Supporting Information

Boosting Nitrate Electroreduction to Ammonia on NbO_x via Constructing Oxygen Vacancies

Experimental Section:

Materials:

Niobium oxalates, ammonium chloride and sodium nitroferricyanide dihydrate were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. Potassium sulfate, salicylic acid, sodium citrate dehydrate, and sodium hypochlorite solution were purchased from Alfa Aesar (China) Chemicals Co., Ltd. Oxalic acid, methanol, ethanol, acetone, sodium nitrate, sodium hydroxide and isopropyl alcohol were provided by Sinopharm Chemical Reagent Co.,Ltd. Nafion solution (5 wt%) were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. Carbon Paper and Nafion N-117 membrane were also purchased from Alfa Aesar China Co., Ltd. All the chemicals and reagents were analytical grade and used as received without further purification in this work. Deionized water was used during all experimental process.

Pre-treatment of carbon paper (CP):

The CPs (1 cm × 1 cm × 0.1 cm) were ultrasonicated with alcohol for 30 min. After rinsing with ultrapure water, the CPs were ultrasonicated with water for 10 min. Finally, CPs were cleaned with acetone and dried at 60 °C for further use.

Pre-treatment of Nafion117 membrane:

Prior to electrochemical tests, Nafion 117 membrane was successively heat-treated in H_2O_2(5%) aqueous solution, 0.5 M H_2SO_4 solution and water for 1 h at 80 °C, respectively. Then membranes were rinsed in water thoroughly. Finally, they were immersed in deionized water for use.

NbO_x preparation:

Typically, 2 mM $C_{10}H_5NbO_{20}\cdot xH_2O$ and 6 mM $H_2C_2O_4$ were dissolved in 12 mL water and stirred at 75 °C for 2 h with stirring speed of 600 rpm. Then 40 mL methanol was added. The obtained aqueous solution was transferred into a 100 mL Teflonlined stainless steel autoclave with liner. The autoclaves kept at 180 °C for 12 h to obtain NbO_x particles. Then the NbO_x was acquire and rinsed with water and ethanol for several times. Finally, the obtained NbO_x was dried at 60 °C overnight.

Nb_2O_5 preparation:

Similarly, 2 mM $C_{10}H_5NbO_{20}\cdot xH_2O$ and 9 mM $H_2C_2O_4$ were dissolved in 40 mL water and stirred at 80 °C for 10min. Then 20 mL ethanol was added. The obtained aqueous solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave with liner. The autoclaves kept at 180 °C for 12 h to obtain white precursor precipitate. Then the white product was rinsed with water and ethanol for several times. Next, the product was dried at 50 °C for 12h. Finally, the obtained material was annealed in a muffle furnace at 550℃ for 4 h under air atmosphere.

Preparation of working electrode:

To prepare the working electrode, 5 mg of the catalyst powders and 30 μL 5 wt% Nafion solution were dispersed in 350 μL isopropyl alcohol. Then the mixed solution was treated by ultrasonic for 30min to form a homogeneous ink. Next, catalyst suspension was drop-casted onto a CP (1×1 cm^2) and dried under room temperature for measurement.

Characterizations:

X-ray powder diffraction (XRD) analysis of the catalysts were conducted on a Rigaku Ultima IV X-ray diffractometer. The diffractometer was conducted at 35 kV and 25 mA with Cu Kα radiation. The diffraction data was recorded in the 2θ range of 5~90°with a scan rate of 10°/min. The morphology of the catalysts was observed by Hitachi S4800 scanning electron microscope (SEM) at 3 kV and transmission electron microscopy (TEM) with a JEOL JEM-2100 microscope at an operating voltage of 300 kV. The chemical states of the catalysts were obtained by X-ray photoelectron spectroscopy (XPS) measurement. The XPS were performed at AXIS Supra surface analysis instrument equipped with an X-ray monochromatic source (combined Al/Ag anode, energy 1486.6/2984.2 eV). Raman spectra were collected on Shimadzu LabRAM HR Evolution with laser wavelength of 532 nm. 1H NMR spectroscopy was conducted on a Bruker Advance 500MHz spectrometer. The absorbance values of spectrophotometer were measured on SHIMADZU UV-2700 ultraviolet-visible (UV-Vis) spectrophotometer.

Electrochemical measurements:

Electrochemical nitrate reduction reaction was performed in a H-type electrolytic cell separated by ion exchange membrane (Nafion117) using CHI660E electrochemical analyzer (Shanghai CH Instruments Co., China), which was similar to that used previously.[1,4,10]. The catalyst powders loaded on CP acted as the working electrode, platinum gauze was used as counter electrode and Ag/AgCl electrode (filled with the saturated KCl solution) served as the reference. 0.5M K_2SO_4 solution(60mL) containing the concentration of 1000 ppm NO_3^- was used as an electrolyte and is divided evenly into cathode compartment for nitrate reduction. Prior to the electrochemical test, the cathode chamber electrolyte was purged with Ar (99.99% purity) for 0.5 h. All the reported potentials were recorded against reversible hydrogen electrode (RHE) via following Equation: $E(\text{vs. RHE}) = E\ (\text{vs. Ag/AgCl}) + 0.197\ \text{V} + 0.059 \times \text{pH}$ in measurements. The linear sweep voltammetry and cyclic voltammetry was performed at a scan rate of 10 mV s^{-1}, and a chronoamperometry test for nitrate reduction was conducted at the different potential for 2 h under stirring rate of 500 rpm. All the polarization curves achieved the steady-state ones after several CV cycles.

Determination of NH_3:

The method used was similar to that reported.[10] The ultraviolet-visible (UV-Vis) spectrophotometer was employed to detect the ammonia concentration of post-test electrolytes. The specific detection methods were spectrophotometrically determined by the indophenol blue method. Details are as follow: 2 mL electrolyte was removed from the cathodic chamber, and then added into 2 mL 1 M NaOH solution containing 5wt% salicylic acid and 5wt% sodium citrate. Next, 1 mL of 0.05 M sodium hypochlorite solution and 0.2 mL of 1wt% sodium nitroferricyanide aqueous solution were also added into the above solution. After standing at room temperature for 60 min, UV-Vis spectrophotometric measurements were performed at wavelength of 655nm. The concentration-absorbance standard curves were calibrated using standard ammonia chloride solution with a various of concentrations. The fitting curve ($y = 0.4331x + 0.0127$, $R^2=0.9994$) shows great linear relation of absorbance value with ammonia concentration.

^{15}N isotope labeling experiments:

The experiments were carried out using the same set-up over the NbO_x with the addition of ^{15}N isotope-labeled nitrate. After the electrocatalytic reaction, 20 mL of the electrolyte was taken out and concentrated to ~1 mL by heating at 75 °C. Then 0.1 mL of the resultant solution was thoroughly mixed with 0.6 mL of DMSO-d_6 for ^1H NMR.

Calculations of Faradaic efficiency and ammonia formation rate:

For nitrate electroreduction, producing one NH_3 molecule needs eight electrons. Thus, the FE_{NH3} can be calculated as following equation: $FE = 8F \times C_{NH3} \times V / 17 \times Q \times 100\%$, and the formation rate of ammonia can be calculated using the following equation: formation rate of ammonia = $(C_{NH3} \times V) / (t \times m)$,where F is the Faraday constant (96485 C mol^{-1}); C_{NH3} is the measured concentration of NH_3; Q is the total charge passing the electrode; V is the electrolyte volume; t is the electrolysis time; m is the mass of the catalyst used.

Detailed experimental method for quasi-operando XPS analysis:

Quasi-operando XPS was carried out with the samples processed in a glove box. After electrolysis, the electrode plate was soaked in acetone solution, and put into the glove box immediately. The obtained electrode plate was cut into 5 × 5 mm and glued on a support. The support could be evacuated into vacuum to prevent the samples to be oxidized by the air. The subsequent testing processes were the same as the common XPS.

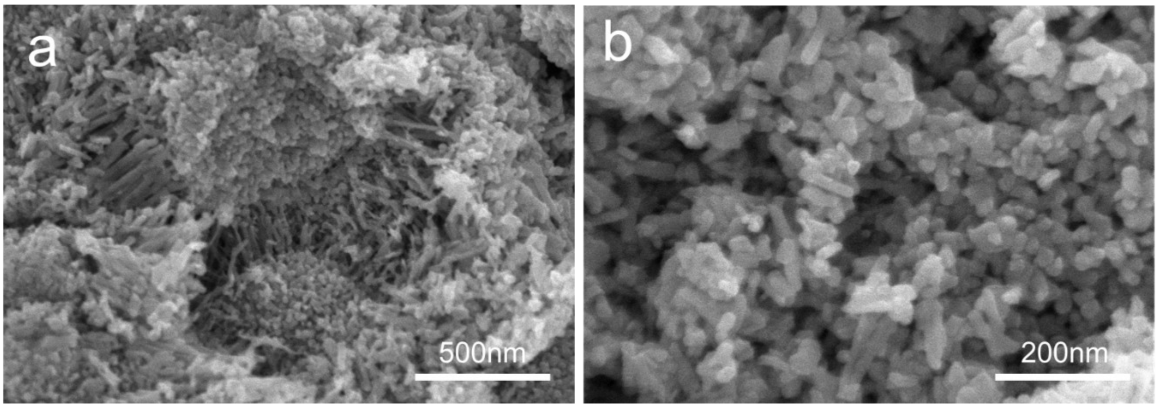

Figure S1. SEM images of Nb_2O_5.

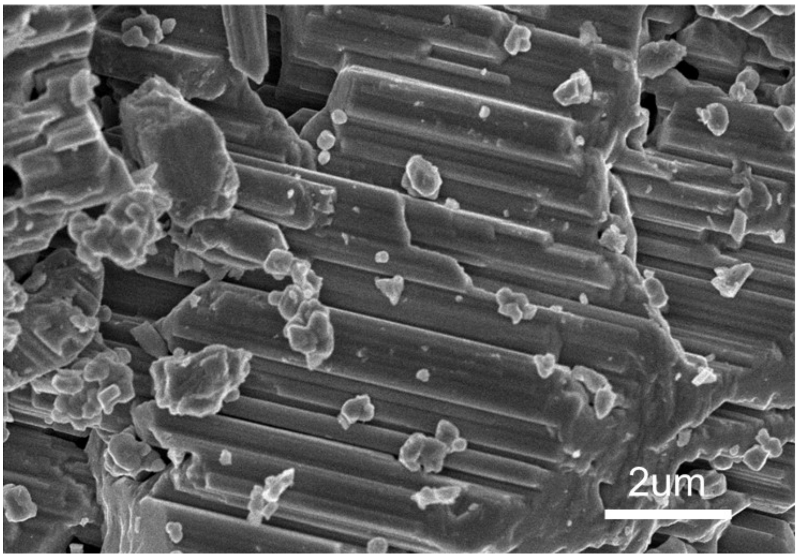

Figure S2. SEM image of commercial Nb_2O_5(c-Nb_2O_5).

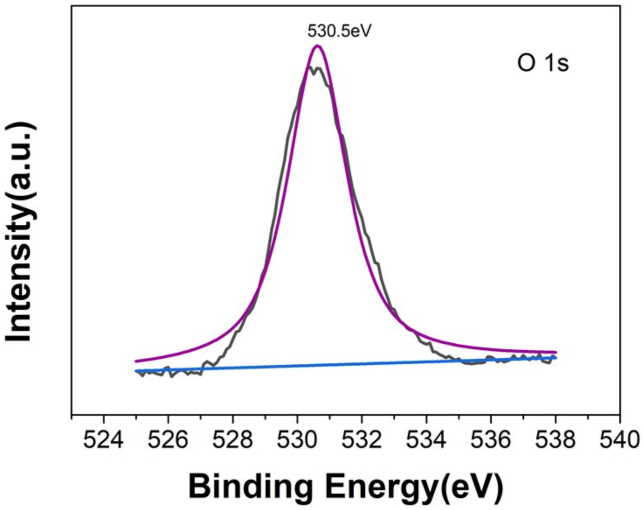

Figure S3. High-resolution XPS spectra of O 1s for the Nb_2O_5.

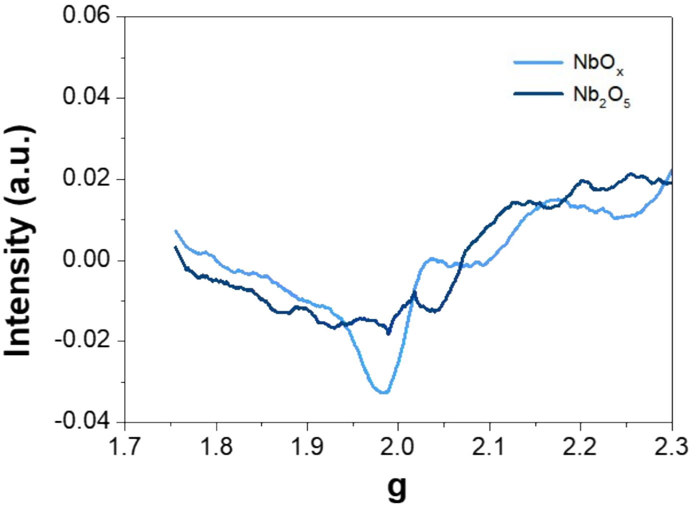

Figure S4. EPR spectra of NbO_x and Nb_2O_5.

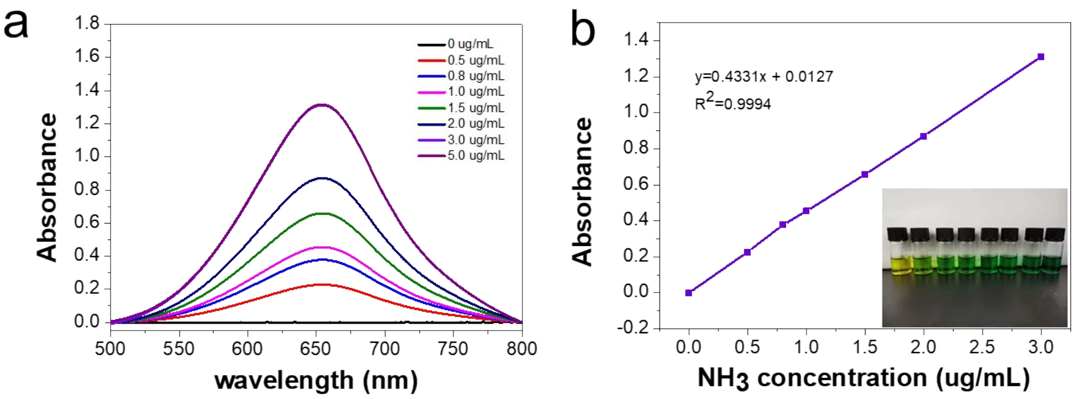

Figure S5. a) UV-Vis absorption spectra of indophenol assays with various NH_3 concentrations after incubated for 2 h at room temperature. b) Calibration curve used for calculation of NH_3 concentrations.

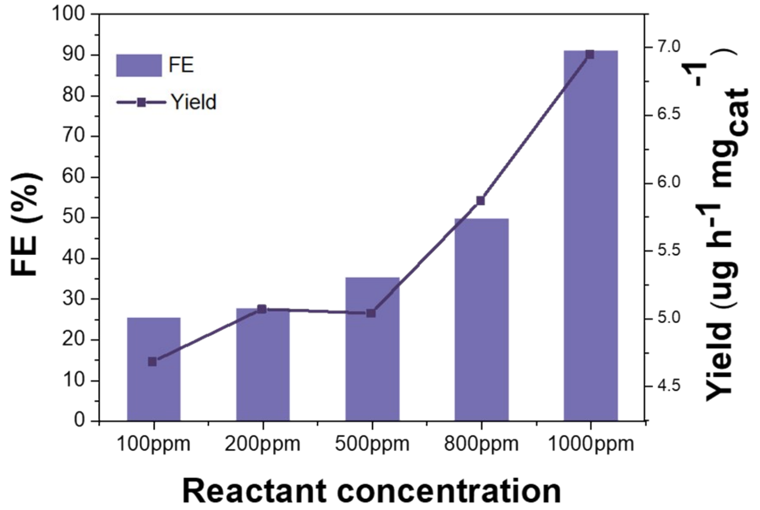

Figure S6. Potentiostatic tests were measured at -0.75 V in the same electrolyte with the addition of different content of NO_3^- (100, 200, 500, 800, and 1000 ppm).

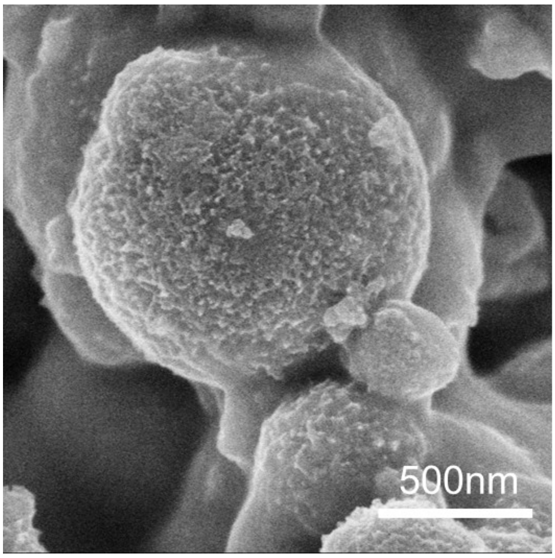

Figure S7. SEM image of the NbO_x after electrolysis.

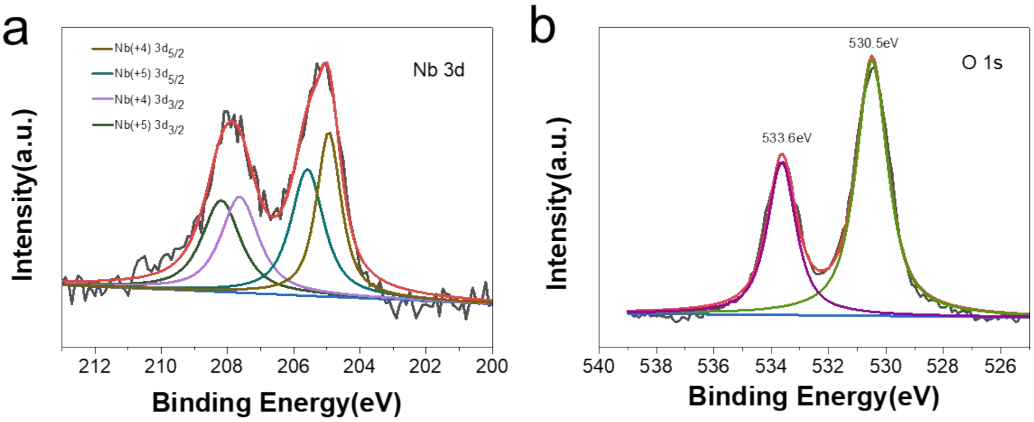

Figure S8. XPS spectra in a) Nb 3d and b) O 1s regions of NbO_x after electrolysis.

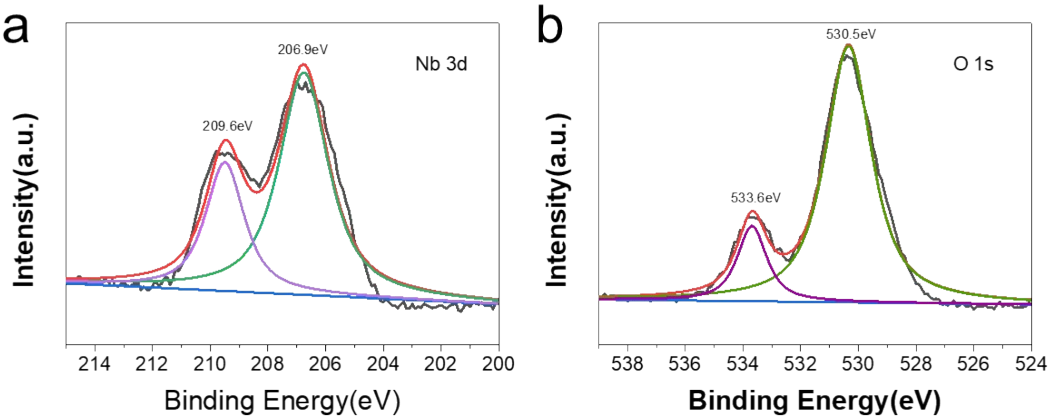

Figure S9. XPS spectra in a) Nb 3d and b) O 1s regions of Nb_2O_5 after electrolysis.

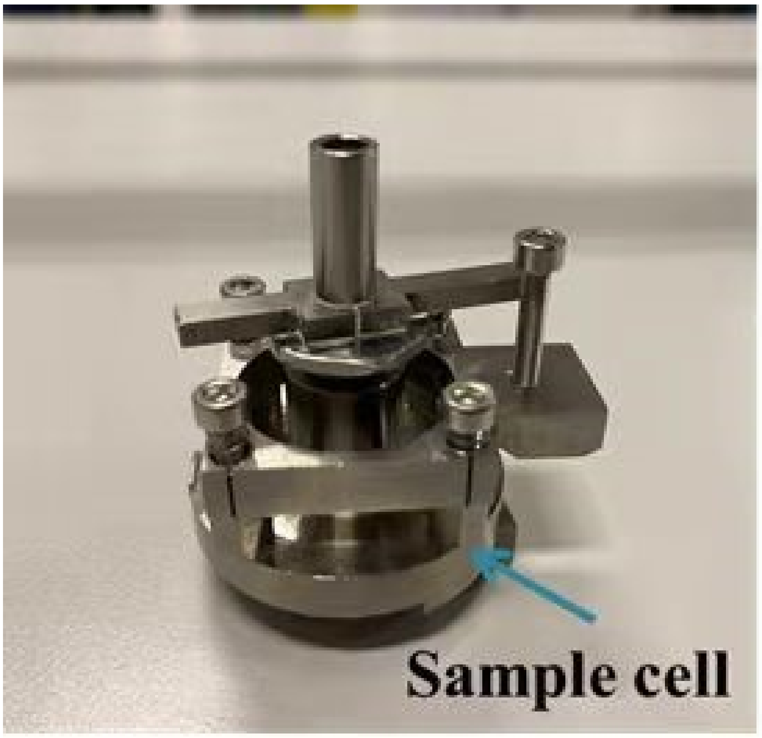

Figure S10. The quasi-operando XPS cell used in this work.

Table S1. Comparison of nitride electroreduction to NH_3 over different catalysts under ambient conditions.

Catalyst	Electrolyte	Potential	FE (%)	Yield rate	Detecting method	Ref.
NbO_x	0.5M Na_2SO_4+1000ppm KNO_3	-0.75 (vs. RHE)	94.5	55.0 ug h^{-1} mg^{-1}	Indophenol blue method	This work
TiO_{2-x}	0.5M Na_2SO_4 +50-400 ppm $NaNO_3$	-1.6V (vs. SCE)	85	0.045 mmol $h^{-1}mg^{-1}$	Nessler's reagent	1
Strained Ru nanoclusters	1M KOH +1M KNO_3	-0.2V (vs. RHE)	-	5.56 mol g^{-1} h^{-1}	Ion chromatograph	2
Cu nanosheets	0.1M KOH + 10 mM KNO_3	-0.15V (vs. RHE)	99.7	390.1 ug mg^{-1} h^{-1}	Berthelot reaction	3
Co3O4 nanorod arrays	0.1M K_2SO_4+ 100g L^{-1} KNO_3	-0.65V (vs. RHE)	-	0.854 mmol h^{-1} cm^{-2}	UV-vis spectroscopy	4
Co/CoO NSAs	0.1M Na_2SO_4+200 ppm $NaNO_3$	-1.3 V (vs. SCE)	93.8	194.46 μmol h^{-1} cm^{-2}	Nessler's reagent	5
Cu/Cu_2O nanowire arrays	0.5M Na_2SO_4+200-2000 ppm $NaNO_3$	-0.85 (vs. RHE)	95.8	0.2449 Mmol h^{-1} cm^{-2}	Nessler's reagent	6
$Cu_{50}Ni_{50}$	1 M KOH + 0.1 M KNO_3	-0.15 (vs. RHE)	99 ± 1	-	Indophenol blue method	7
Ti foil	0.4 M NO_3^- at pH~0.77	−1 V (vs. RHE)	82	-	Indophenol blue method	8
Au nanorods	0.1 M KOH	-0.2 (vs. RHE)	4.02	1.65 ug cm^{-2} h^{-1}	Nessler's reagent	9
Au-TiO_2 subnanocluster	0.1 M HCl	-0.2 (vs. RHE)	8.11	21.4 ug h^{-1} mg^{-1}	Indophenol blue method	10
Pd/C	0.1 M PBS	0.1 (vs. RHE)	8.2	4.5 ug h^{-1} mg^{-1}	Indophenol blue method	11
$Bi_4V_2O_{11}$-CeO_2 nanofibers	0.1 M HCl	-0.2 (vs. RHE)	10.16	23.21 ug h^{-1} mg^{-1}	Indophenol blue method	12
MoN nanosheets	0.1 M HCl	-0.3 (vs. RHE)	1.15	3.01×10^{-10} mol s^{-1} cm^{-2}	Indophenol blue method	13
$FeMoO_4$ nanorods	0.1 M Na_2SO_4	-0.6 (vs. RHE)	10.53	17.51 ug h^{-1} mg^{-1}	Indophenol blue method	14
Ti^{3+}–TiO_{2-x}/TM	0.1 M Na_2SO_4	-0.55 (vs. RHE)	14.62	$3.51x10^{-10}$ mol s^{-1} cm^{-2}	Indophenol blue method	15

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