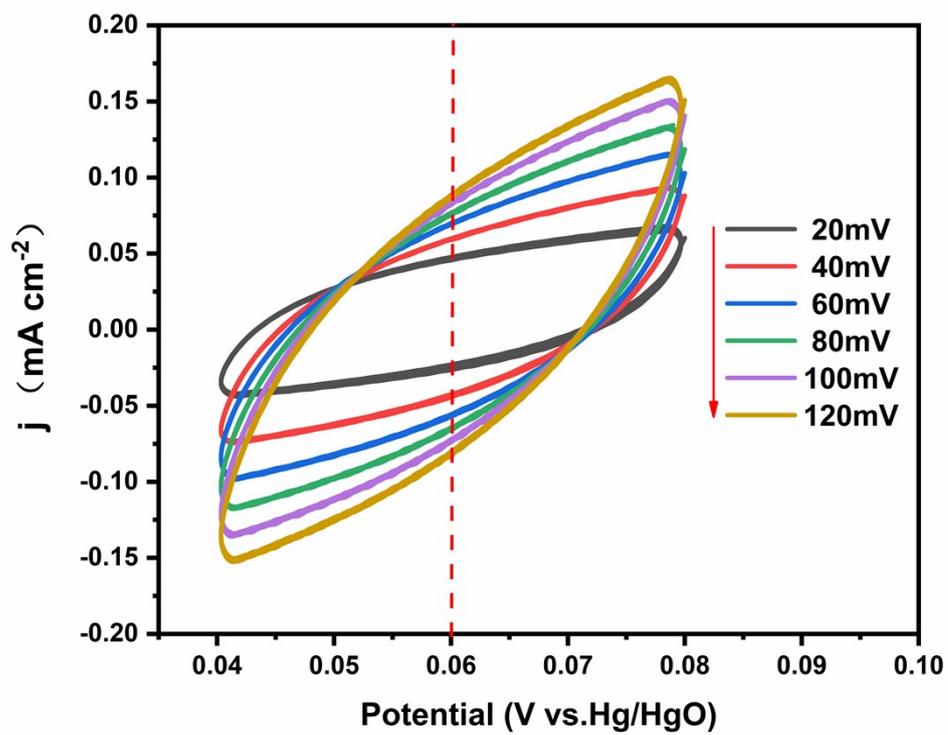


Fig. S11. CV curves of V/NiO at various scan rates

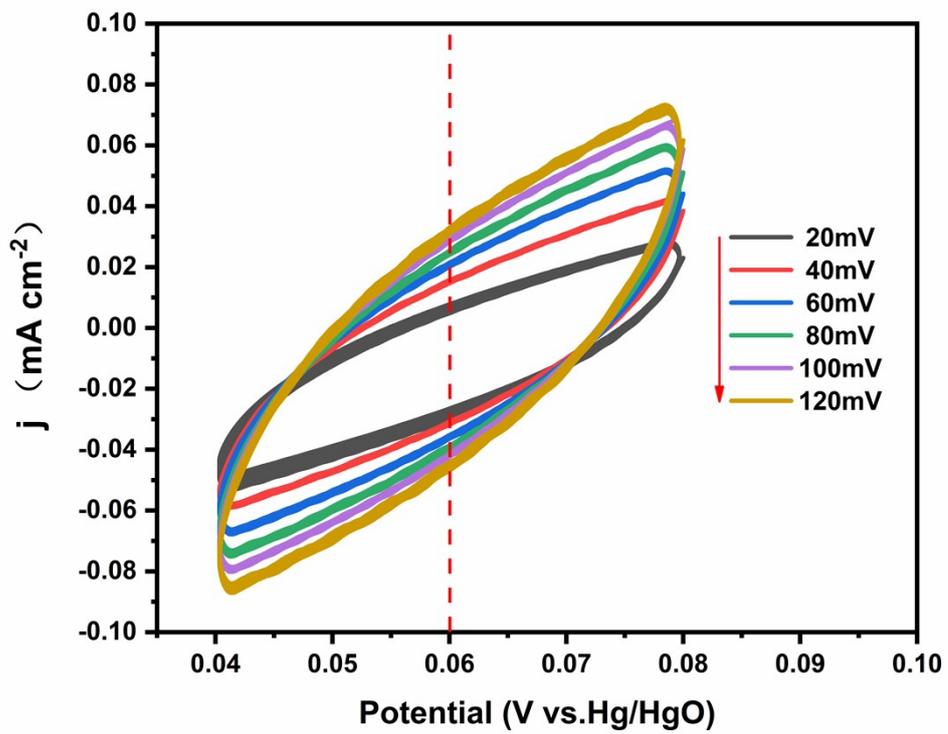
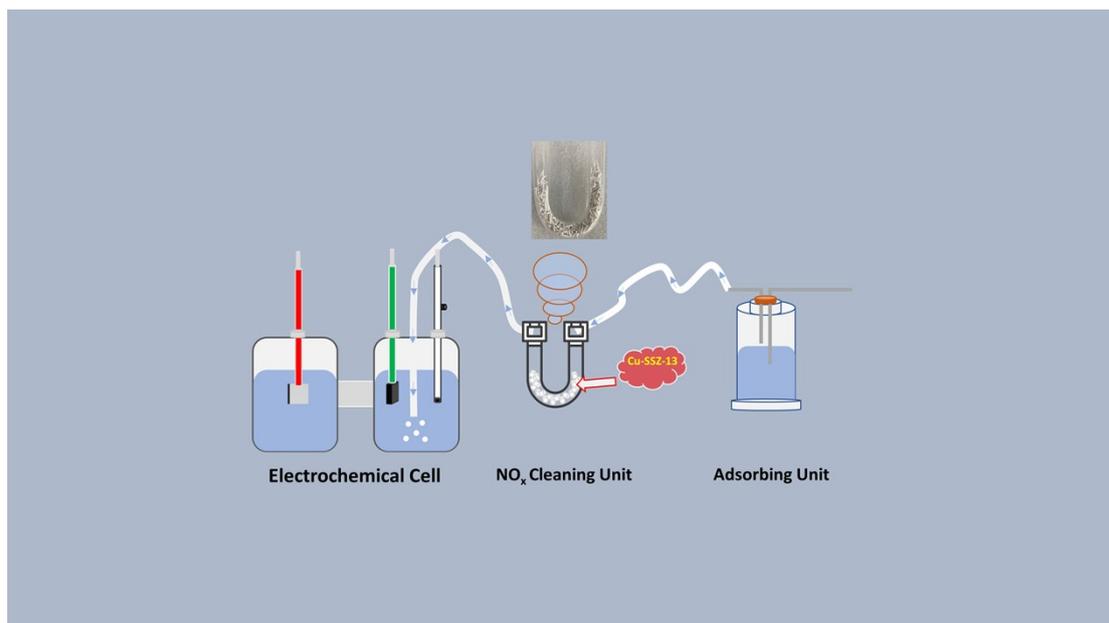


Fig. S12. CV curves of NiO at various scan rates



**Fig. S13. Schematic diagram of test setup**

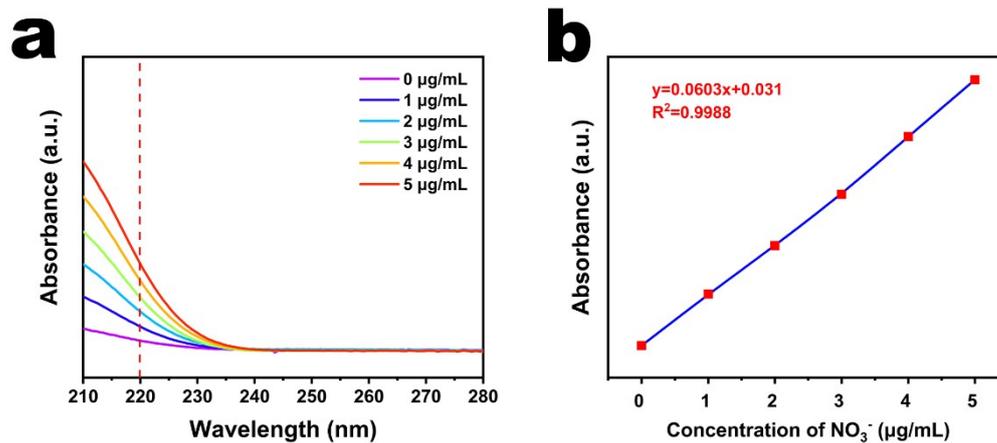


Figure S14. (a) UV-Vis spectra of various  $\text{NO}_3^-$  concentrations after incubated for 15min at room temperature. (b) Calibration curve used for calculation of  $\text{NO}_3^-$  concentrations.

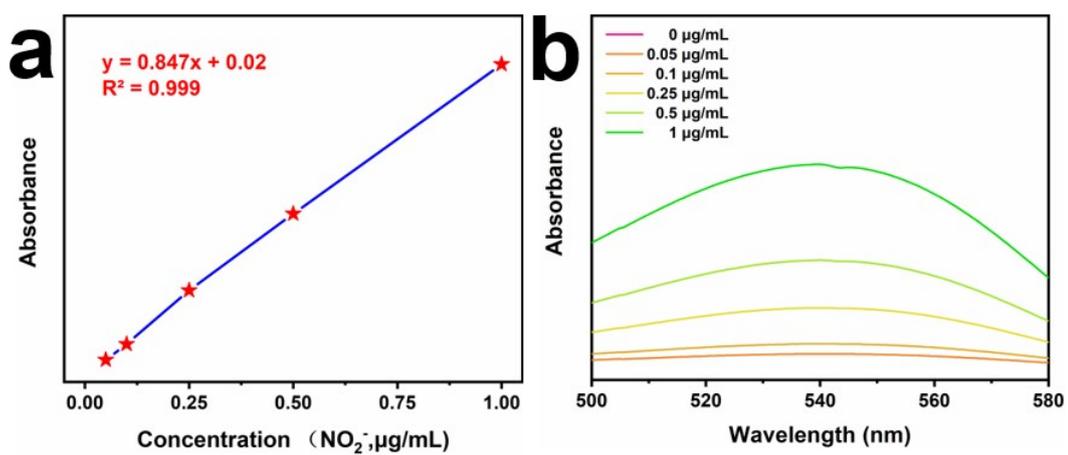


Fig. S15 (a) Calibration curve used for calculation of nitrite concentrations

(b) UV-Vis spectra of various nitrite concentrations.

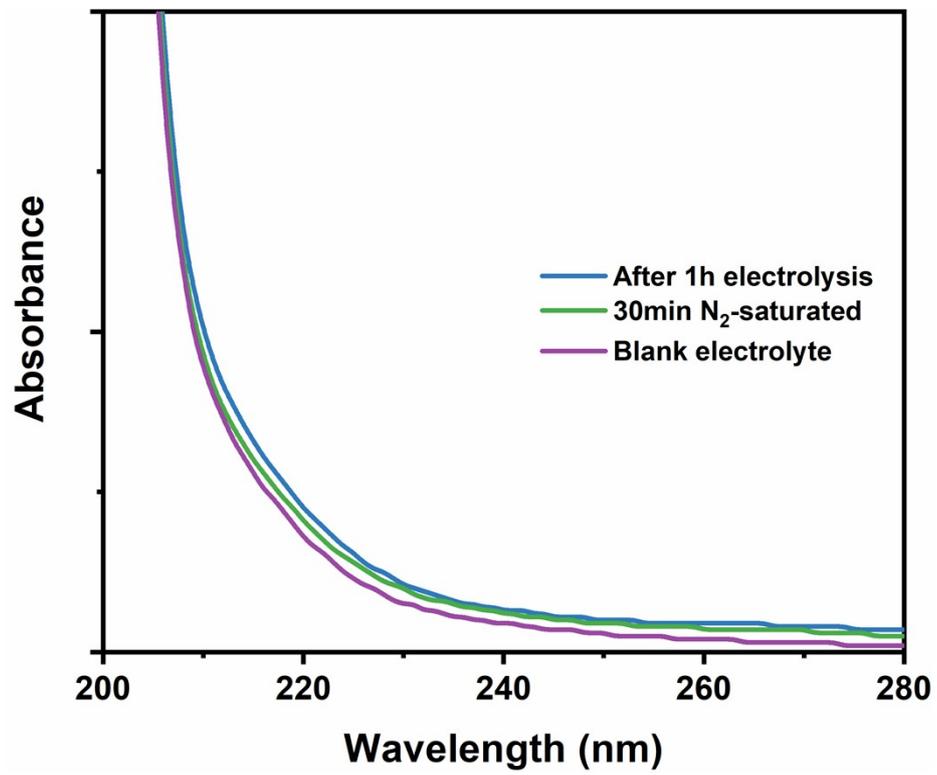


Fig. S16 UV-Vis spectra of nitrate of select stages

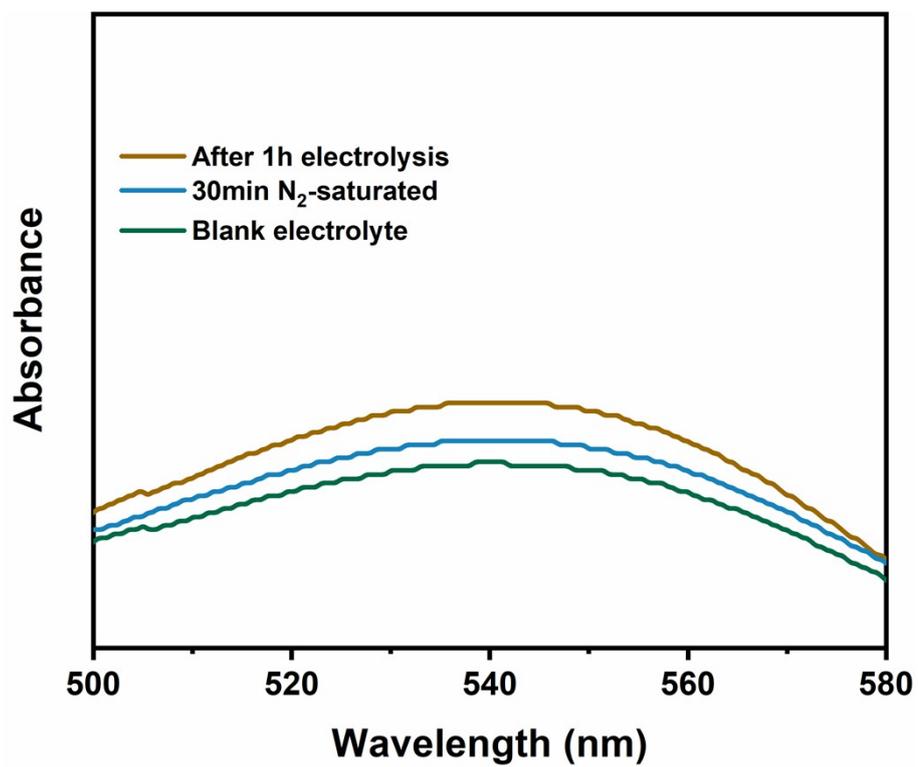


Fig. S17 UV-Vis spectra of nitrite of select stages

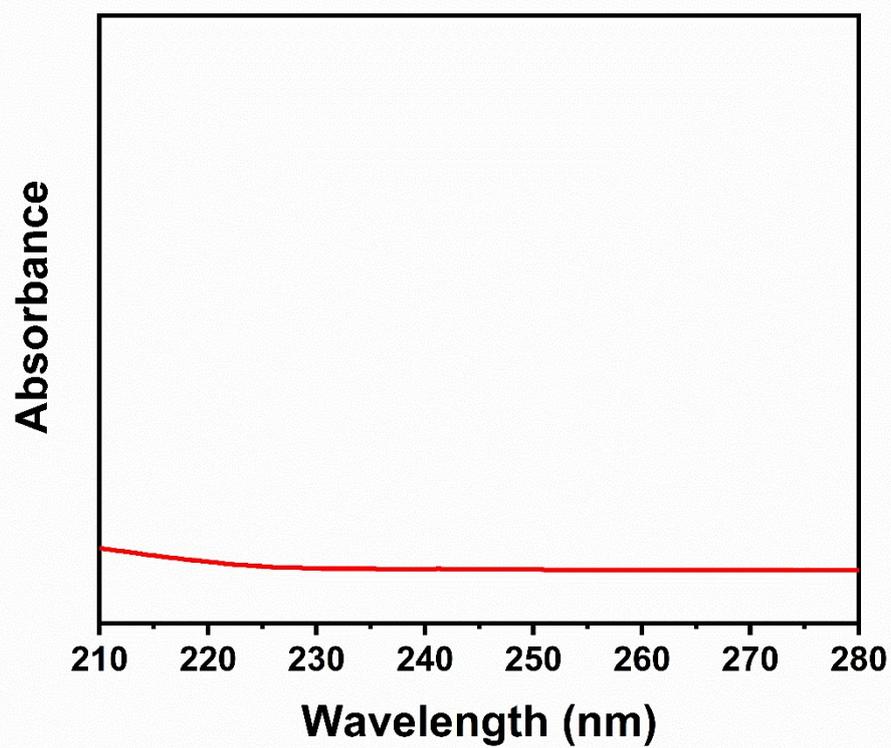


Figure S18. UV-Vis spectra of  $\text{NO}_3^-$  concentration after 1h electrocatalysis at -0.6V

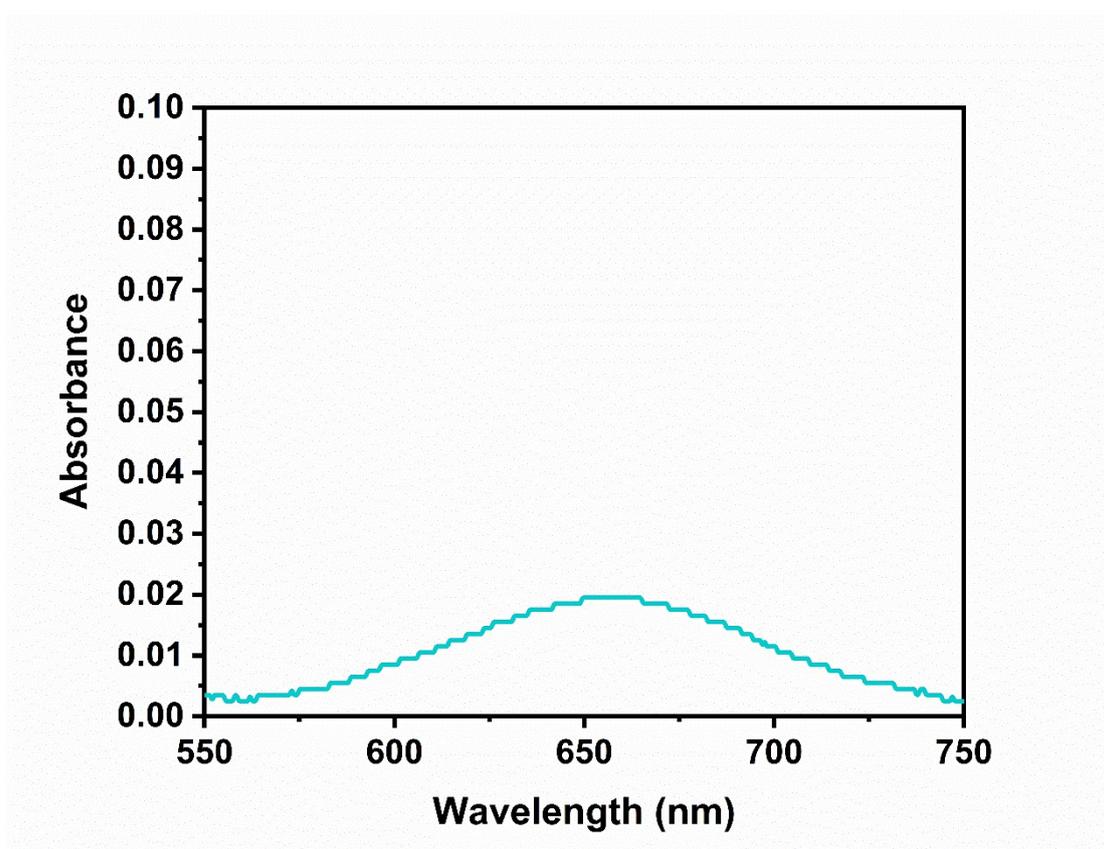
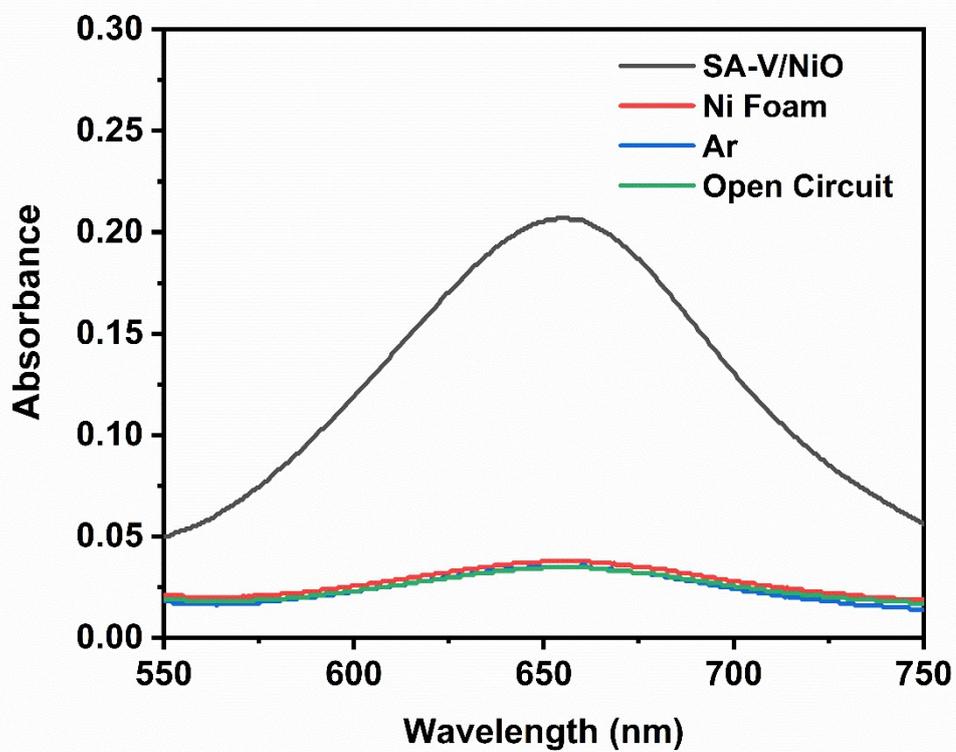


Figure S19. UV-Vis spectra of NH<sub>3</sub> concentration after 1h electrocatalysis at -0.6V



**Fig. S20.** UV-vis absorption spectra of V/NiO in N<sub>2</sub>-saturated 0.1M KOH, V/NiO in Ar-saturated 0.1M KOH, open circuit test in N<sub>2</sub>-saturated 0.1M KOH and Ni Foam in N<sub>2</sub>-saturated 0.1M KOH.

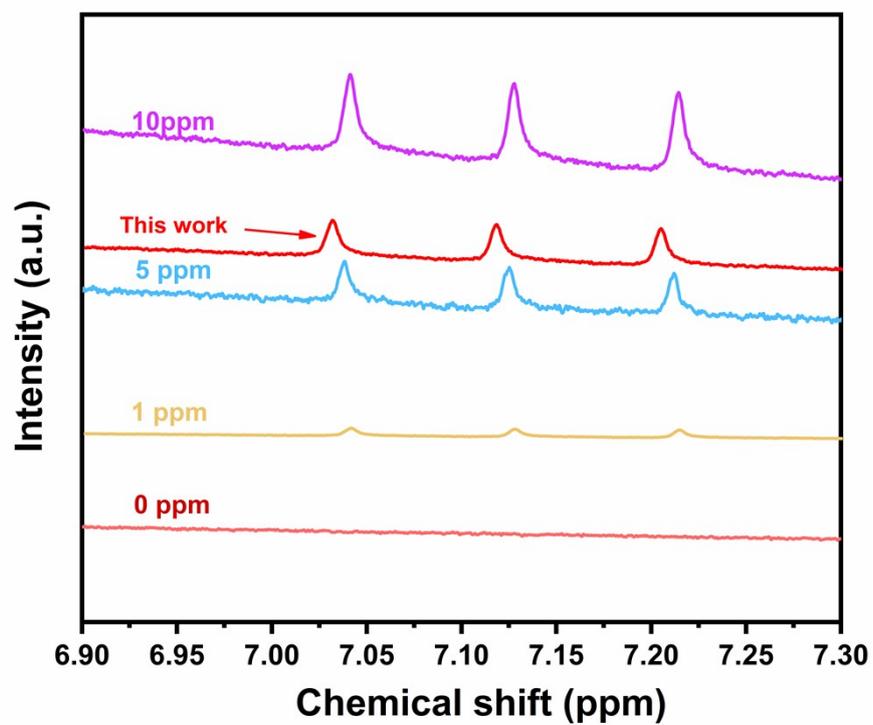


Figure.S21.  $^1\text{H}$  NMR measurements

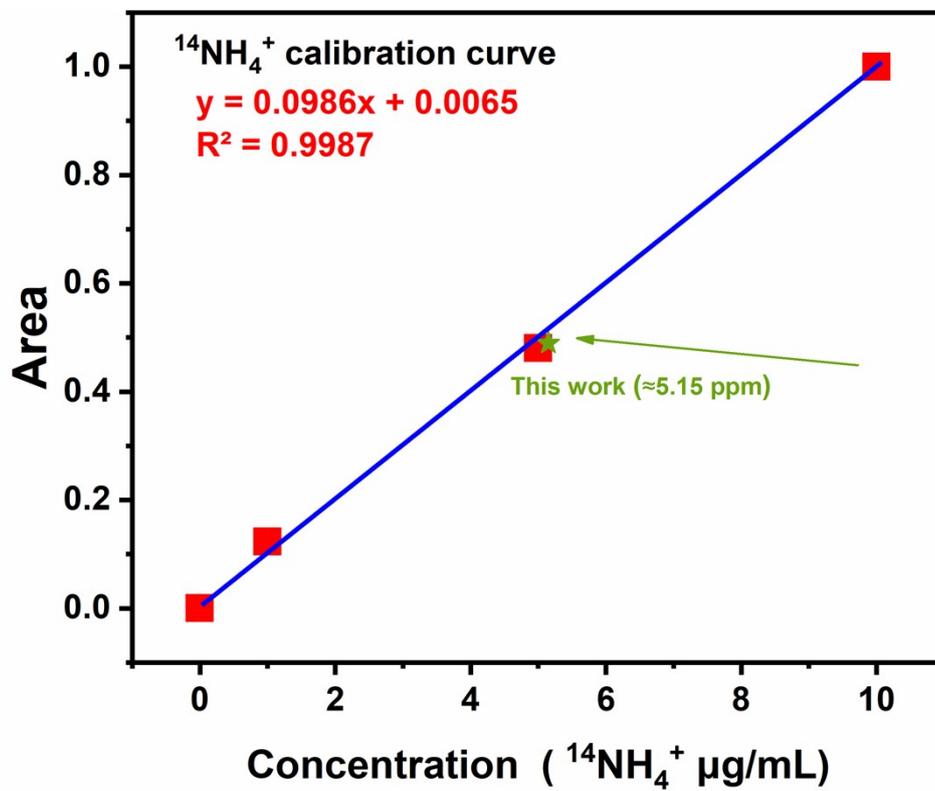


Figure S22. Calibration curve of  $^1\text{H}$  NMR

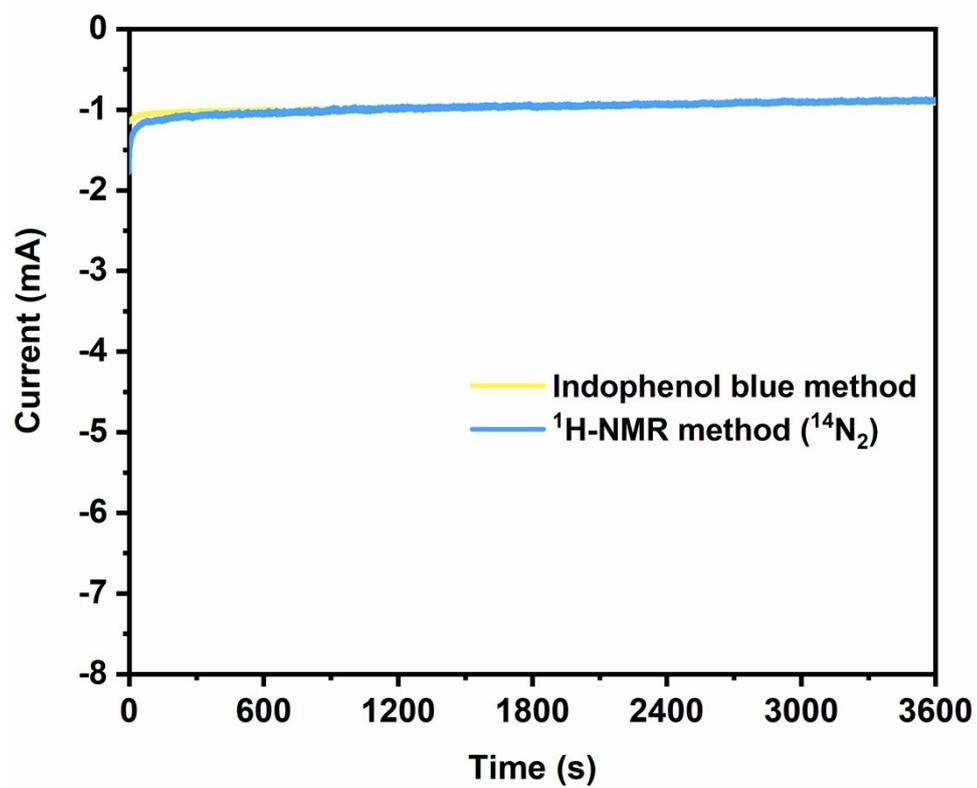


Figure S23. Chronoamperometry curves

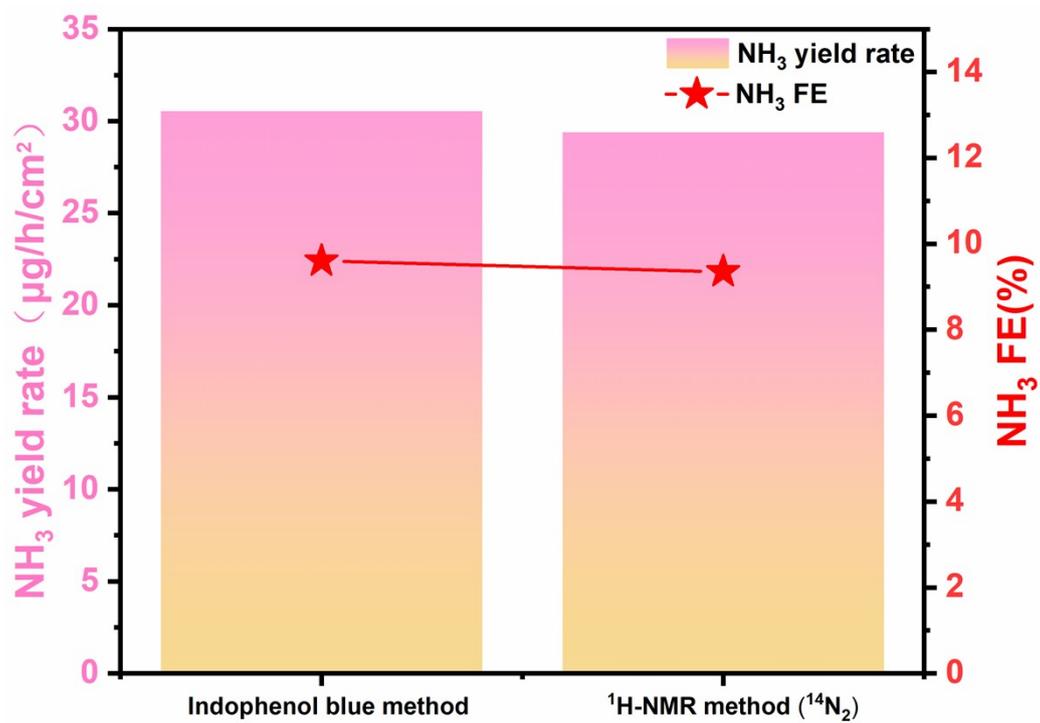


Figure .S24. Comparison of NH<sub>3</sub> yield rates and NH<sub>3</sub> Fes between different quantitative methods

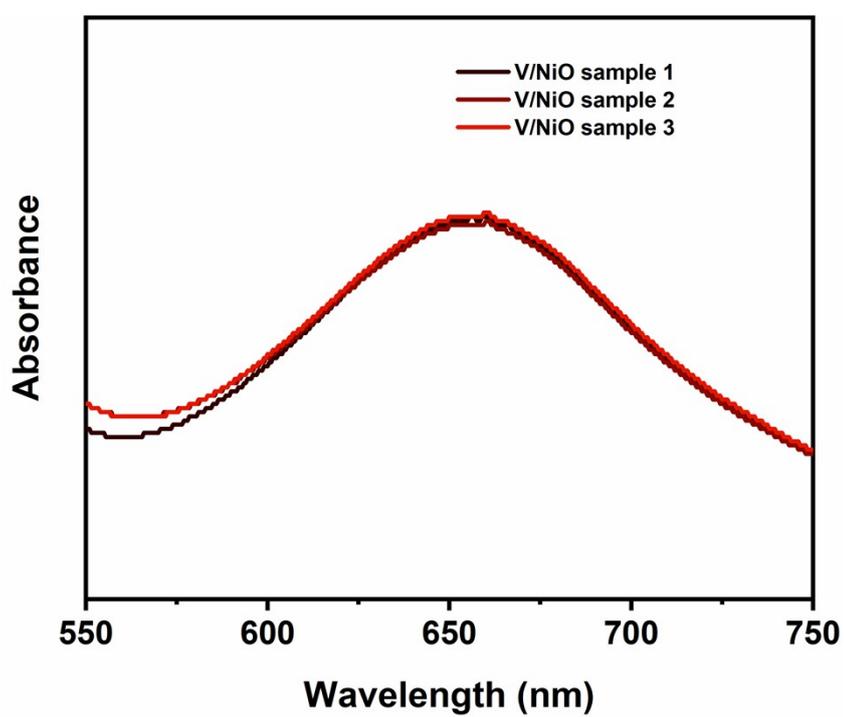


Fig. S25. UV-vis spectra of three independent samples

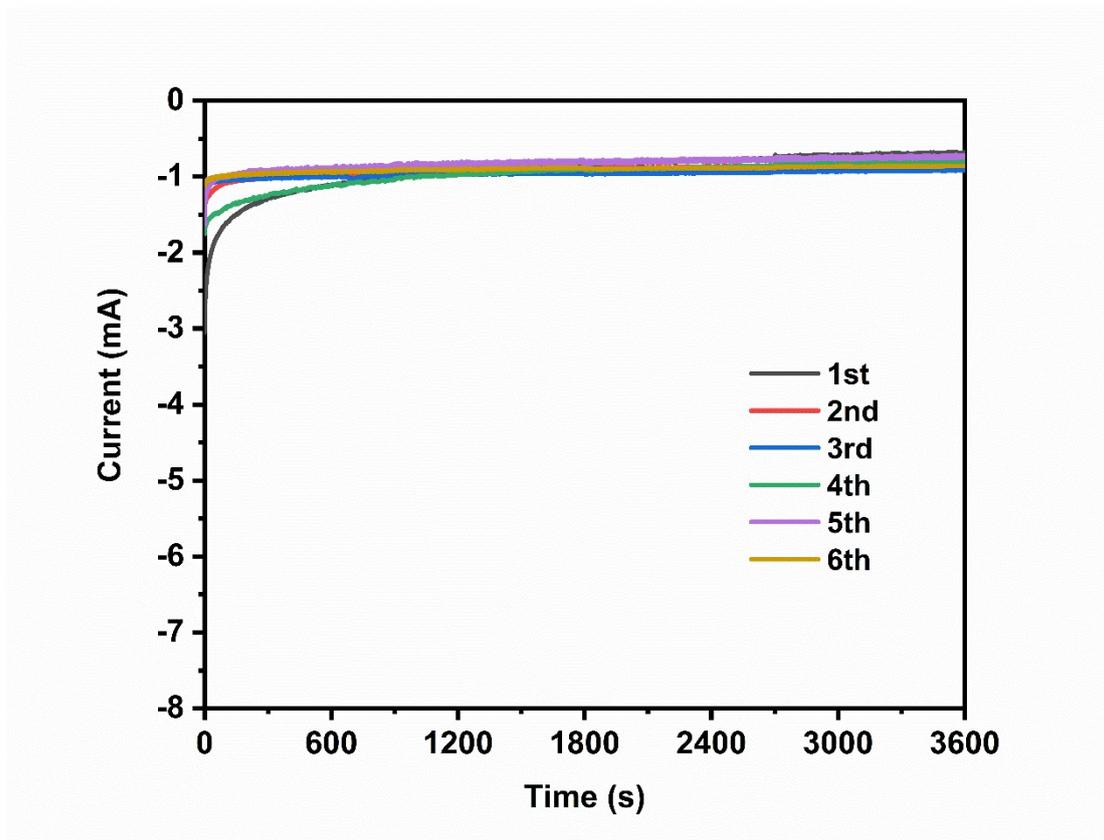


Figure S26. Chronoamperometry tests of six time recycle test.

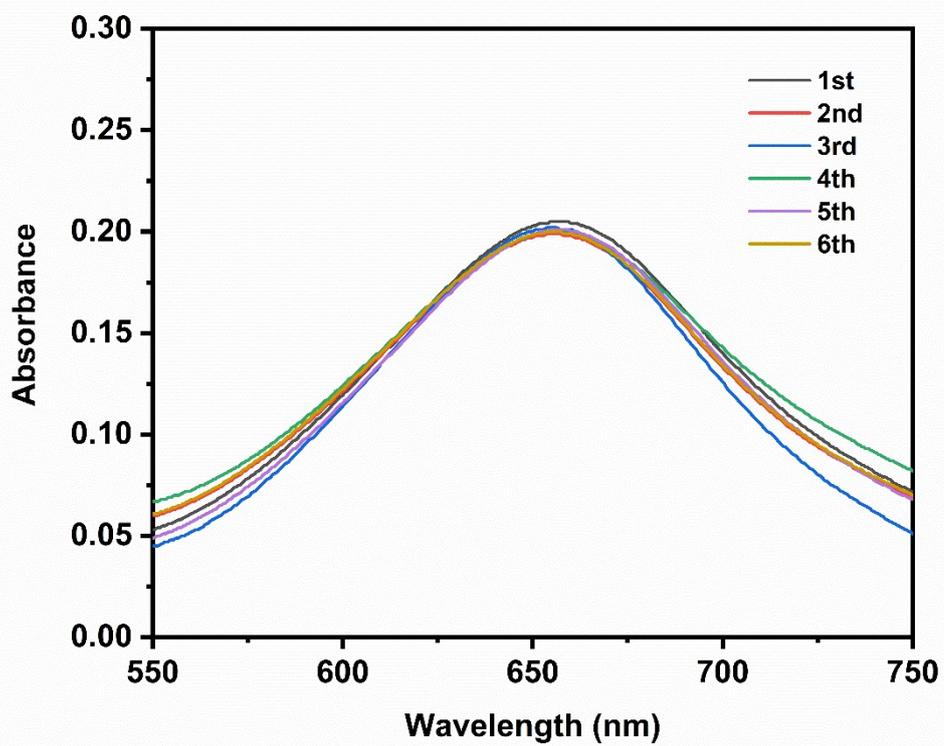


Fig. S27. UV-vis absorption spectra of six time recycle test.

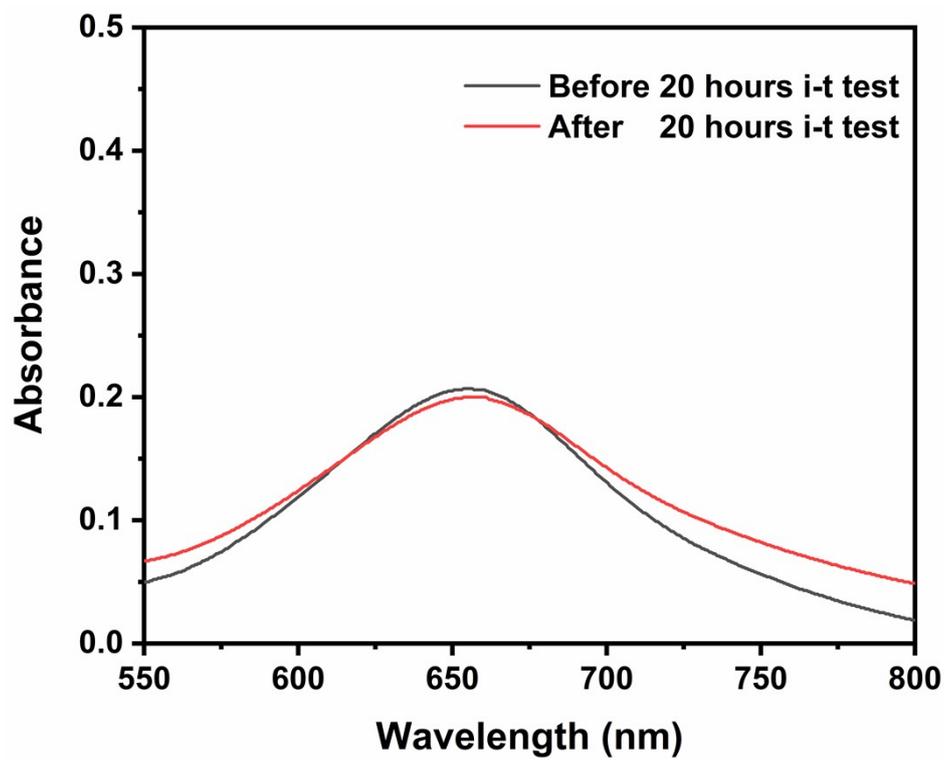


Figure.S28. UV-vis absorption spectras.

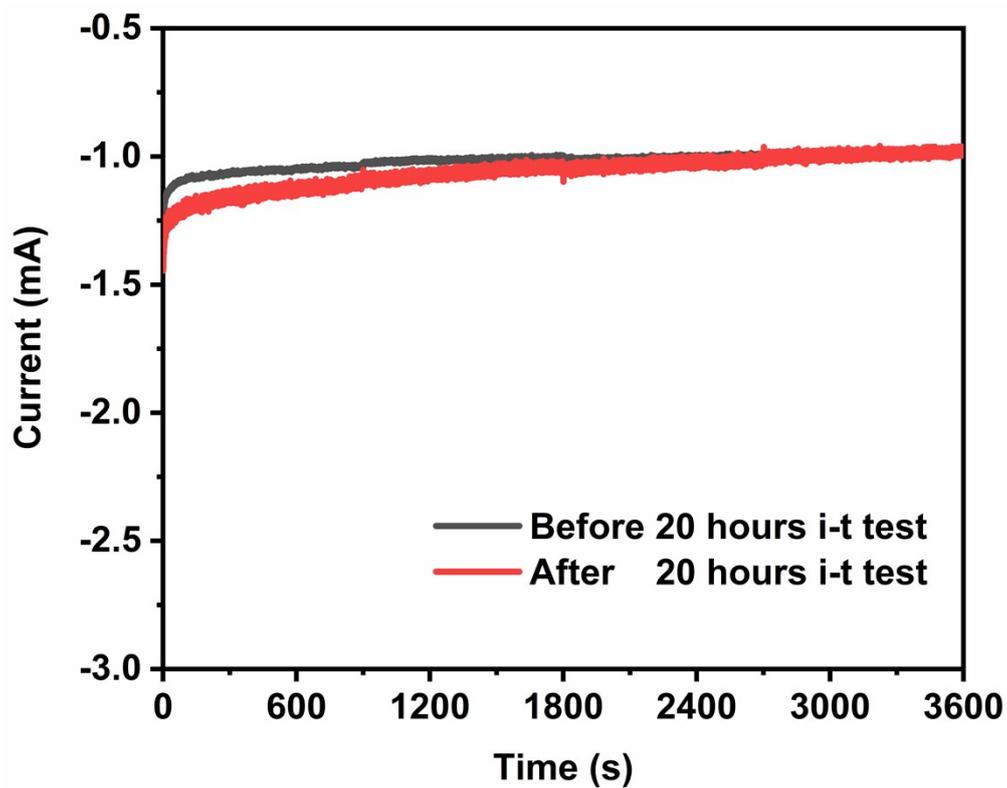
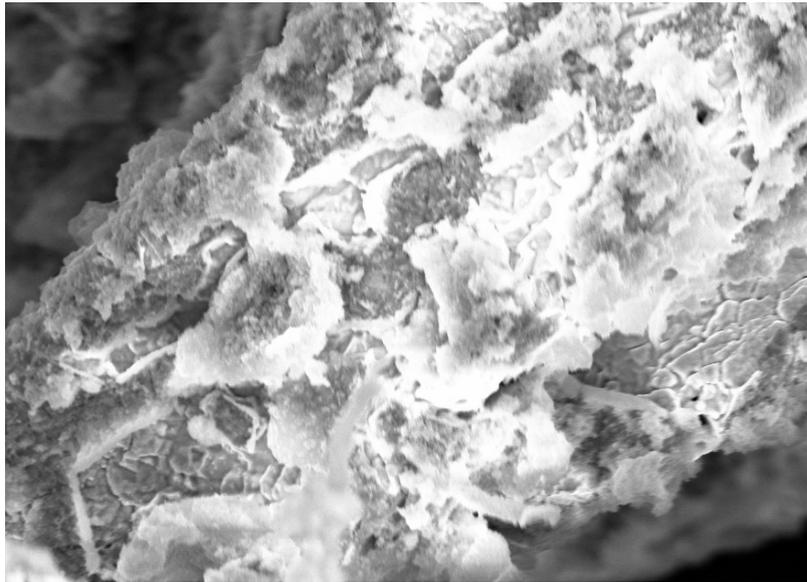


Figure S29. Chronoamperometry curves



**Fig. S30.** SEM image of V/NiO after six times cycle tests.

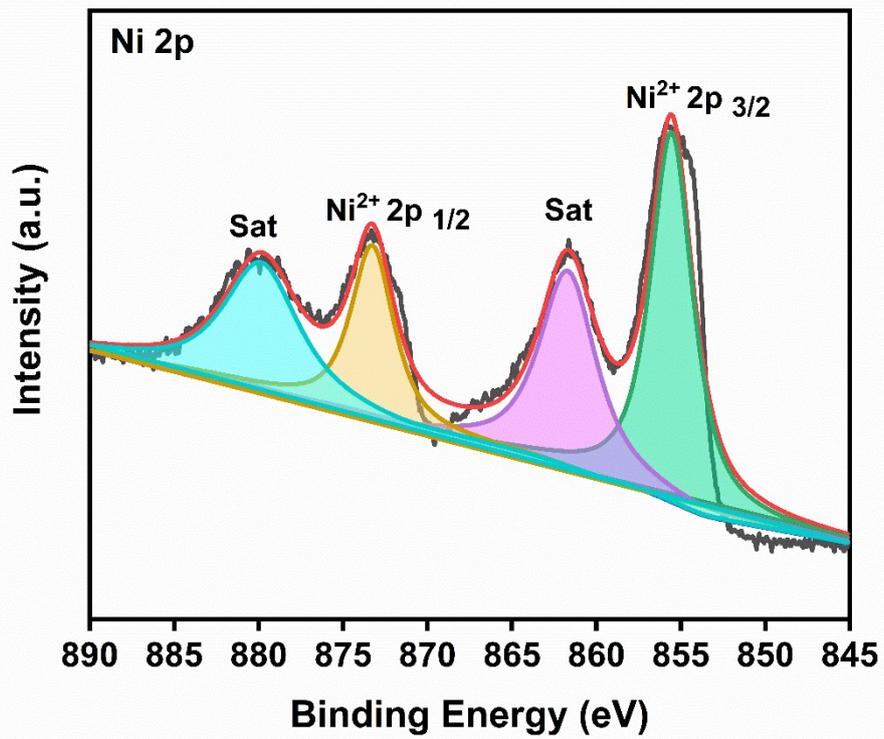


Fig. S31. High resolution XPS of Ni 2p after six times cycle tests.

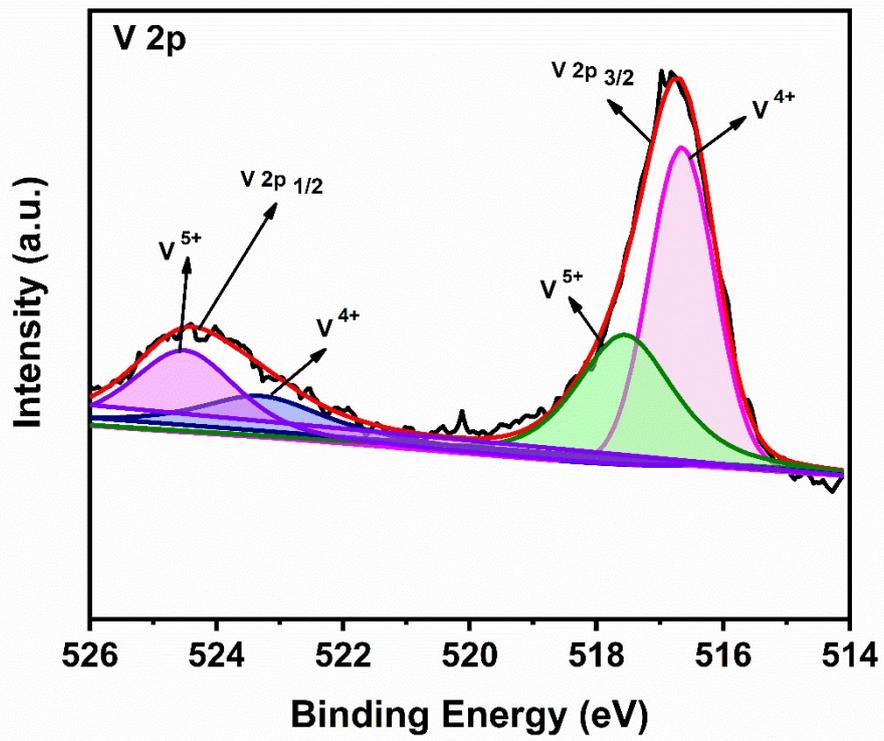


Fig. S32. High resolution XPS of V 2p after six times cycle tests.

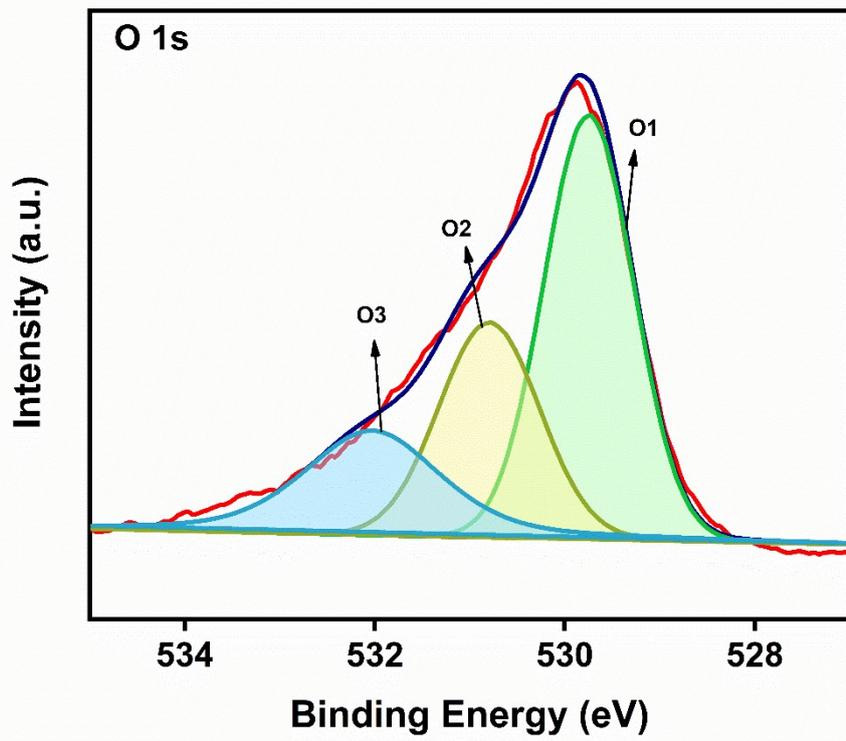


Fig. S33. High resolution XPS of O 1s after six times cycle tests.

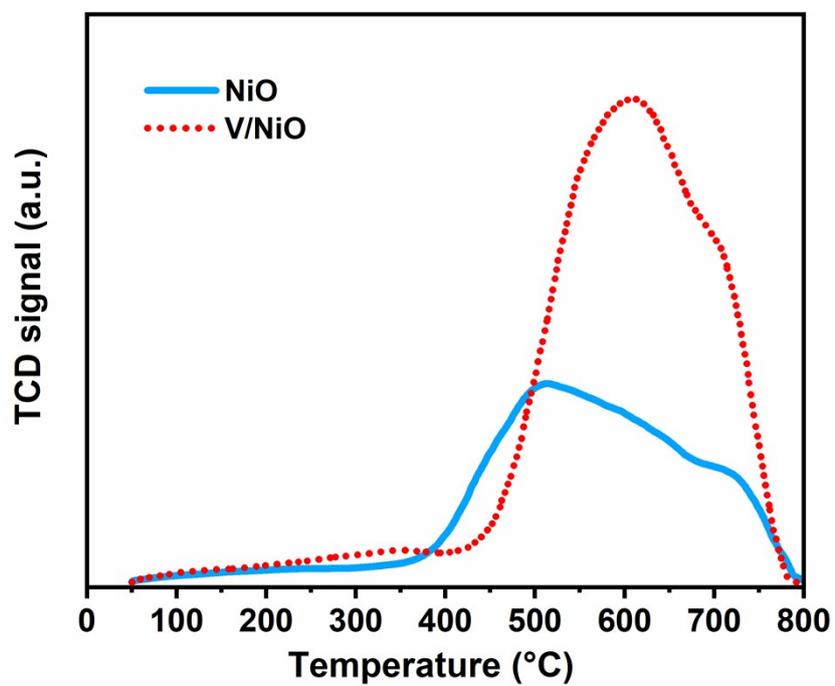


Fig. S34. N<sub>2</sub>-TPD of -V/NiO and NiO.

**Table S1. Comparison with various electrocatalysts for ENRR.**

Catalyst	NH <sub>3</sub> yield	FE(%)	Detection method	Electrolyte	Ref.
V/NiO	30.55μg/ h/cm <sup>2</sup>	11%	Indophenol blue	0.1M KOH	This work
Amorphous Bi <sub>4</sub> V <sub>2</sub> O <sub>11</sub>	23.21μg/ h/mg	10.16%	Indophenol blue	0.1M KOH	4
V-doped TiO <sub>2</sub>	17.73μg/ h/mg	15.3%	Indophenol blue	0.5M LiClO <sub>4</sub>	5
VN@NSC	20.5μg/ h/mg	8.6%	Indophenol blue	0.1M HCl	6
N-NiO/CC	22.7μg/ h/mg	7.3%	Indophenol blue	0.1M LiClO <sub>4</sub>	7
P-NiO/CC	29.1μg/ h/mg	10.8%	Indophenol blue	0.1M Na <sub>2</sub> SO <sub>4</sub>	8
NC@NiO/GP	14.02μg/ h/mg	30.43%	Indophenol blue	0.1M HCl	9
Au-Fe <sub>3</sub> O <sub>4</sub> nanoparticles	21.42μg/ h/mg	10.54%	Indophenol blue	0.1M KOH	10
Fe-MoS <sub>2</sub> /CC	12.5μg/ h/mg	10.8%	Indophenol blue	0.1M KOH	11
AuPd NSs	16.9μg/ h/mg	15.9%	Indophenol blue	0.1M Na <sub>2</sub> SO <sub>4</sub>	12
Zn nanosheets	25.3μg/ h/mg	11.7%	Indophenol blue	0.5M LiClO <sub>4</sub>	13
BiNi alloys	17.5μg/ h/mg	13.8%	Indophenol blue	0.1M Na <sub>2</sub> SO <sub>4</sub>	14

## References

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