

RESEARCH ARTICLE

BiVO₄/TiO₂ heterojunction with rich oxygen vacancies for enhanced electrocatalytic nitrogen reduction reaction

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SUPPLEMENTARY MATERIAL

1 Experimental section

Materials: Titanium foil, Ammonium metavanadate (NH₄VO₃), Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O), glycol, ammonium fluoride (NH₄F) ammonium chloride (NH₄Cl), sodium hypochlorite (NaClO), sodium hydroxide (NaOH), sodium salicylate (C₇H₅O₃Na), were bought from Beijing Chemical Corporation. Para-(dimethylamino) benzaldehyde (C₉H₁₁NO), sodium nitroferricyanide (III) dihydrate (Na₂Fe(CN)₅NO·2H₂O), and Nafion were purchased from Aladdin Ltd. (Shanghai, China). The water used throughout all experiments was purified through a Millipore system Chemical Corp. (China). All reagents were analytical reagent grade without further purification.

Characterizations: The X-ray diffraction (XRD) patterns were obtained from a LabX XRD-6100 X-ray diffractometer with Cu K α radiation (40 kV, 30mA) of wavelength 0.154 nm (SHIMADZU, Japan). Scanning electron microscope (SEM) measurements were recorded on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) images were obtained on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) operated at 200 kV. X-ray photoelectron spectroscopy (XPS) data of the

samples were collected on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. The absorbance data of spectrophotometer were measured on SHIMADZU UV-2700 ultraviolet-visible (UV-Vis) spectrophotometer. The N₂ temperature-programmed desorption (N₂-TPD) curves were characterized on an AutoChem II 2920 (Micromeritics).

Electrochemical measurements: NRR measurements were carried out in a two-compartment cell under room temperature and pressure condition, which was separated by Nafion117 membrane. Such membrane was protonated by first boiling in ultrapure water for 1 h and treating in H₂O₂ (5 wt %) aqueous solution at 80 °C for another 1 h, respectively. And then, the membrane was treated in 0.5 M H₂SO₄ for 3 h at 80 °C and finally in water for 6 h. All electrochemical tests were performed with a CHI 660E electrochemical workstation (CH Instruments, Inc., Shanghai) in a standard three-electrode system. BiVO₄/TNT, a graphite plate and Ag/AgCl electrode were used as the working electrode, counter electrode and reference electrode, respectively. The potentials reported in this work were converted to RHE other than especially explained via calibration with the following equation: $E \text{ (vs. RHE)} = E \text{ (vs. Ag/AgCl)} + 0.059 \times \text{pH} + 0.197 \text{ V}$ and the presented current density was normalized to the geometric surface area. For electrochemical N₂ reduction, chronoamperometry tests were conducted in N₂-saturated 0.1M Na₂SO₄ solution. The electrolyte after 7200s measurement was collected and the next potential test was performed in fresh electrolyte using the same electrode.

Determination of NH₃: The amount of ammonia was estimated by the reaction of salicylate and nitroprusside into the intense blue indophenol complex. In detail, 2 mL of the corresponding solution was removed from electrochemical reaction cell. Then 2 mL of 1 M NaOH solution containing 5 wt% salicylic acid and 5 wt % Sodium citrates, followed by addition of 1 mL 0.05 M NaClO and 0.2 mL of an aqueous solution of 1 wt % C₅FeN₆Na₂O (sodium nitroferricyanide), and then were set aside for 2 h in the dark at room temperature. The absorption spectrum was measured by using an ultraviolet-visible (UV-Vis) spectrophotometer. The formed indophenols blue was detected by absorbance at a wavelength of 655 nm. In order to quantify the produced NH₃, the calibration curves were built using a series of standard NH₄Cl solutions in the presence of 0.1 M Na₂SO₄ or 0.05 M H₂SO₄, as shown in Fig. SI 1 and Fig. SI 2. The measurements with the background solutions (no NH₃) were performed for all experiments. The sample absorbance at

655 nm was used to quantitatively measurement of ammonia based on the calibration standards.

Determination of N₂H₄: The amount of hydrazine was measured by the method of Watt and Crisp. A mixture 4-(dimethylamine) benzaldehyde (5.99g), HCl (concentrated, 30mL) and ethyl alcohol (300mL) was used as color reagent. In detail, 5 mL electrolyte was removed from the electrochemical reaction cell, and added into 5 mL as-prepared color reagent and stirred 10-15 min at room temperature. The absorbance of the resulting solution was estimated at 455 nm. The calibration curves were shown in Figure.S3.

Faradic efficiency and yield rate. The faradic efficiency for the NRR was defined using the following equation:

$$FE = 3 \times F \times [\text{NH}_3] \times V / (17 \times Q) \times 100\%. \quad (1)$$

NH₃ yield was calculated using the following equation:

$$\text{NH}_3 \text{ yield} = [\text{NH}_3] \times V / (m_{\text{cat.}} \times t), \quad (2)$$

where F is the Faraday constant, $[\text{NH}_3]$ is the measured NH₃ concentration, V is the volume of the electrolyte in the cathode chamber, Q is the total quantity of applied electricity; t is the reduction time; $m_{\text{cat.}}$ is the catalyst loaded mass.

Double layer capacitance (C_{dl}) measurements: To measure the electrochemical capacitance, the potential was swept between -1.5 V to -1.3V vs. Ag/AgCl at different scan rates (10, 20, 30, 40 and 50 mV s⁻¹) with an assumption of double layer charging in the potential range. The capacitive currents at -1.4 V vs. Ag/AgCl were measured and plotted as a function of scan rate. A linear fit determined the double layer capacitance.

2 Calculation section

The DFT calculation is carried out via Vienna Ab-initio Simulation Package (VASP) [1]. The pseudo-potential is projected-augmented plane wave (PAW) [2] method while the exchange-correlation functional adopts Perdew-Burke-Ernzerhof (PBE) functional of generalized gradient approximation (GGA) [3, 4]. The energy cut-off is 400eV and structure are relaxed until the atomic force is less than 0.05eV/Å. Since the BiVO₄ films and TNT attach randomly, we do not study every possible interface, but simply study an interface which makes interfacial coherent strain reasonably small. According to the previous XRD analysis, the crystal structures of TiO₂

(Figure S4a) and BiVO_4 (Fig. S4b) are obtained from JCPDS Card NO.21-1272 and JCPDS Card NO.14-0688, respectively. The structure of TiO_2 is tetragonal with three lattice parameters $a = b = 3.8\text{\AA}$ and $c = 9.5\text{\AA}$. The structure of BiVO_4 is defined as monoclinic, however, it is very close to an orthogonal structure, and the three lattice parameters a , b and c are 5.1\AA , 5.1\AA and 11.6\AA . The (100) plane ($3b \times c$, $11.4\text{\AA} \times 9.5\text{\AA}$) of TiO_2 and the (010) plane ($c \times 2a$, $11.6\text{\AA} \times 10.2\text{\AA}$) of BiVO_4 are selected as interfacial plane.

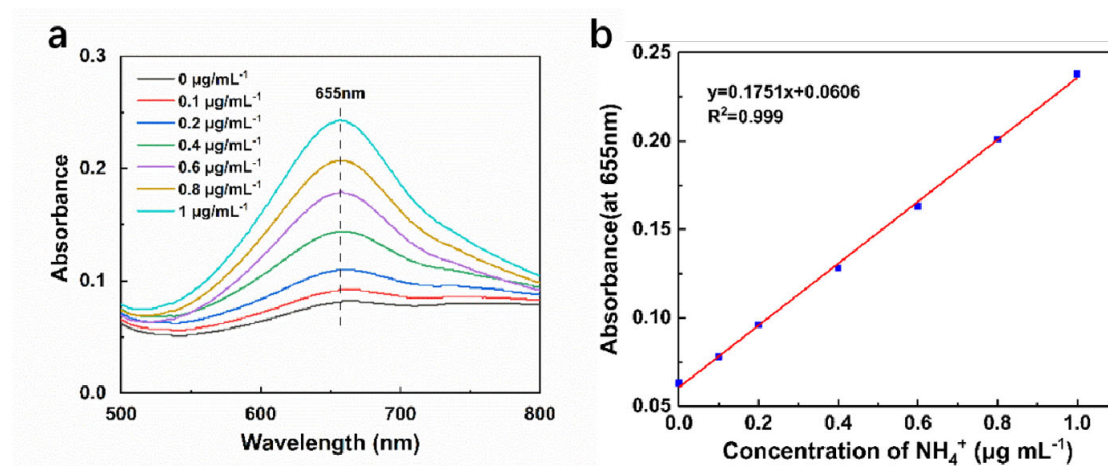


Fig. SI 1 (a) UV-Vis absorption spectra of indophenol assays with NH_3 after incubated for 1 h at room temperature in $0.1\text{M Na}_2\text{SO}_4$. (b) Calibration curve used for determination of NH_3 concentration.

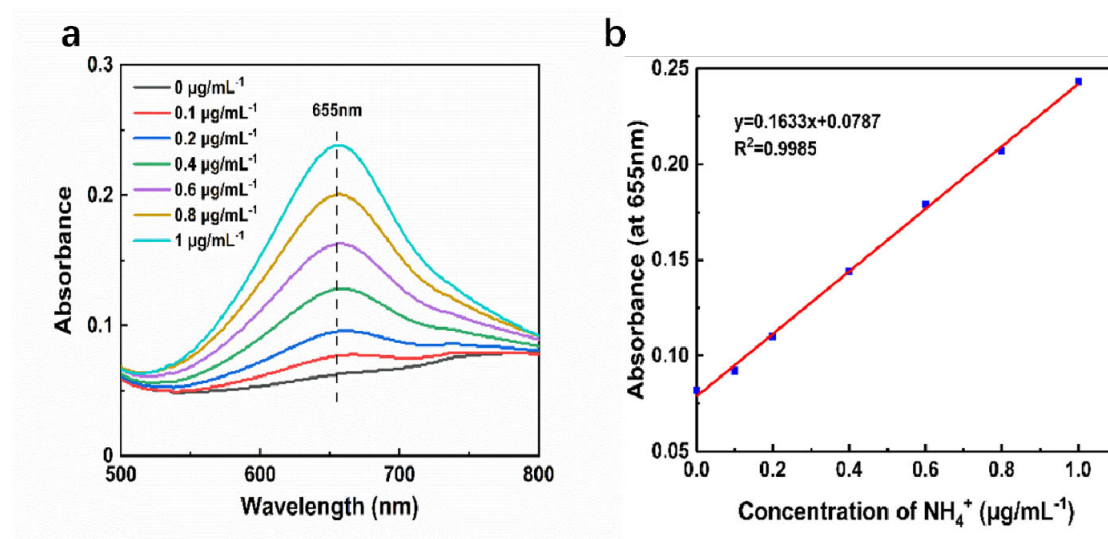


Fig. SI 2 (a) UV-Vis absorption spectra of indophenol assays with NH_3 after

incubated for 1 h at room temperature in 0.05M H₂SO₄. **(b)** Calibration curve used for determination of NH₃ concentration.

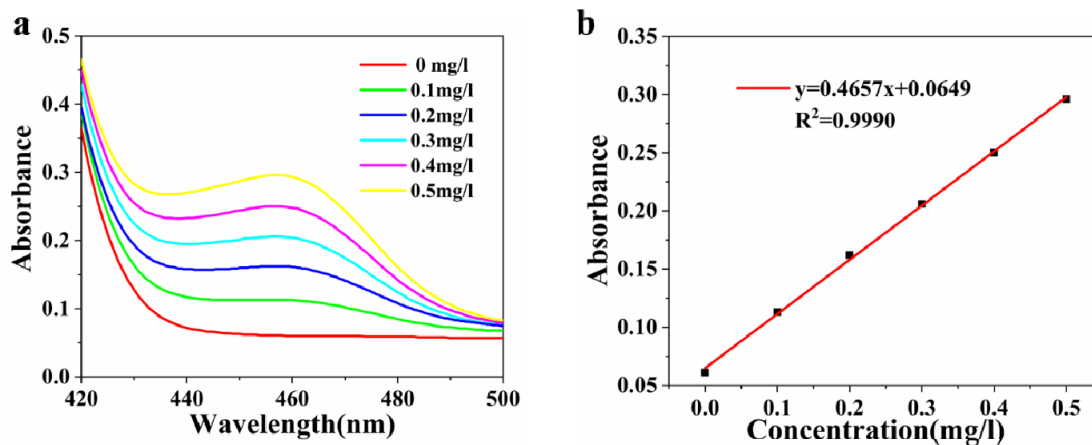


Fig. SI 3 (a) UV-Vis absorption spectra of various N₂H₄ concentrations after incubated for 20 min at room temperature. **(b)** Calibration curve used for determination of N₂H₄ concentration.

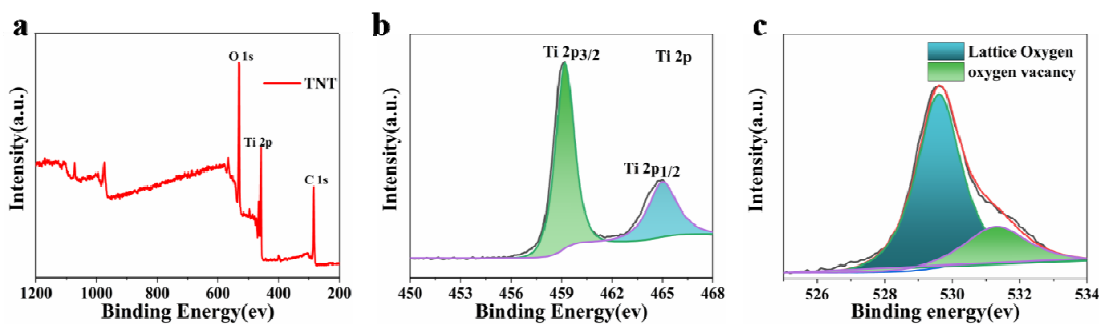


Fig. S1 XPS spectra of TNT: **(a)** Survey; **(b)** Ti 2p; **(c)** O1s.

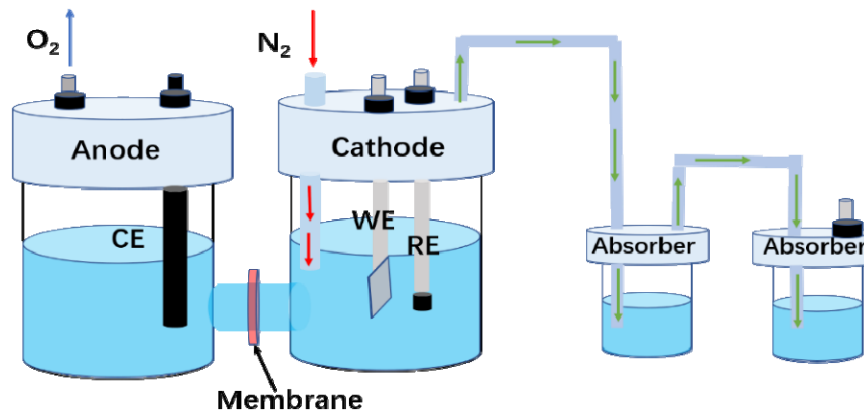


Fig. S2 Electrocatalysis nitrogen fixation device.

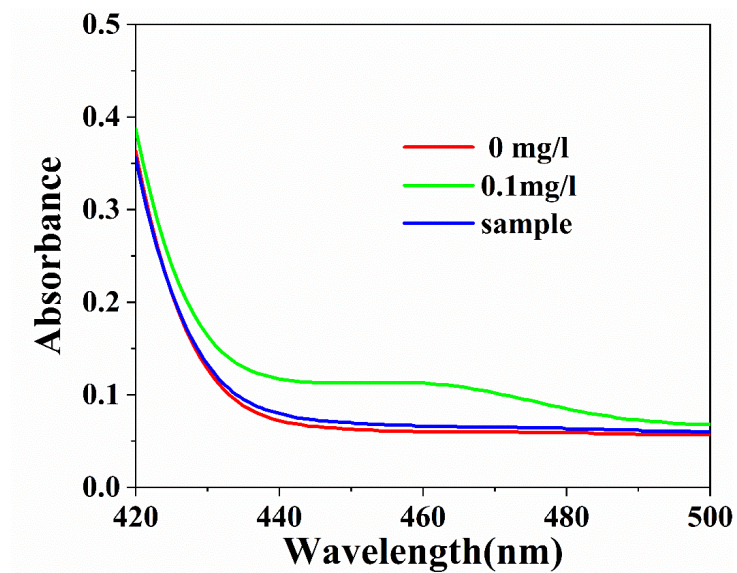


Fig. S3 The N_2H_4 concentration of sample in -0.8V vs. RHE in $0.1\text{M Na}_2\text{SO}_4$.

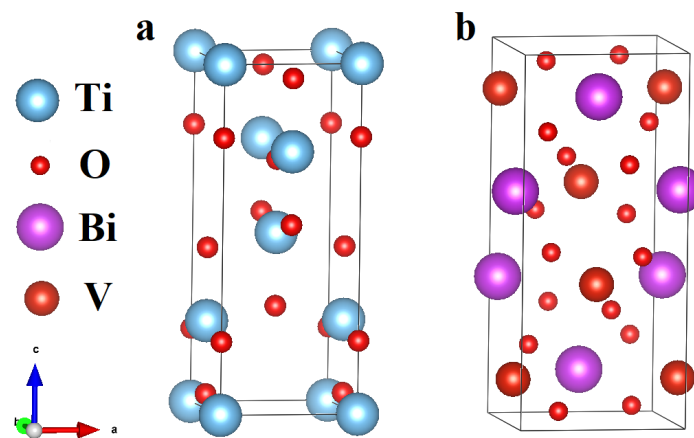


Fig. S4 The crystal structure of (a) TiO_2 and (b) BiVO_4 .

References

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