Introducing oxygen vacancies in bi-metal oxide nanosphere for promoting electrocatalytic nitrogen reduction

Heen Li [a]，Xiaoyue Xu [a], Xiaohu Lin [b], Jianmin Chen [a]，Kunling Zhu [a], Fei Peng [b] , Faming Gao* [a]

a. Key Laboratory of Applied Chemistry, Yanshan University, Qinhuangdao 066004, P. R. China

b. Analyses and Testing Center，Hebei Normal University of Science and Technology, Qinhuangdao 066000, P. R. China

Corresponding Author

*Faming Gao: E-mail: fmgao@ysu.edu.cn

Supporting information

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. Raman spectroscopy (WITec, alpha300R, excited by a 512 nm laser) was also performed. 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. Electron spin resonance (ESR) measurements were performed using the Bruker ER 200D spectrometer at room temperature. N_2-TPD (Autosorb-iQ-C chemisorption analyzer，Quantachrome，USA) was also performed.

Quantification of ammonia

When tested in 0.1M KOH solution, we used spectrophotometry method to detect the quantification of ammonia. 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% $C_5FeN_6Na_2O\cdot 2H_2O$ were add 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_4^+ calibration curve was calculated by using a series of different concentrations standard NH_3 Solution (0μg/mL,0.25μg/mL,0.5μg/mL,0.75μg/mL,1μg/mL).NH_4Cl was dried in oven before used. Calibration curve showed good linear relationship (y=0.3148x+0.0352 R^2=0.998).

Quantification of hydrazine

The quantification of hydrazine was detected by the method of Watt and Chrisp. 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 (0μg ,0.5μg,1ug,1.5μg,2μg)The calibration curve showed good linear relationship (y=1.153x+0.048 R^2=0.999).

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 = 0.0631x + 0.021, $R^2 = 0.998$).

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 $NaNO_2$ solutions and the corresponding absorbance. It showed an excellent linear relationship between the absorbance value and the $NaNO_2$ concentration from the fitting curve (y = 0.785x + 0.031 $R^2 = 0.9998$).

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_3 concentration, V is the volume

of the electrolyte, and Q is the quantity of electric charge for one electron of NRR testing.

The NH_3 formation rate was determined using the following equation:

$$r(NH_3) = (c \times V)/(t \times m)$$

where c is the measured NH_3 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).

$^{15}N_2$ isotope labelling experiments

^{15}N isotopic labeling experiment was conducted using $^{15}N_2$ as the feeding gas (99%, supplied by Shanghai Shoucheng Biotechnology Co.Ltd.) with identical experimental procedure as that of $^{14}N_2$ experiment. The yielded $^{15}NH_3$ was detected using ^{1}H-NMR (Bruker Avance-600 MHZ). The reference $^{15}NH_4Cl$ sample was dissolved in 0.1 M KOH solution for the measurement, and 10ml electrolyte obtained from $^{15}N_2$-saturated 0.1 M KOH solution with a reaction time of 1 h and a concentration time of 12 h at 80℃ to concentrate electrolyte to 1ml . At last,0.5ml Dimethyl sulfoxide-d6(DMSO-d6) was added into 1ml concentrated KOH, and 1-3 drops of 0.5M H_2SO_4 was added to adjust pH to1-2 for the ^{1}H-NMR measurement.

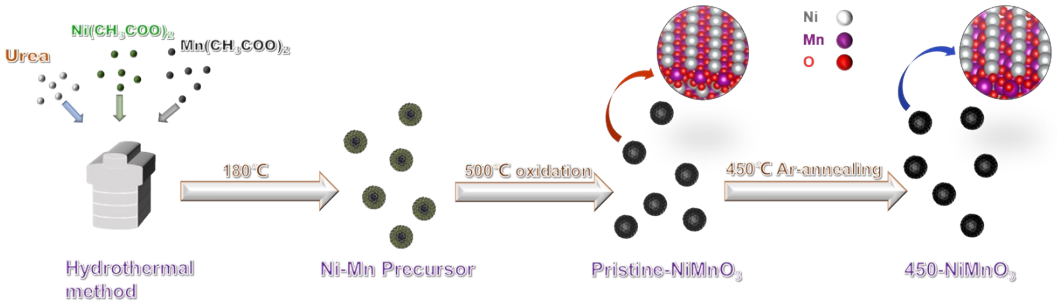

Fig. S1 Schematic illustration of the synthesis process of 450-$NiMnO_3$.

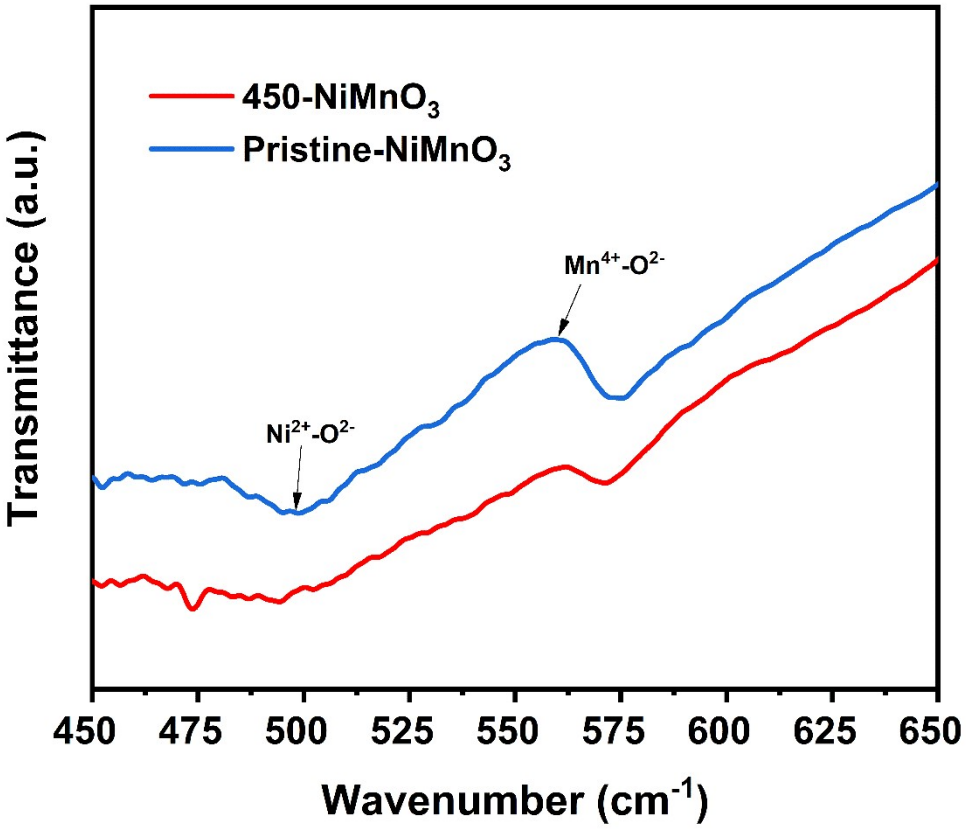

Fig. S2 FT-IR spectra of pristine-$NiMnO_3$ and 450- $NiMnO_3$

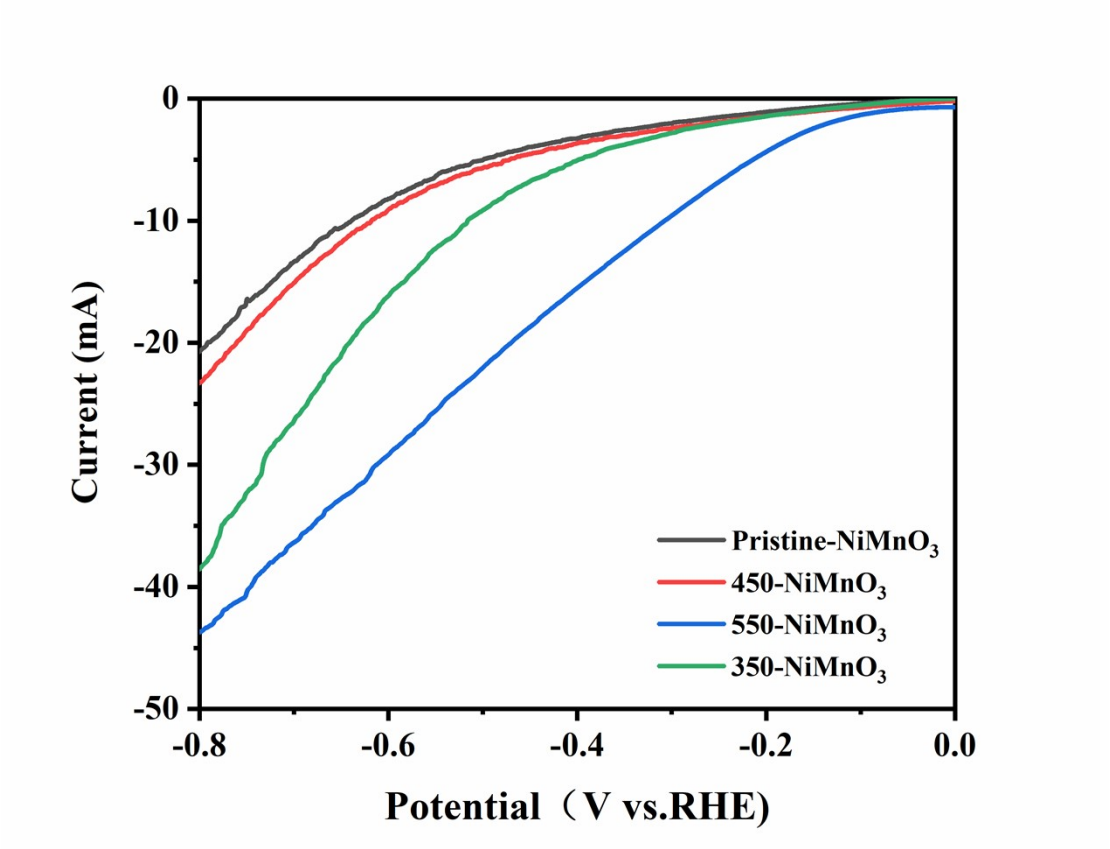

Fig. S3 LSV curves of Pristine-NiMnO , 350-$NiMnO_3$, , 450-$NiMnO_3$ and 550-$NiMnO_3$

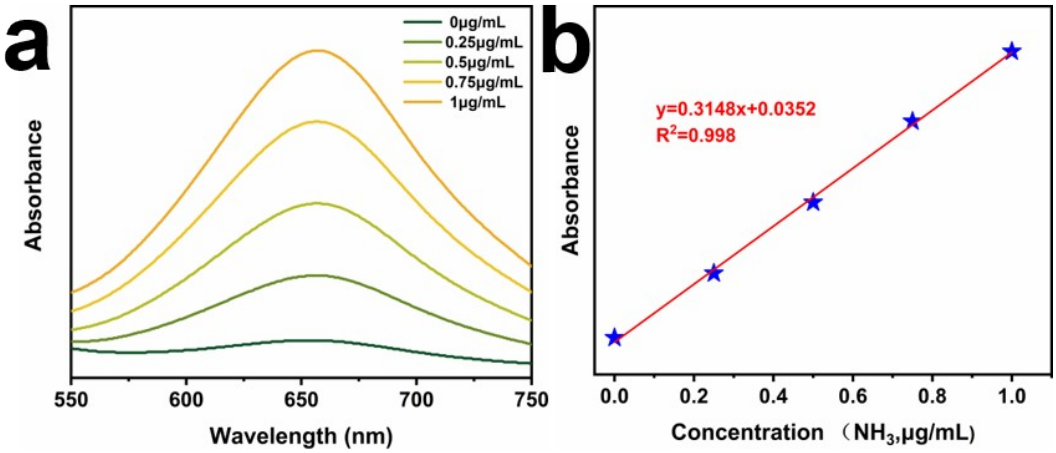

Fig. S4 (a) UV-Vis spectra of various NH_3 concentrations (mother solution: 0.1M KOH) after incubated for 1 h at room temperature. (b) Calibration curve used for calculation of NH_3 concentrations.

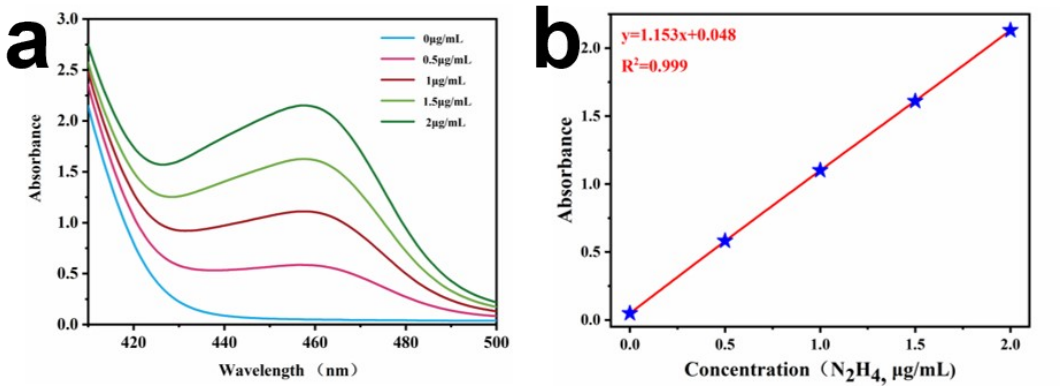

Fig. S5. (a) UV-Vis spectra of various N_2H_4concentrations (mother solution: 0.1M KOH) after incubated for 20min at room temperature. (b) Calibration curve used for calculation of N_2H_4concentrations.

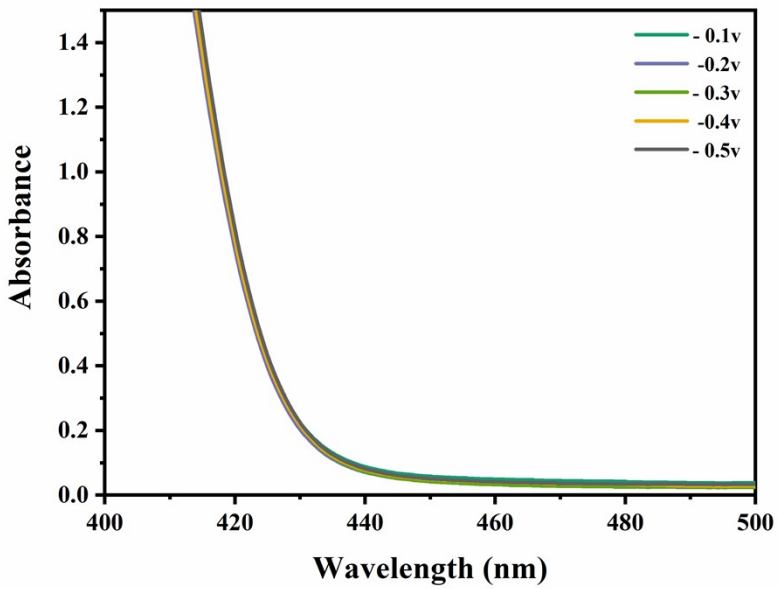

Fig. S6. UV–Vis spectra of the N_2H_4

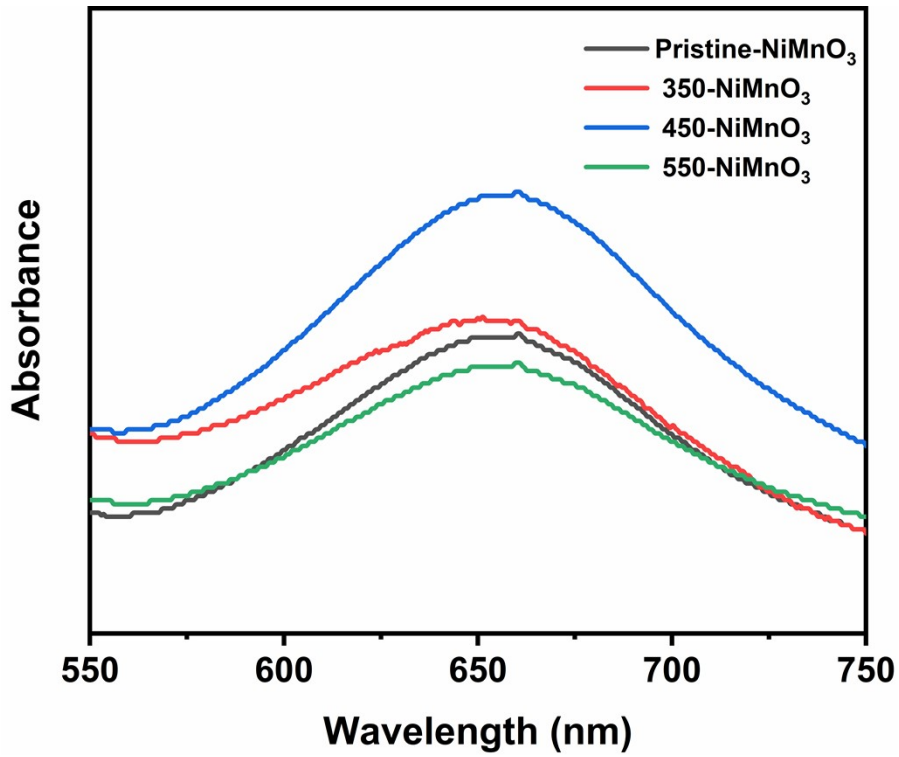

Fig. S7 UV-vis spectra of Pristine-$NiMnO_3$,350-$NiMnO_3$, 450-$NiMnO_3$,and 550-$NiMnO_3$

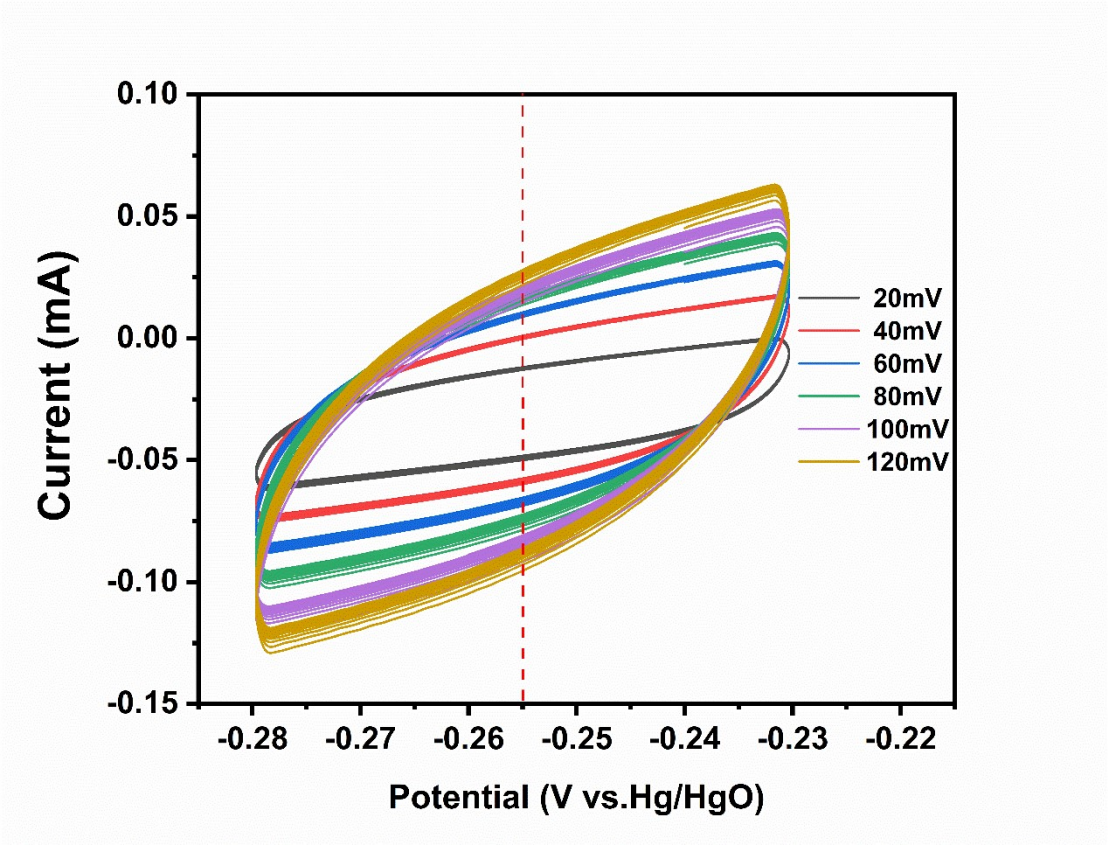

Fig. S8. CV curves of 450-$NiMnO_3$

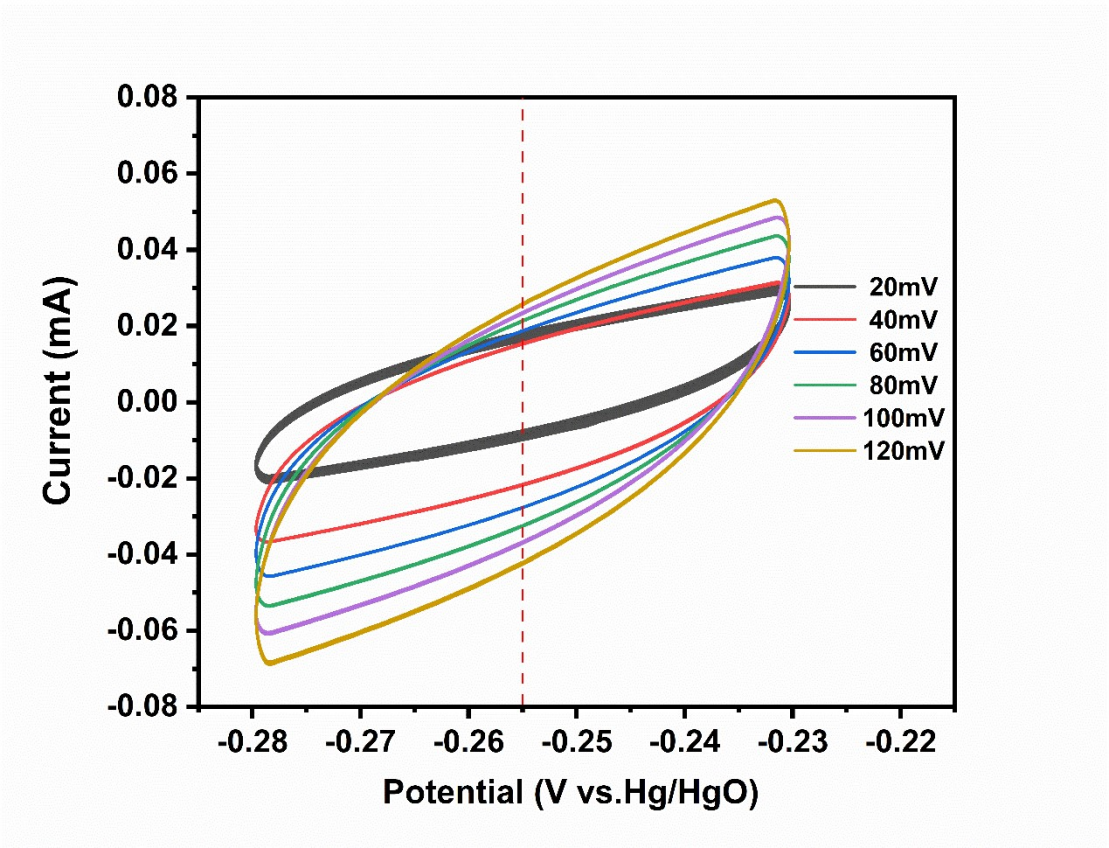

Fig. S9. CV curves of 350-$NiMnO_3$

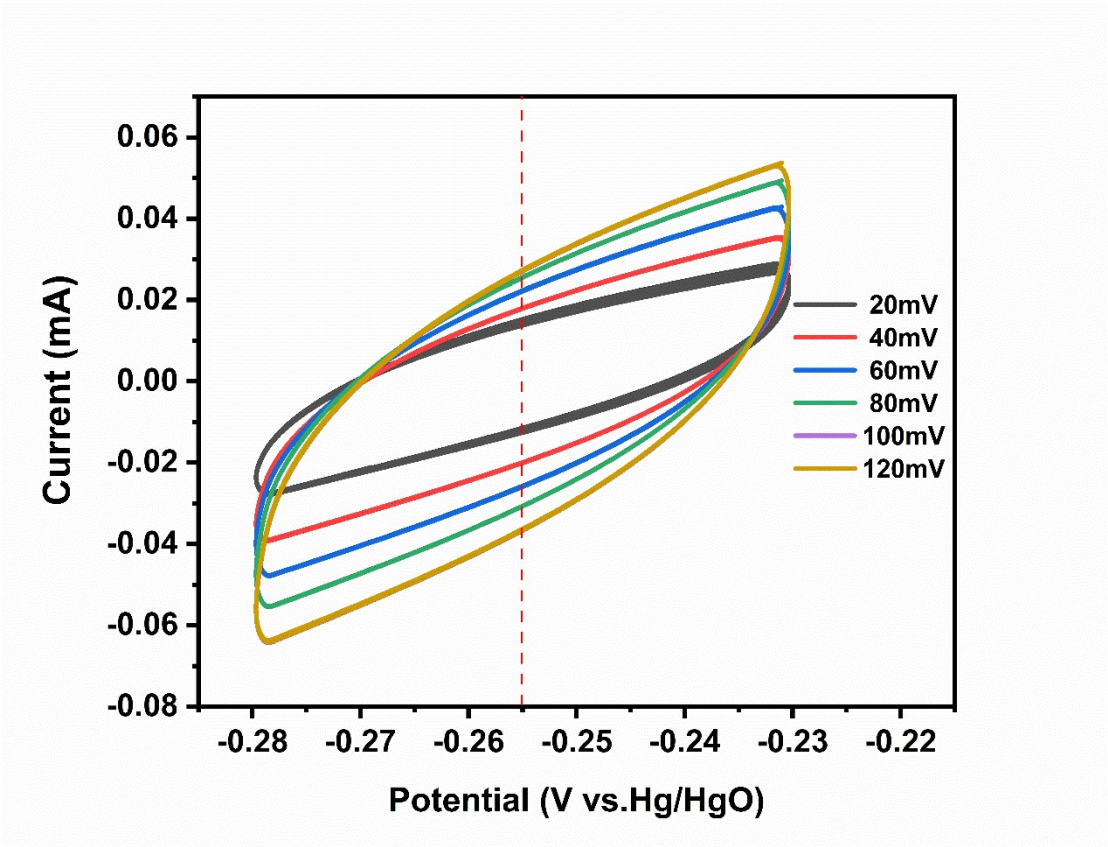

Fig. S10. CV curves of Pristine-$NiMnO_3$

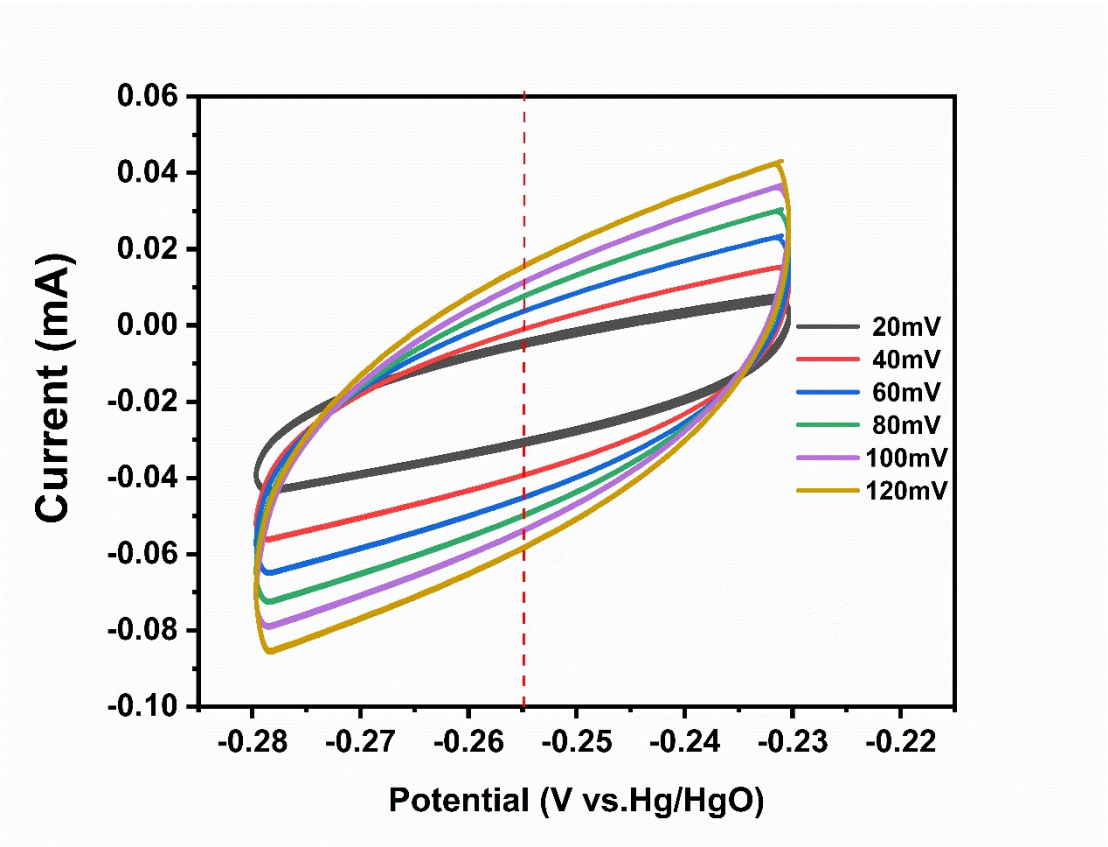

Fig. S11. CV curves of 550-$NiMnO_3$

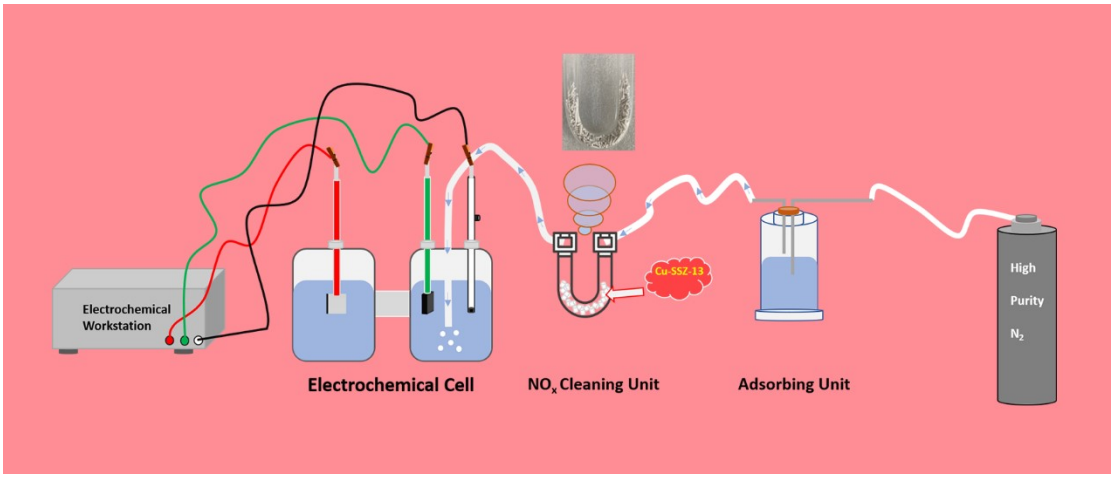

Fig. S12. Schematic diagram of test setup

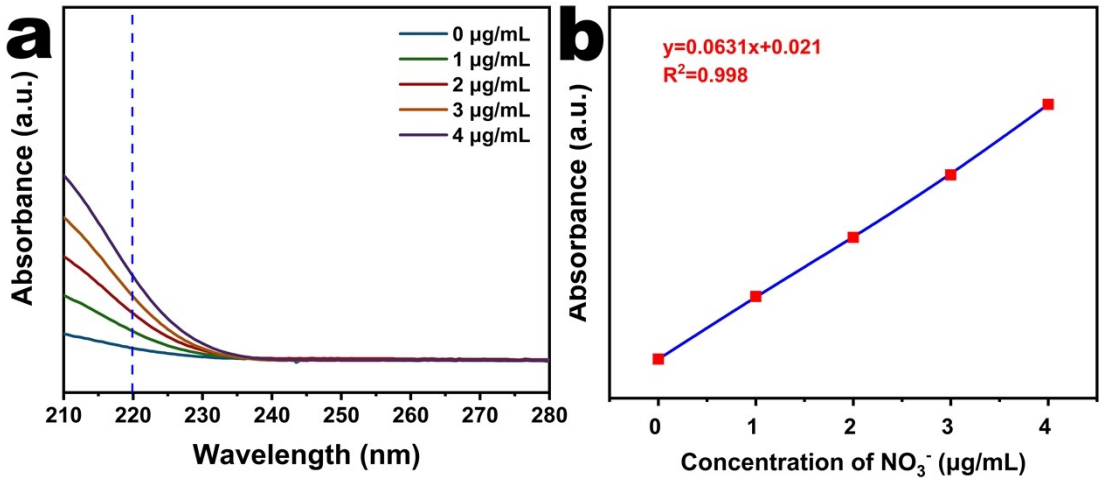

Fig. S13 (a) UV-Vis spectra of various nitrateconcentrations. (b) Calibration curve used for calculation of nitrateconcentrations.

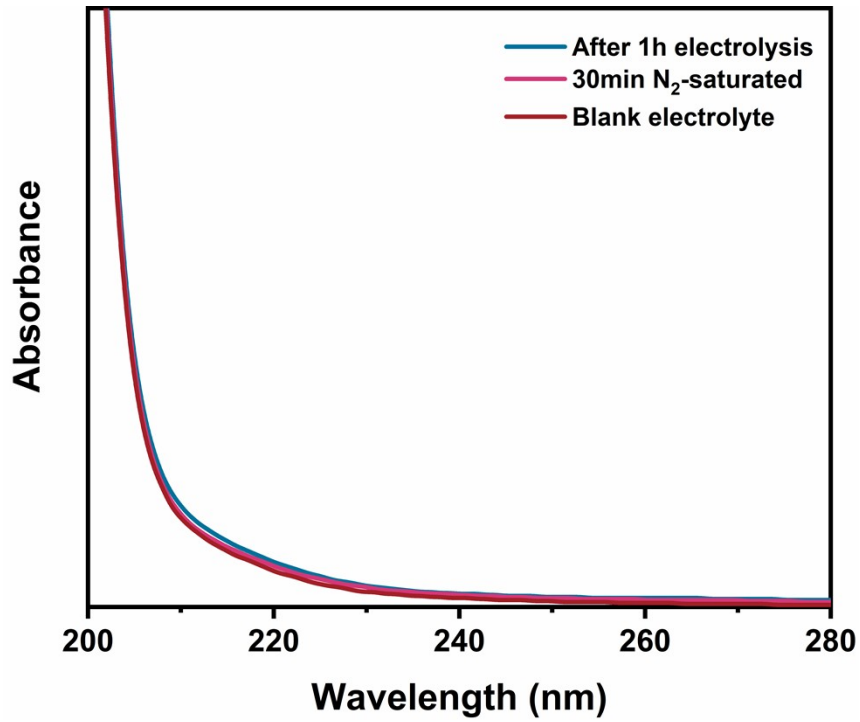

Fig. S14 UV-Vis spectra of nitrate of select stages

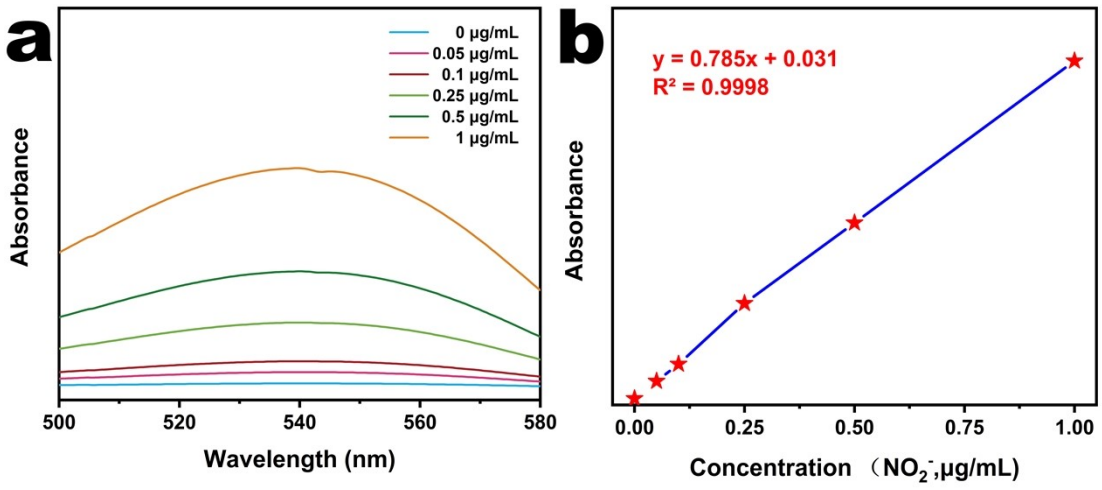

Fig. S15 (a) UV-Vis spectra of various nitrite concentrations. (b) Calibration curve used for calculation of nitrite concentrations

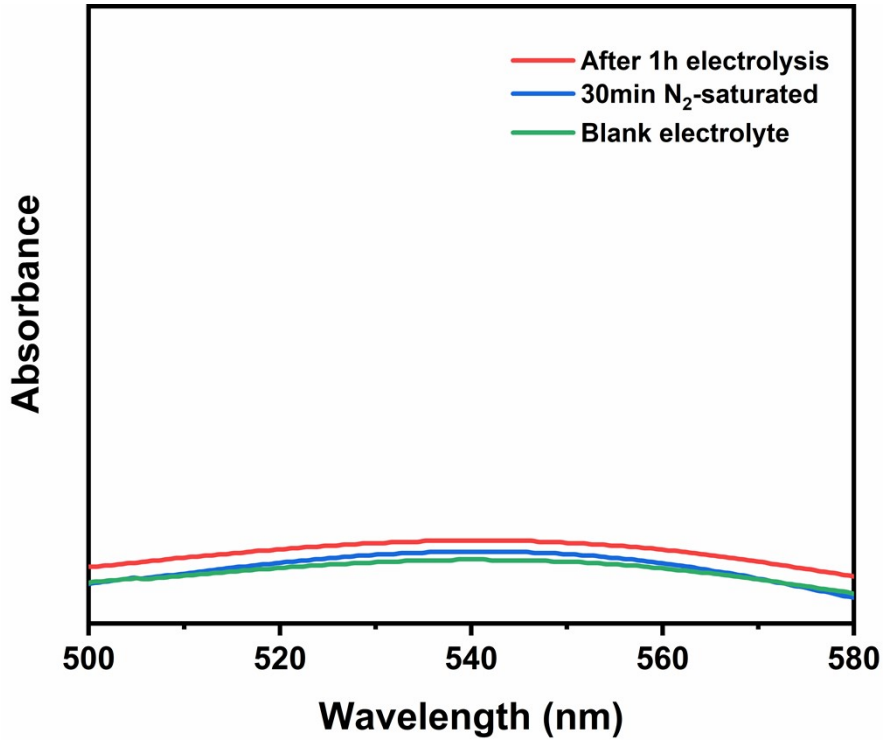

Fig. S16 UV-Vis spectra of nitrite of select stages

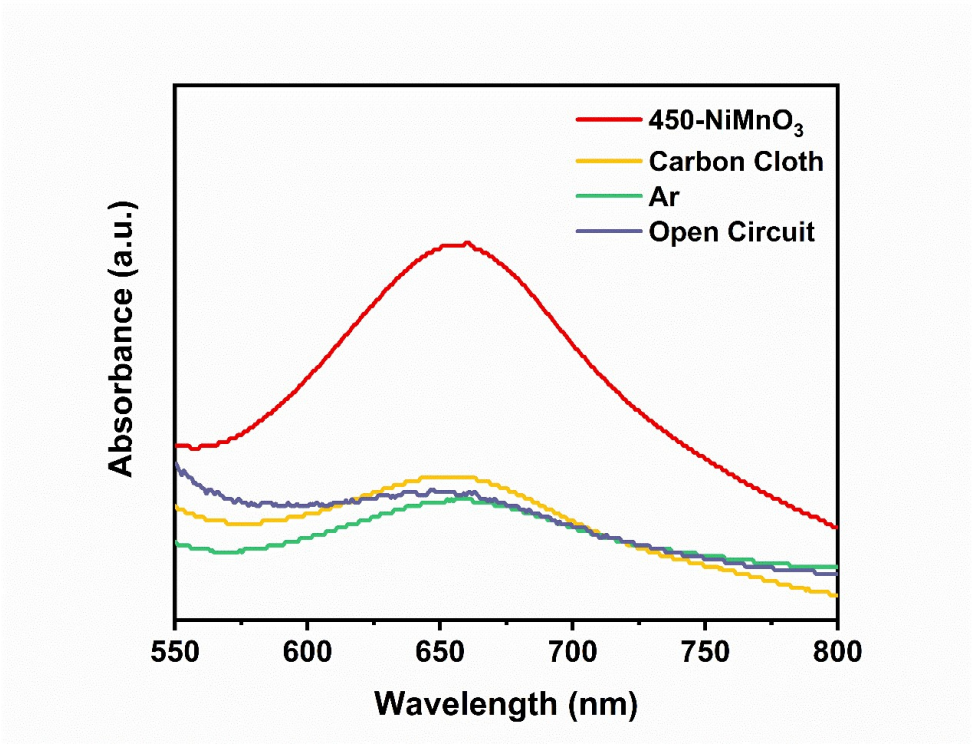

Fig. S17. UV-vis spectra of blank control

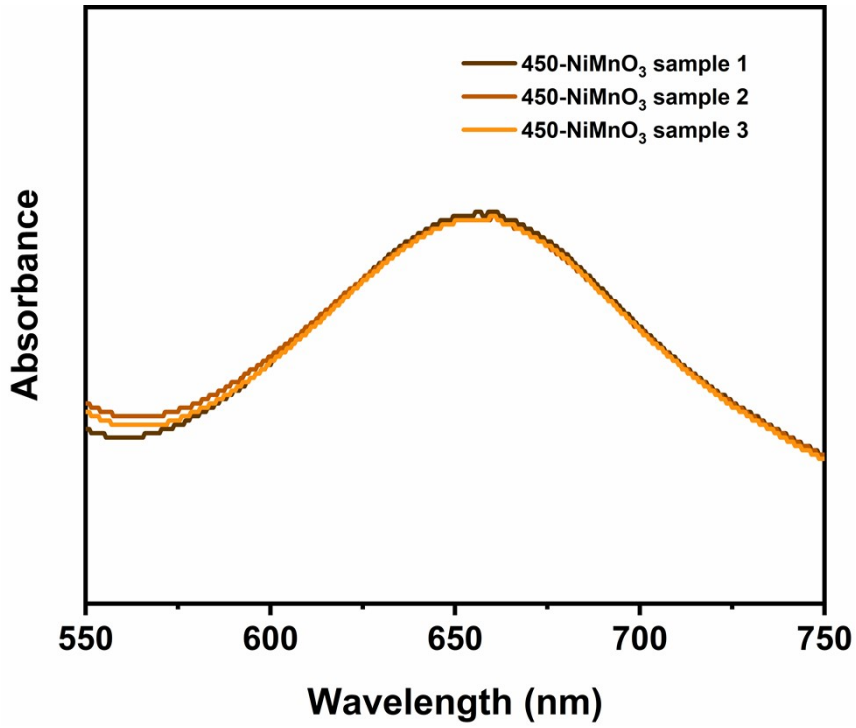

Fig. S18. UV-vis spectra of three independent samples

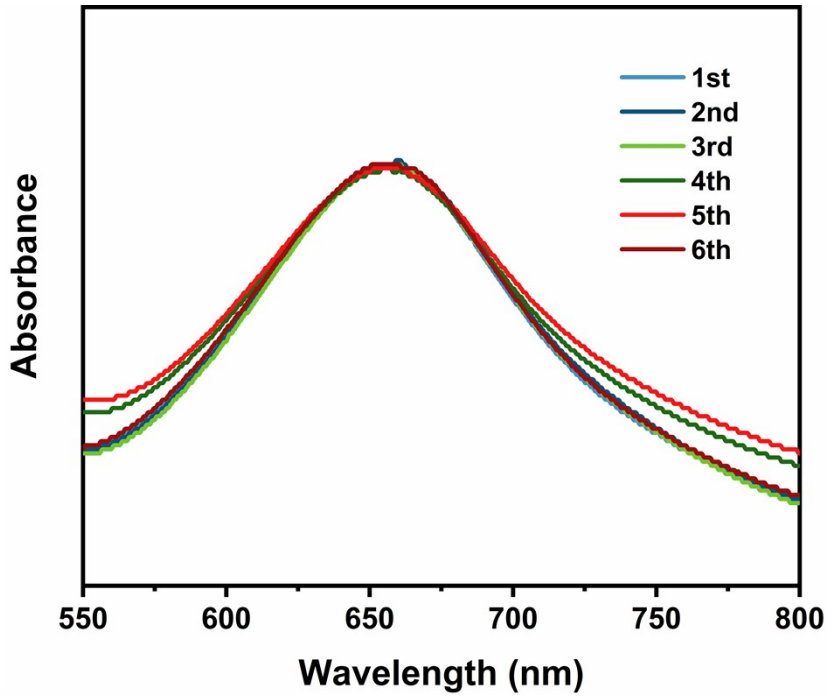

Fig. S19. UV-vis spectra of six-time cycle test

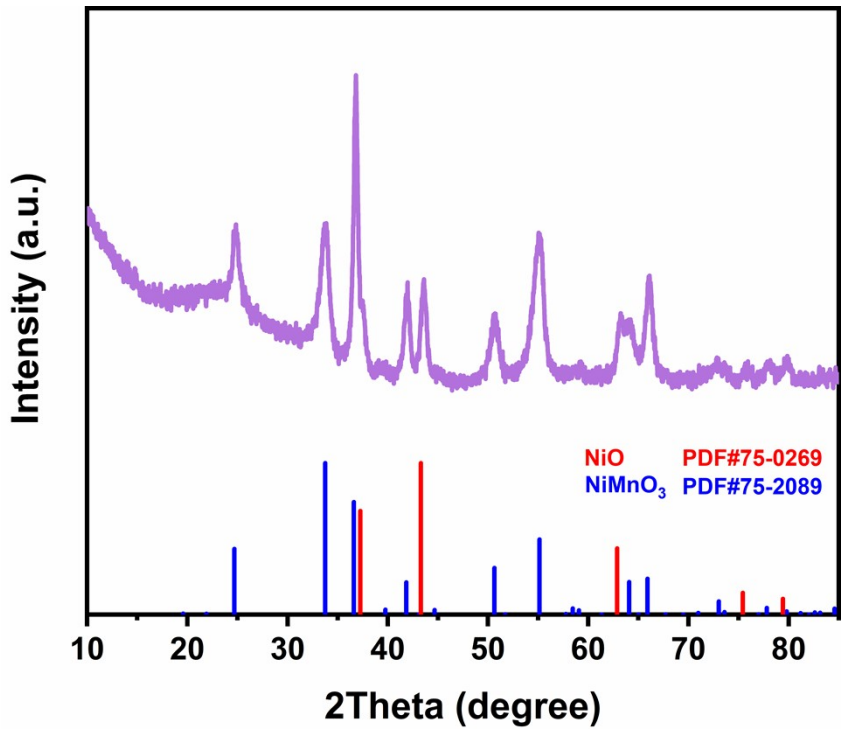

Fig. S20. XRD of 450-$NiMnO_3$ after cycle test

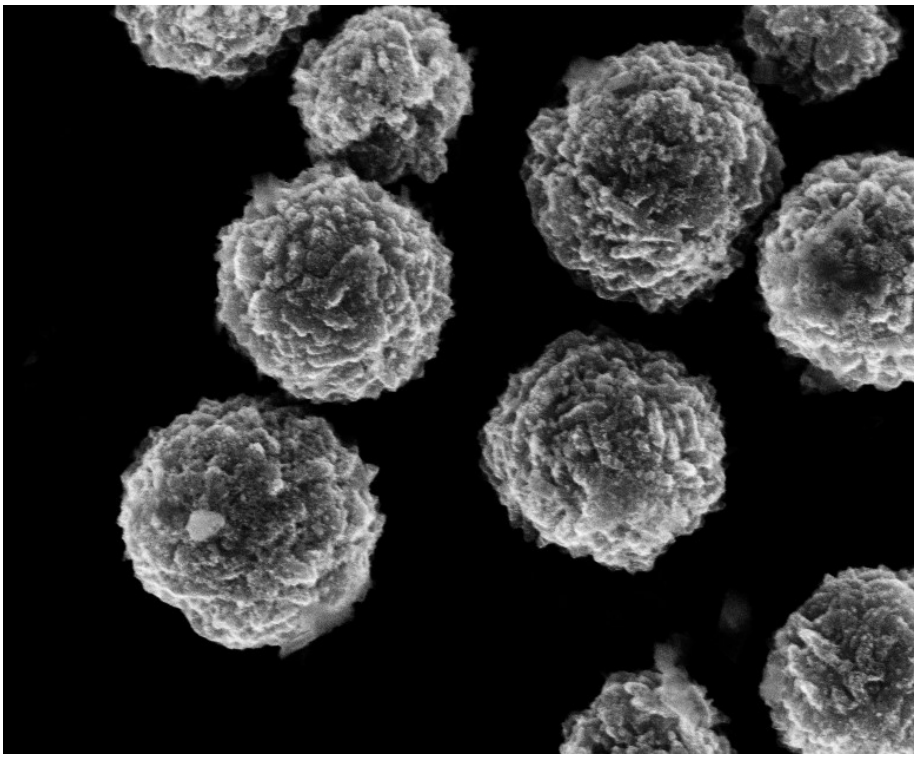

Fig. S21. SEM image of 450-$NiMnO_3$ after cycle test

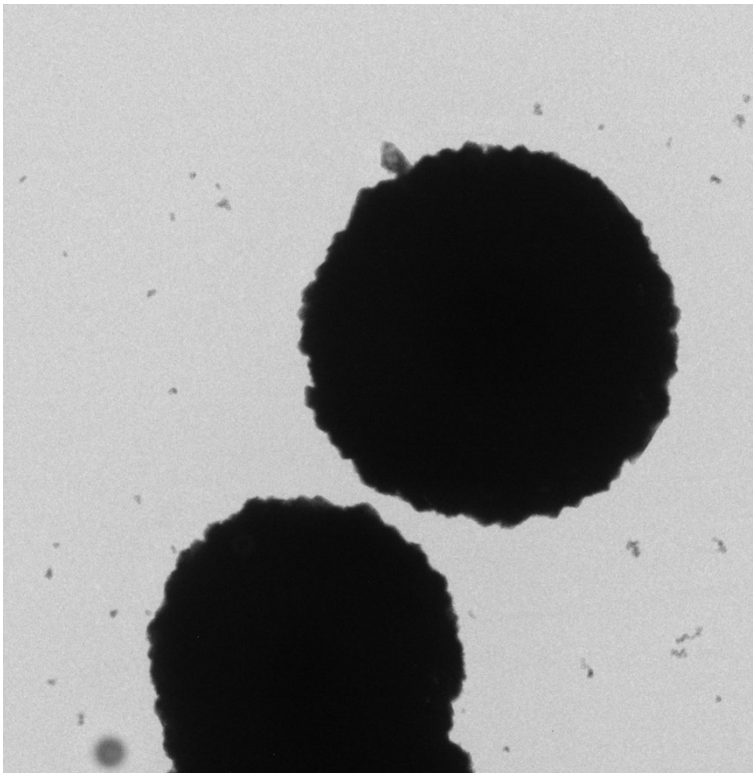

Fig. S22. TEM image of 450-$NiMnO_3$ after cycle test

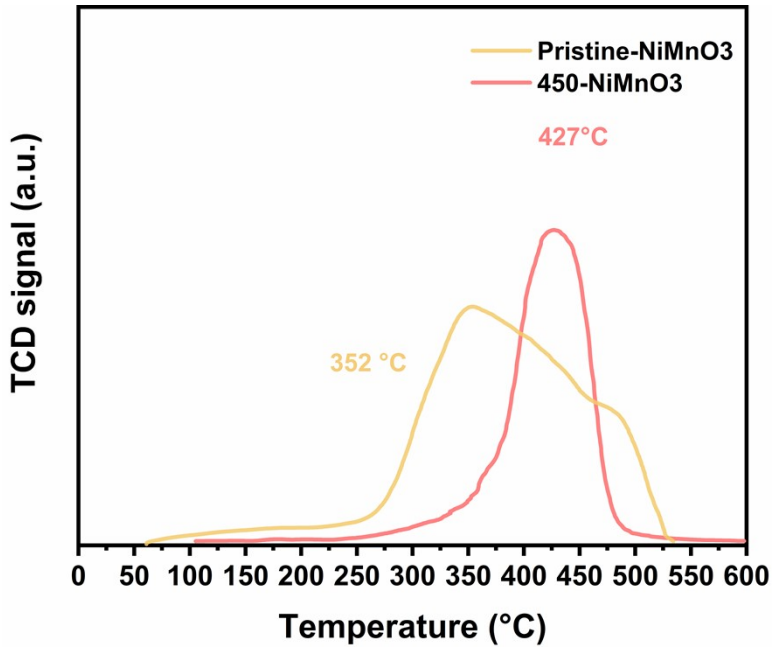

Fig. S23. N_2-TPD measurements **of 450-$NiMnO_3$ and pristine $NiMnO_3$**

Table S1. The gas analysis of $^{14}N_2$

Items	Results
N_2 gas purity	≥99.999
Oxygen content	≤ 0.2 ppm
CO,CO2,CH4 total content	≤ 0.7 ppm
H2O content	≤ 0.2 ppm
N_2O content	≤ 0.15 ppm

Table S2. The gas analysis of $^{15}N_2$

Items	Results
$^{15}N_2$ gas purity	≥99
Ar/O_2 content	≤ 300 ppm
CO_2	≤ 100 ppm
$^{15}N_2O$	≤ 50 ppm

Table S3.Comparison with various electrocatalysts for ENRR.

Catalyst	NH_3 yield	FE(%)	Detection method	Electrolyte	Ref.
450-$NiMnO_3$	**31.44μg/ h/mg (9.825μg/ h / cm^2)**	**14.5%**	**Indophenol blue**	**0.1M KOH**	**This work**
OV-MnO_2	**9.79μg/ h/cm^2**	**11.4%**	**Indophenol blue**	**0.1M KOH**	**1**
MnO_2–$Ti_3C_2T_x$	**34.1μg/ h/mg**	**11.39%**	**Indophenol blue**	**0.1M KOH**	**2**
MnO–CNF	**35.9μg/ h/mg**	**1.52%**	**Indophenol blue**	**0.1M Na_2SO_4**	**3**
Mn_3O_4 nanocubes	**11.6μg/ h/mg**	**3%**	**Indophenol blue**	**0.1M Na_2SO_4**	**4**
OV-TiO_2	**3μg/ h/mg**	**6.5%**	**Indophenol blue**	**0.1M KOH**	**5**
N-NiO/CC	**22.7μg/ h/mg**	**7.3%**	**Indophenol blue**	**0.1M $LiClO_4$**	**6**
NiO	**29.1μg/ h/mg**	**10.8%**	**Indophenol blue**	**0.1M Na_2SO_4**	**7**
Perovskite $LaCrO_3$	**24.8μg/ h/mg**	**15%**	**Indophenol blue**	**0.1M KOH**	**8**
$FeMoO_4$	**17.51μg/ h/mg**	**10.53%**	**Indophenol blue**	**0.1M Na_2SO_4**	**9**

Perovskite $La_2Ti_2O_7$	**25.15μg/h/mg**	**4.55%**	**Indophenol blue**	**0.1 M HCl**	**10**
Au/WO_{3-x}	**23.15μg/h/mg**	**14.72%**	**Indophenol blue**	**0.1 M HCl**	**11**
$CoFe_2O_4$	**2.57μg/h/mg**	**6.2%**	**Indophenol blue**	**0.1M Na_2SO_4**	**12**

References

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