

Supporting Information

Bismuth-doped manganese molybdenum bimetallic oxide nanorods as a highly efficient nitrogen reduction catalyst

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1. Sample characterization and electrochemical testing

Field emission scanning electron microscopy (FESEM) was used to measure the morphology of catalysts on a Zeiss Sigma 300 EDS instrument, with an acceleration voltage of 0.02 kV-30 kV. X-ray diffraction (XRD) with Cu K α Radiation LabX XRD-6000 X-ray diffractometer ($\lambda_{1/4}=1.5406 \text{ \AA}$) was collected, and diffraction data was recorded at 2θ from 10 to 80°. Within the range, the scanning rate is 5°/min. X-ray photoelectron (XPS) spectroscopy using Al K α Thermo Scientific K-Alpha+ X-ray photoelectron spectrometer with source. Use high-resolution transmission electron microscopy (HRTEM, JEM-2100) under 200 kV operation to test the TEM images of the catalyst. Measure and record the UV-vis spectrum of the electrolyte using a UV-1800 UV spectrophotometer.

The electrochemical workstation (CS310M) is connected to an H-type sealed electrolytic cell containing a three electrode system, with 0.1 M Na₂SO₄ as the electrolyte. The blank carbon cloth coated with catalyst material is used as the working electrode (WE), saturated Ag/AgCl as the reference electrode (RE), and the blank carbon cloth as the counter electrode (CE). All potentials were tested using a reversible hydrogen electrode as a reference. The formula is as follows: $E_{\text{RHE}}(\text{V})=E_{\text{Ag/AgCl}}+0.197+0.059 \times \text{pH}$. Before NRR measurement, soak the electrolyte in ultra-high purity N₂ (99.999%) for 30 minutes. Then, use ultra-high purity N₂ to blow the electrode plates throughout the entire electrolysis process.

Weigh 5 mg of synthesized manganese molybdate based catalyst and place it in a 1 mL centrifuge tube. Then, add 10 μL of Nafion solution, 490 μL of ethanol, and 500 μL of deionized water to the centrifuge tube to form a mixed solution. Then, sonicate

the mixed solution for 60 minutes to form a uniform suspension. Next, apply the suspension evenly with a 20 μL pipette to the working area of the treated strip carbon cloth 1 cm x 1 cm. Each time, take 20 μL of the suspension and dry it in a 50 $^{\circ}\text{C}$ oven for 5 minutes. Then, take it out and continue the coating for a total of 5 times (a total of 100 μL , with a catalyst mass of about 0.5 mg). After all coatings are completed, dry in a 50 $^{\circ}\text{C}$ oven for 8 hours to obtain a working electrode that can be used directly.

2. Measurement of ammonia

The concentration of synthetic ammonia in the experiment was determined by the indophenol blue method. Firstly, prepare a chromogenic agent solution, weigh 10 g of salicylic acid and 10 g of sodium citrate dihydrate, and dissolve them in 2 M NaOH solution to obtain chromogenic agent solution A; First prepare 1 M NaOH solution for later use, then measure 3.63 mL of NaClO and add it to a 100 mL volumetric flask. Further add 1 M NaOH solution to obtain reagent solution B; Add 0.2 g of nitroprusside to 20 mL of deionized water to obtain reagent solution C. Then take 2 mL of the tested electrolyte and sequentially add 2 mL of developer A, 1 mL of developer B, and 0.2 mL of developer C. Shake the above mixture well and let it stand at room temperature in the dark for 1 hour. Collect the UV visible absorption spectra of the mixed solution at a wavelength of approximately 653 nm. Using 0.1 M Na_2SO_4 solution as the solvent, different concentrations of $(\text{NH}_4)_2\text{SO}_4$ were added to obtain ammonia nitrogen working solutions of different concentrations. The standard curve for detecting ammonia using indophenol blue method was obtained through fitting: $y = 0.239x + 0.0354$ ($R^2 = 0.999$), and the NH_3 concentration in the unknown sample was calculated. (Fig. S1a and S1b)

Measure each sample at least three times. The NH₃ yield and FE rate are calculated using the following formula:

$$\text{NH}_3 \text{ yield } (\mu\text{g h}^{-1} \text{ mg}^{-1}) = \frac{c_{\text{NH}_3} \times V}{m \times t} \quad (1)$$

$$\text{FE } (\%) = \frac{3 \times F \times c_{\text{NH}_3}}{17 \times Q} \times 100\% \quad (2)$$

Among them, c_{NH_3} ($\mu\text{g mL}^{-1}$) is the measured concentration of NH₃ in aqueous solution, V (mL) is the volume of electrolyte, t (h) is the electroreduction reaction time, m (mg) is the effective weight of the catalyst on the working electrode, F is the Faraday constant (96500 C mol^{-1}), and Q is the applied electricity (C) during the reaction.

3. Determination of by-product hydrazine

Evaluate the concentration of hydrazine in the electrolyte using the Watt Chrisp method. Firstly, add 2.0 g of dimethylaminobenzaldehyde (p-C₉H₁₁NO) and 10 mL of concentrated hydrochloric acid to 100 mL of anhydrous ethanol to prepare the colorimetric reagent. Subsequently, take 5 mL of the tested electrolyte and 5 mL of the colorimetric reagent, shake the mixed solution evenly, and place it in a dark place, away from light, and let it stand for 20 minutes. Record the absorbance at a wavelength of 455 nm using a UV spectrometer. Using 0.1 M Na₂SO₄ as a solvent, different concentrations of hydrazine hydrochloride were added to obtain hydrazine working solutions. Finally, the standard curve for detecting hydrazine by Watt Christian method was obtained through fitting: $y = 0.981x + 0.211$ ($R^2 = 0.999$), estimating the N₂H₄ content produced after electrolysis. (Fig. S1c and S1d)

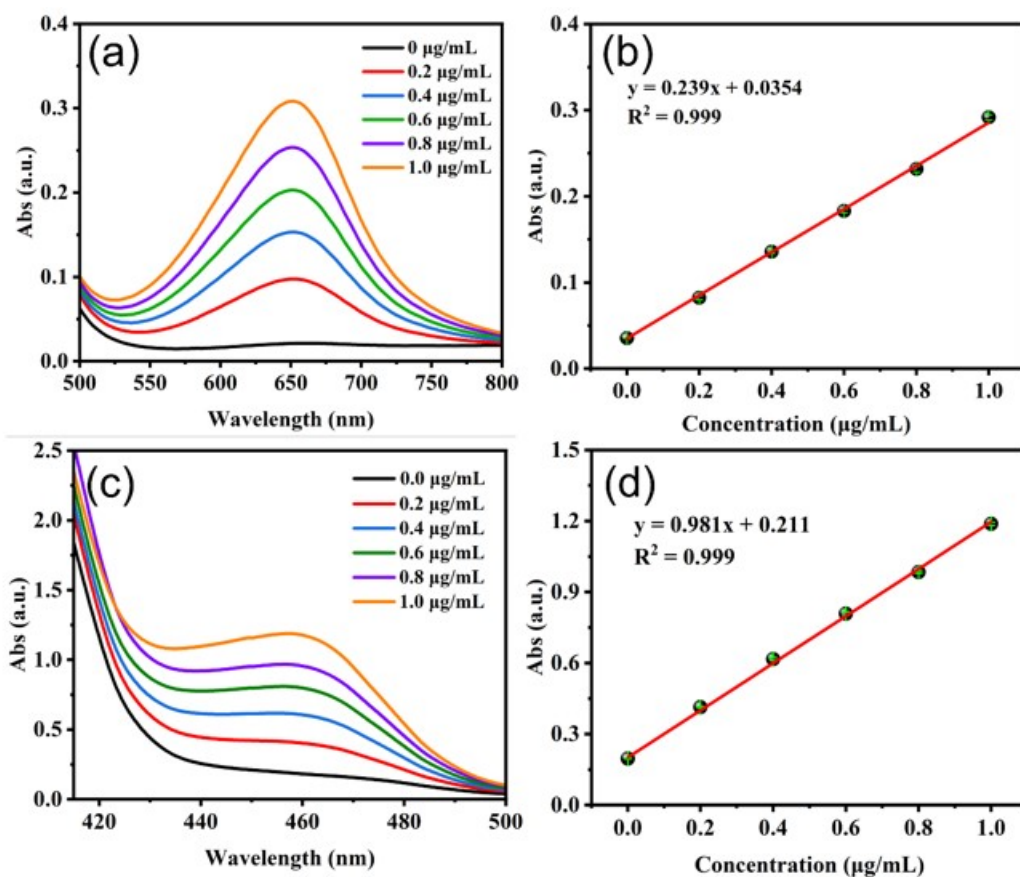


Fig. S1. (a) UV-vis absorption spectra obtained using indophenol blue method at different NH_3 concentrations and (b) fitting curves. (c) Use Watt-Chrisp method to obtain UV-vis absorption spectra and (d) fitting curves at different N_2H_4 concentrations.

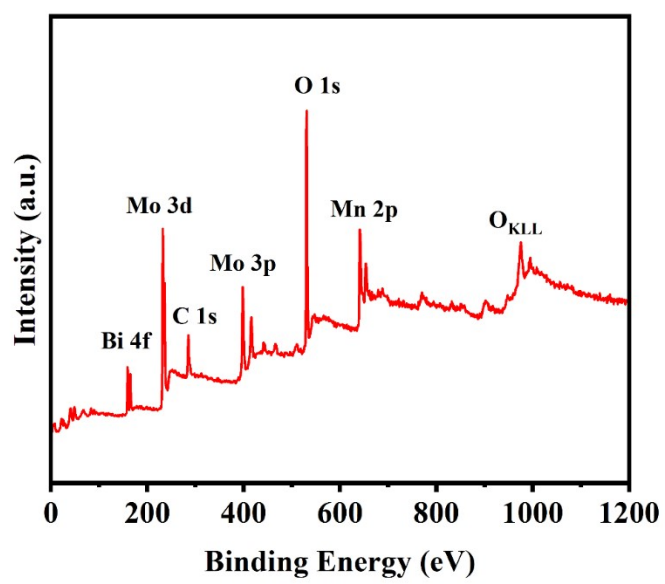


Fig. S2. XPS full spectrum of 6%Bi-MnMoO₄ after electrolysis.

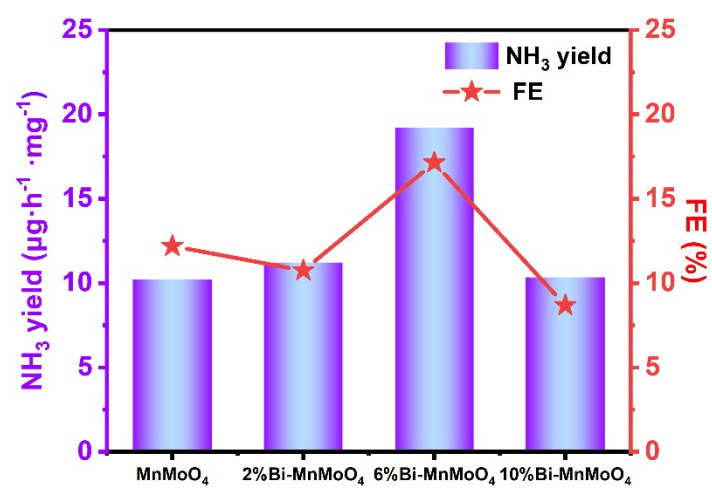


Fig. S3. Comparison of catalytic performance of four samples.

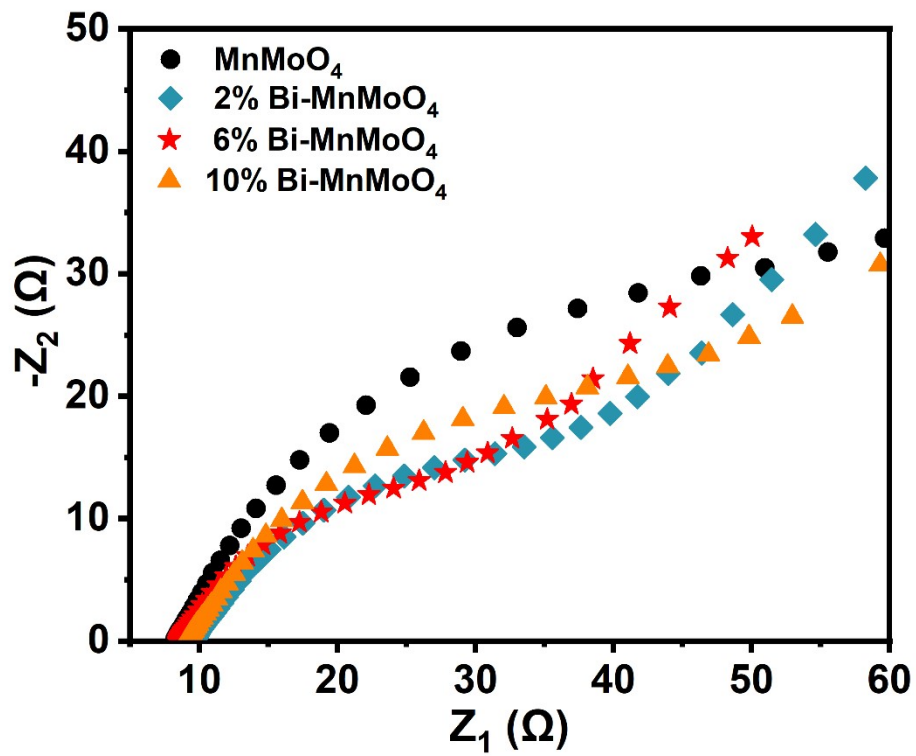


Fig. S4. EIS of MnMoO₄ and Bi-MnMoO₄ samples.

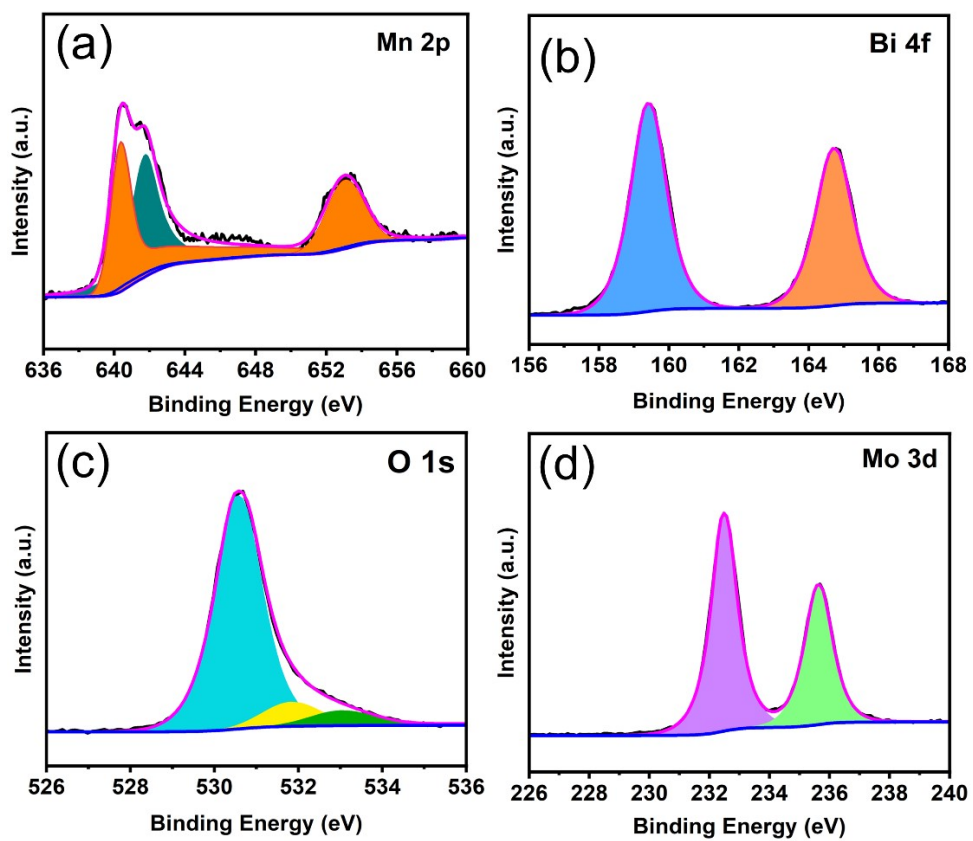


Fig. S5. XRD and XPS spectra of 6%Bi-MnMoO₄ after electrolysis.

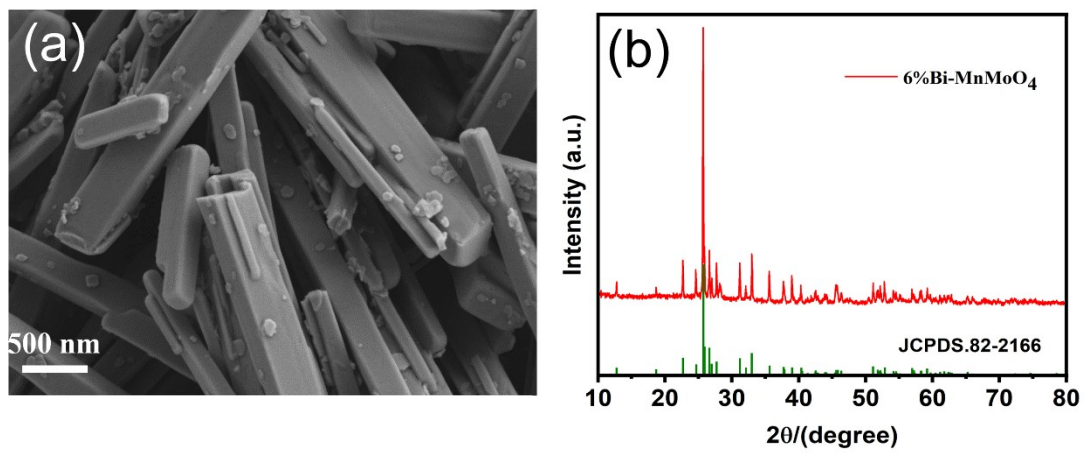


Fig. S6. (a) SEM image and (b) XRD spectra of 6%Bi-MnMoO₄ after electrolysis.