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Support Information

Understanding Z-Scheme Heterojunction of $BiVO_4$/PANI for Photoelectrochemical Nitrogen Reduction

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Materials

All chemical reagents are of analytical grade and used without further purification. Bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$), ammonium vanadate (NH_4VO_3), ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), sodium hydroxide (NaOH), ammonium chloride (NH_4Cl), hydrazine hydrate ($N_2H_4 \cdot H_2O$), aniline (C_6H_7N), nitric acid and sulfuric acid potassium sodium tartrate ($NaKC_4H_4O_6$), Nessler's reagent, hydrogen nitrate (HNO_3, 65%~68%) were all obtained from Aladdin Reagent Co. The FTO glass substrates used in the experiment were washed by acetone and ethanol for 25 minutes in advance.

Characterization

The morphology of samples was investigated by transmission electron microscopy (TEM, Tecnai G2 F20 S-Twin electron microscope (FEI Co.)), and scanning electron microscopy (SEM, Hitachi S-4800 25.0kV 7.5mm×40.0 SE(U)). The crystal structure was collected by high-resolution transmission electron microscope (HRTEM) and X-ray diffractometer (XRD, Bruker D8 ADVANCE). The valence state and composition of elements were detected by X-ray photoelectron spectroscopy (XPS, Thermos Fisher Scientific, Escalab 250Xi, Al Ka). Photoelectrochemical impedance spectroscopy (PEIS) and Mott-Schottky data were tested by electrochemical instrumentation (Princeton, VersaSTAT 3). The absorption spectra were tested by UV–Vis 2550 (Shimadzu, Japan). All photoelectrochemical tests were carried out on the electrochemical system (CHI-852, China).

Preparation

$BiVO_4$ was prepared through hydrothermal method according to literature.[S1] The synthetic procedure of $BiVO_4$ was as follows: 1.94 g $Bi(NO_3)_3 \cdot 5H_2O$ and 1.49 g EDTA-2Na were added into 40 mL HNO_3 (2 M) solution. 0.47 g NH_4VO_3 and 1.49 g EDTA-2Na were dissolved in 80 mL NaOH (1 M) solution. Then, the mixture was transfer into a 50 ml Teflon-lined autoclave. The FTO glass was put into the Teflon-lined stainless autoclave at an angle against the wall. Then, the autoclave was sealed and transferred to an oven at 160 °C for 12 h. Subsequently, $BiVO_4$ sample was repeatedly rinsed with deionized water and dried at room temperature.

$BiVO_4$/PANI was fabricated by an in-situ typical electrodeposition method.[S2] Briefly, 0.9 mL C_6H_7N was dispersed in 50 mL aqueous solution (0.1 M H_2SO_4). The electrodeposition was carried out in a three-electrode cell with $BiVO_4$ as working electrode, Ag/AgCl as reference electrode, and Pt wire as counter electrode. Cathodic deposition was performed at 0.79 V vs. Ag/AgCl for 20 min (room temperature). Similarly, $BiVO_4$/PANI sample was repeatedly rinsed with deionized water and dried at room temperature.

PEC Measurements

In this work, PEC measurements were carried out in a double-chamber H-type cell with good airtightness (0.1 M Li_2SO_4 electrolyte). For PEC NRR activity tests, $BiVO_4$/PANI was used as the working electrode, Pt electrode and Ag/AgCl (saturated KCl) electrode were used as counter electrodes and reference, respectively. In the reaction process, N_2 was continuously introduced into the reactor to make the whole reaction system reach N_2 saturation. As a conclusion, the good airtightness and

saturated N_2 atmosphere of the cell provide the only N_2 source for the formation of NH_3. The light source directed at the H-type PEC cell (300 W xenon lamp; 100 mW/cm^2). The linear sweep voltammogram (LSV) test was carried out with a voltage from -0.4 to 0.2 V vs. RHE (scanning rate is 50 mV/s). The Mott-Schottky plots and photoelectrochemical impedance spectra (PEIS) were measured by an electrochemical analyzer (Princeton, VersaSTAT 3).

Determination of NH_3

The NH_3 yield rate was quantitatively determined by the Nessler's reagent method through ultraviolet−visible (UV−vis) spectrophotometry. 50 mL reaction solution was mixed with 1 mL Nessler's reagent and 1 mL potassium sodium tartrate solution. The mixture stood for 15 min, and the absorbance at 425 nm was measured by UV-vis spectrometer. A series of concentration-absorbance curves were calibrated with standard NH_4Cl solution (Fig. S1a). As shown in Fig. S1b, the calibration curve ($Y = 0.1730X - 0.0007$, $R^2 = 0.9997$) shows an excellent linear relation of absorbance value with NH_3 concentration. The r_{NH3} and FE were calculated using the following formula:

$$r_{NH3} = (C_{NH3} \times V)/(A \times t)$$

$$FE_{NH3} = (3 \times F \times C_{NH3} \times V)/(17 \times Q) \times 100\%$$

Among them, A is the area of catalyst, F is the Faraday constant (96485 C mol^{-1}), C_{NH3} is the concentration of NH_3, V is the volume of reaction liquid, t is the reaction time, Q is the total electricity consumption.

Determination of hydrazine hydrate (N_2H_4)

The concentration of N_2H_4 was estimated by Watt and Chrisp method. The color reagent is composed of 6.0 g para-(dimenthylamino) benzaldehyde, 30 mL concentrated hydrochloric and 300 mL ethanol. In detail, 15 mL as-prepared color reagent was mixed with 15 mL electrolyte solution. After 10 min, the concentration-absorbance was measured by UV-vis spectrophotometer at 455 nm with a series of standard N_2H_4 solutions (Fig. S2a). As shown in Fig. S2b, the calibration curve ($Y = 0.4194X - 0.0018$, $R^2 = 0.9991$) shows excellent linear relation of absorbance value with N_2H_4 concentration.

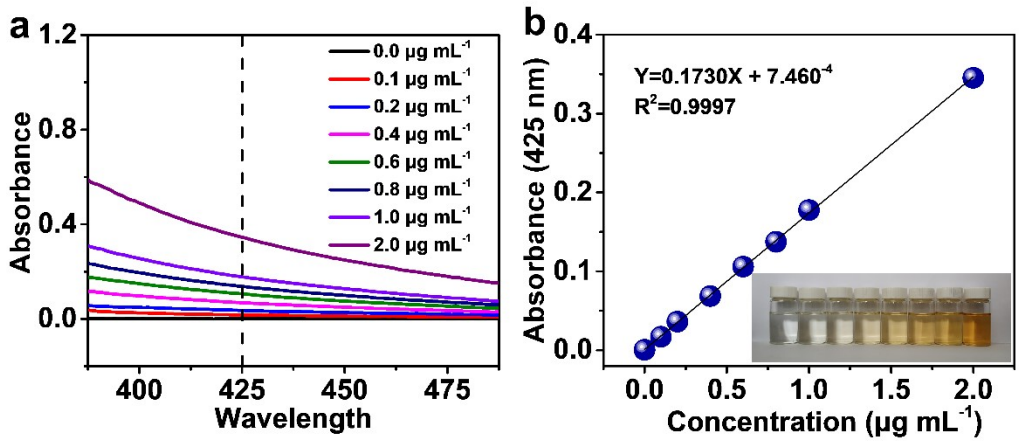


Fig. S1 (a) Standard absorbance curve of NH_3 yield by Nessler reagent spectrophotometry. (b) Calibration curve.

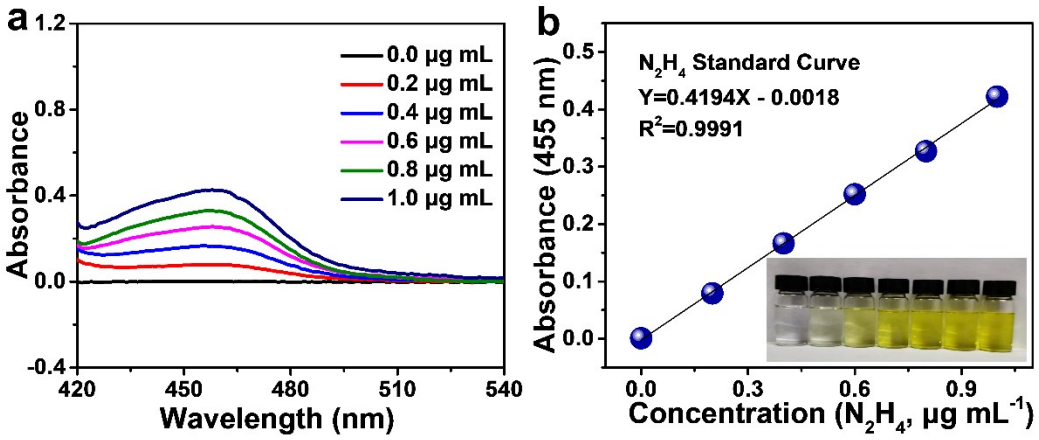


Fig. S2 (a) Standard absorbance curve of N_2H_4 yield by Watt and Chrisp method. (b) Calibration curve.

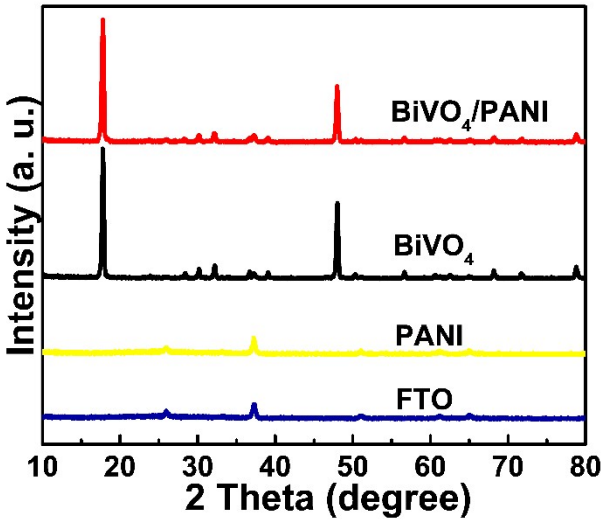


Fig. S3 XRD patterns of FTO, PANI, $BiVO_4$ and $BiVO_4$/PANI.

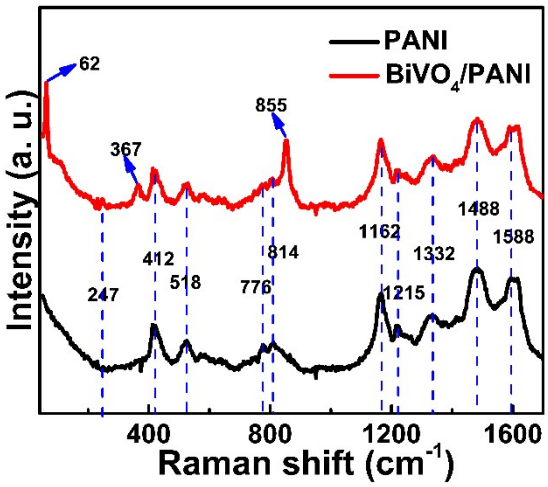


Fig. S4 Raman spectra of PANI and $BiVO_4$/PANI.

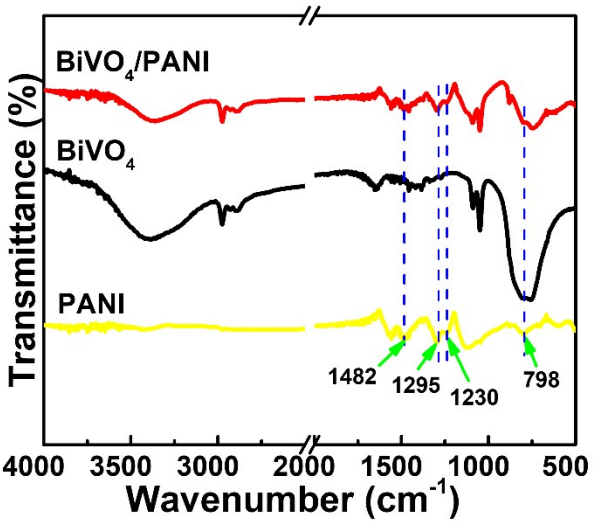


Fig. S5 FTIR spectra of PANI, $BiVO_4$ and $BiVO_4$/PANI.

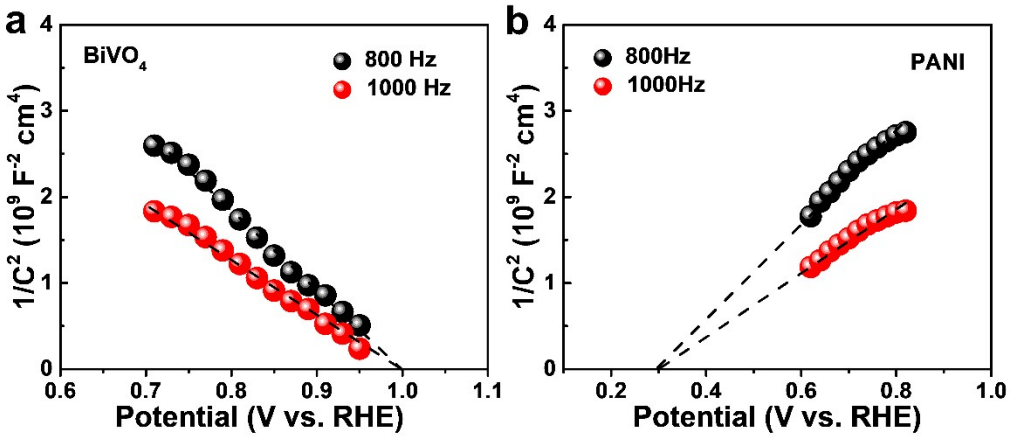


Fig. S6 Mott−Schottky plots at different frequency: (a) $BiVO_4$, (b) PANI.

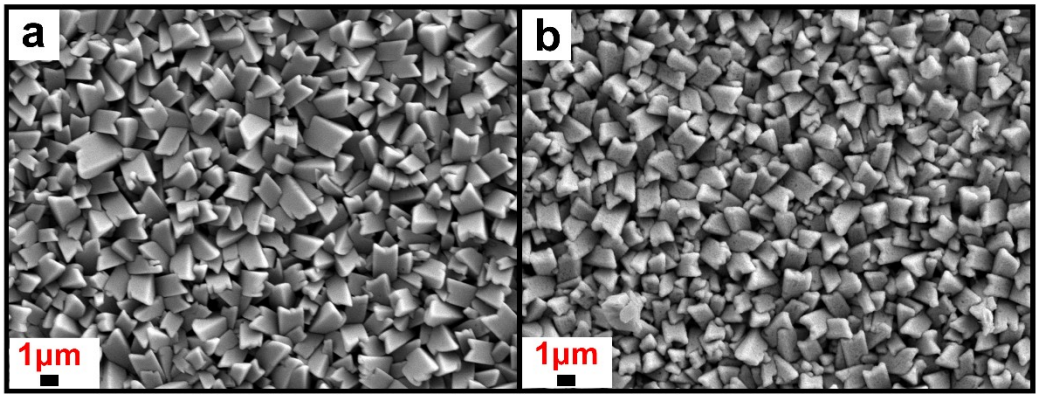


Fig. S7 (a) SEM images of $BiVO_4$ and (b) $BiVO_4$/PANI.

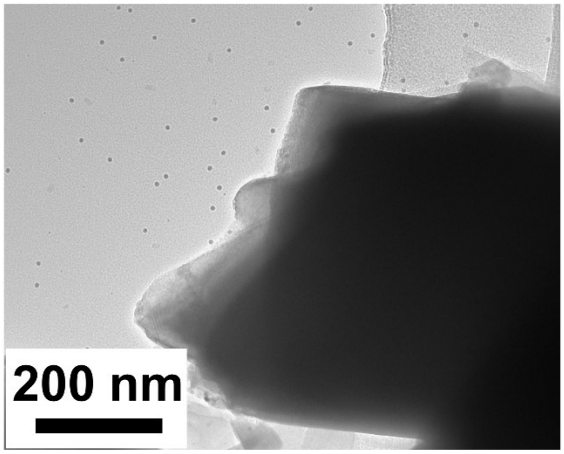


Fig. S8 (a) TEM image of $BiVO_4$/PANI.

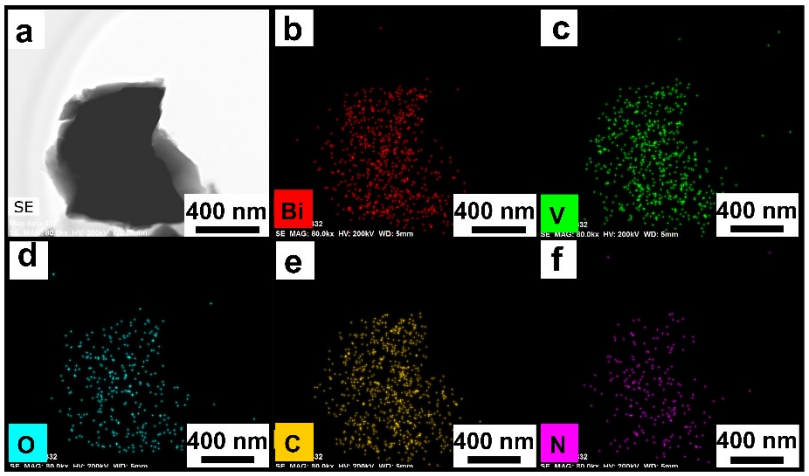


Fig. S9 (a-f) STEM-EDX EDX mapping of $BiVO_4$/PANI.

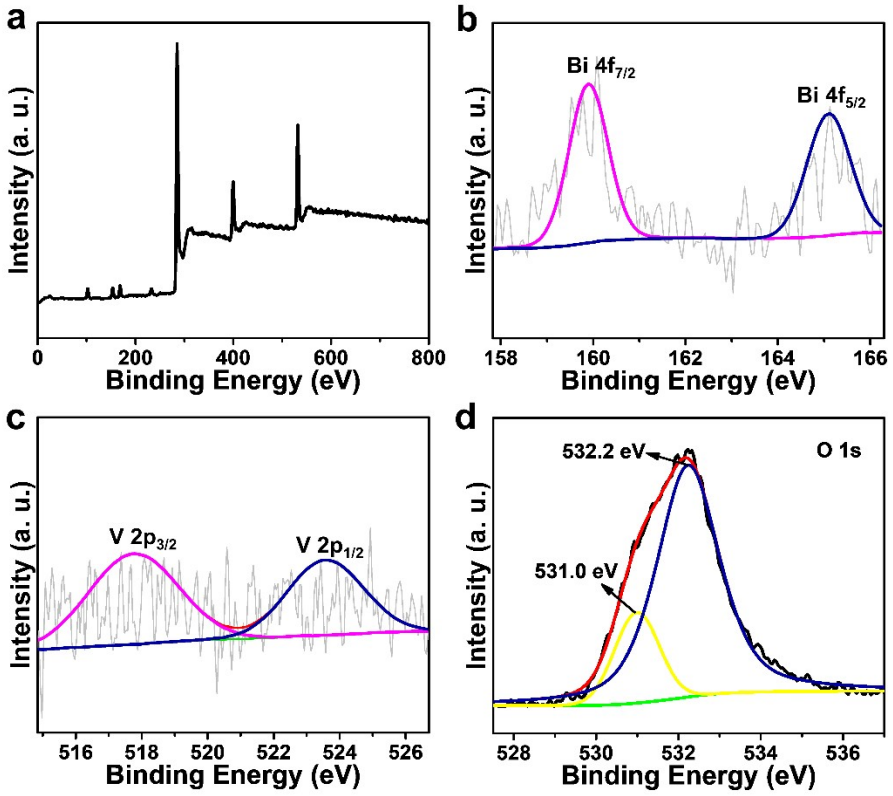


Fig. S10 XPS spectra of $BiVO_4$/PANI: (a) Survey of XPS spectra of (b) Bi 4f, (c) V 2p, (d) O 1s.

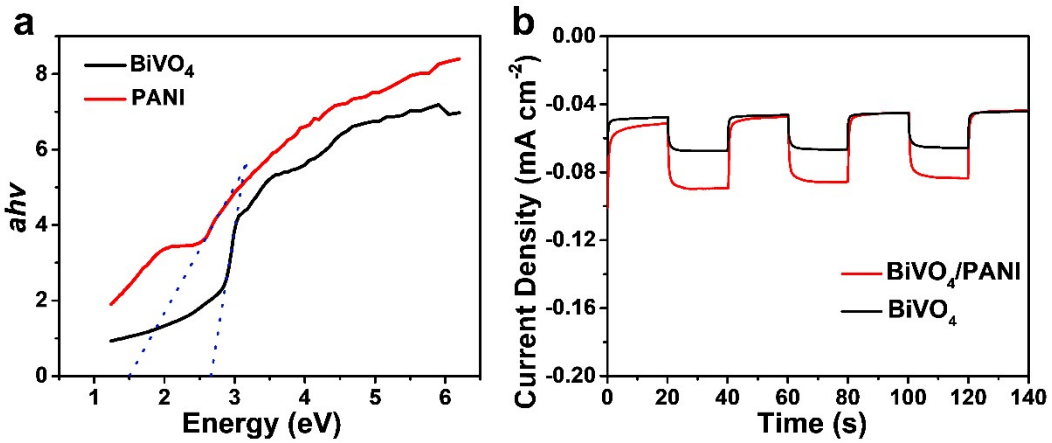
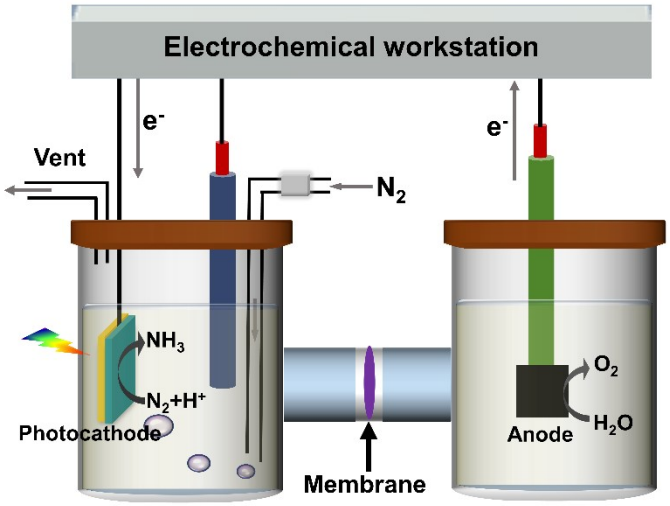


Fig. S11 (a) Tauc plots of $BiVO_4$ and PANI. (b) Transient photocurrent curves under 100 mW/cm^2 illumination (-0.1 V vs. RHE, scan rate: 50 mV/s).



Scheme S1 Schematic diagram for PEC NRR configuration.

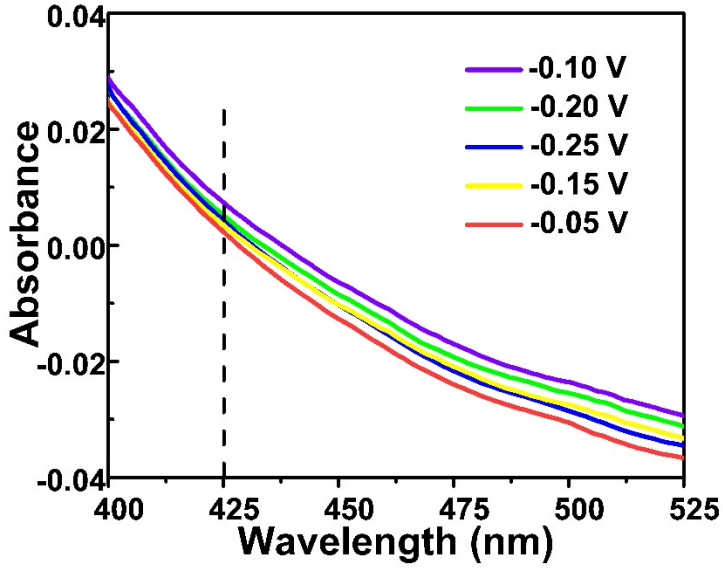


Fig. S12 UV-vis absorption spectra of different electrolytes colored by the Nessler's reagent.

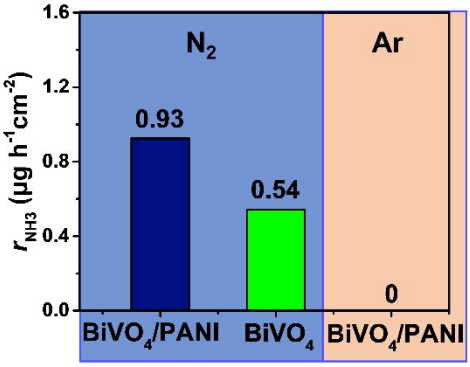


Fig. S13 r_{NH3} in N_2 ($BiVO_4$ and $BiVO_4$/PANI) and Ar ($BiVO_4$/PANI) atmosphere.

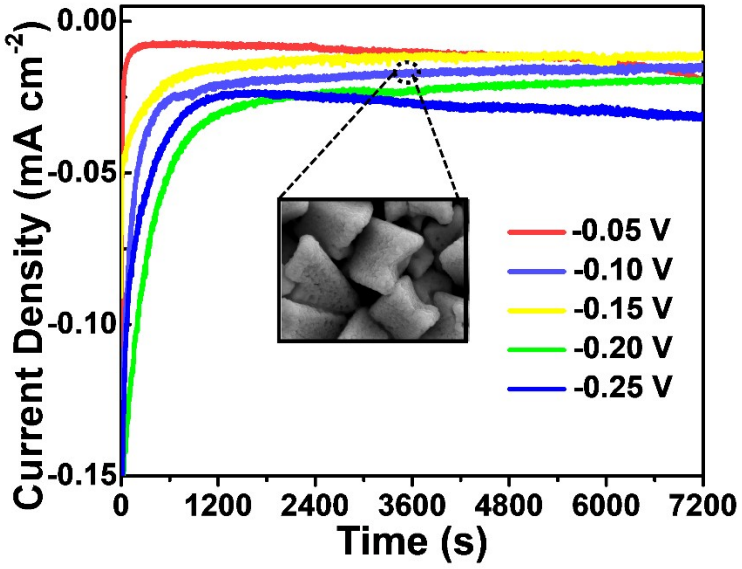


Fig. S14 Chronoamperometry results of $BiVO_4$/PANI at different potentials.

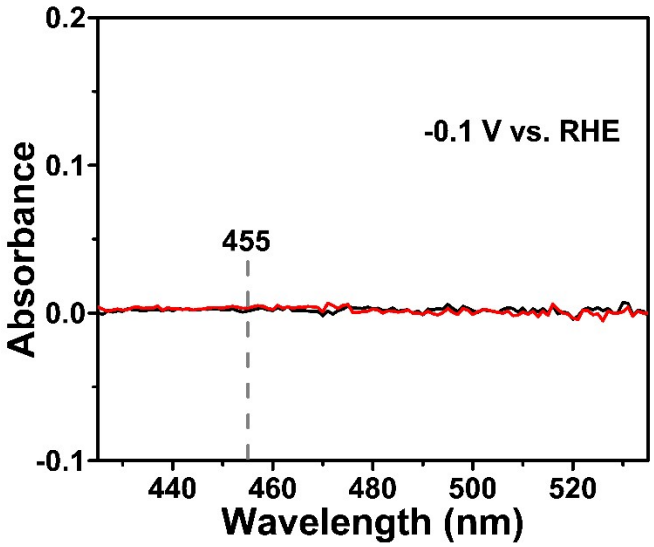


Fig. S15 UV-vis absorption spectra of N_2H_4 at –0.1 V vs. RHE.

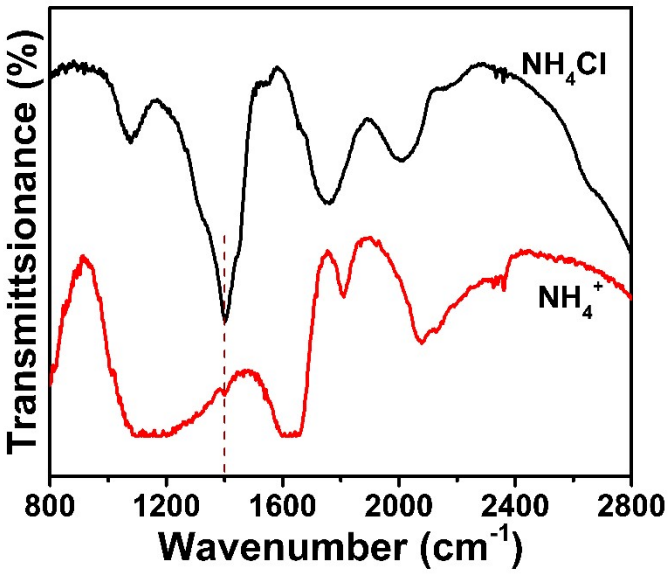


Fig. S16 FT-IR spectra for standard NH_4Cl and reaction solution dripped with HCl.

References

S1. J. Wang, Y. Song, J. Hu, Y. Lia, Z. Wang, P. Yang, Q. Ma, Q. Che, Y. Dai, B. Huang, *Appl. Catal. B-Environ.* 2019, **251**, 94−101.

S2. A. I. Inamdar, H. S. Chavan, H. Kim, H. Im, *Sol. Energ. Mat. Sol. C.* 2019, **201**, 110121.