

Supporting information

for

Oxygen vacancy in Bi_2WO_6 enables a robust nitrate reduction reaction catalysis

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Experimental section

Preparation of Bi₂WO₆: First, dissolve 122.5 mg of Bi(NO₃)₃·5H₂O in 10 mL of ultrapure (UP) water, and 83 mg of Na₂WO₄ in 20 mL of UP water. Once both solutions are fully dissolved, mix them together. Adjust the pH to a range of 5-7, transfer the mixture into a 50 mL PTFE-lined container, and heat it hydrothermally at 160 °C for 14 hours. After the reaction, centrifuge using a 50 mL centrifuge tube, and wash the precipitate multiple times with UP water and anhydrous ethanol to obtain Bi₂WO₆.

Preparation of Bi₂O₃: Disperse 0.25 g of Bi(NO₃)₃·5H₂O in 30 mL of UP water. Gradually add 10 mL of 0.5 M NaOH while stirring at 500 rpm for 0.5-2 minutes. Transfer the mixture to a reaction vessel and conduct hydrothermal treatment at 160 °C for 14 hours. After the reaction, collect the product by centrifugation and wash it repeatedly with UP water and anhydrous ethanol to get Bi₂O₃.

Preparation of WO₃: Disperse 0.33 g of Na₂WO₄ in 40 mL of UP water. Slowly add 8 mL of concentrated hydrochloric acid while stirring at 500 rpm for 0.5-2 minutes. Transfer the mixture to a reaction vessel and conduct hydrothermal treatment at 160 °C for 14 hours. After the reaction, collect the product by centrifugation and wash it repeatedly with UP water and anhydrous ethanol to get WO₃.

Material Characterization: The crystal structure and physical phases of the as-prepared electrocatalysts were examined using X-ray diffraction spectroscopy (XRD, D8 Advance) with Cu K α radiation over a range of 5-90°. The morphologies and microstructures were observed using a Field Emission Scanning Electron Microscope

(FE-SEM, FEI, SU8010) and Transmission Electron Microscopy (TEM, FEI Talos F200x G2). X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) with non-monochromatized Al-K α X-ray as the excitation source was employed to determine the surface chemical states and electronic structure. The recorded binding energy was corrected by referencing the C 1s peak at 284.6 eV, and peak fitting was performed using the Shirley background and XPSPEAK41 software.

Electrochemical measurement: The electrochemical performance of all catalyst materials is tested using a Gamry electrochemical workstation under ambient conditions in an H-type electrolytic cell. A pre-treated Nafion 212 membrane is used to separate the anode and cathode chambers. A three-electrode system is used for the tests, with a glassy carbon electrode (d=3 mm) modified with the catalyst material as the working electrode, a carbon rod as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. A 200 ppm KNO₃ and pH=1 H₂SO₄ solution is used as the electrolyte. The performance of the modified electrode for electrocatalytic ammonia synthesis is tested at room temperature. Before the tests, argon is bubbled for half an hour to remove dissolved impurity gases from the electrolyte. Various electrochemical methods such as Linear Sweep Voltammetry (LSV), Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), and Chronoamperometry (CA) are employed to evaluate the catalyst's basic electrochemical performance. LSV tests are conducted in the voltage range of 0.2 to -0.6 V vs. RHE, with a scan rate of 5 mV s⁻¹. CA tests for double-layer capacitance are performed in the voltage range of 0.16 to 0.26 V vs. RHE, with scan rates of 10, 20, ...

100 mV s⁻¹. EIS tests the impedance of the catalyst with an open-circuit voltage of -0.4 V vs. RHE and a frequency range of 10⁵ to 10⁻² Hz. During CA testing, the voltage is set at the value where 10 mA cm⁻² current density is reached during LSV testing, and the duration is set to 2 hours. After the reaction, the product is collected for further concentration determination.

***in-situ* Raman Testing:** To elucidate the reaction mechanism of nitrate reduction to ammonia on Bi₂WO₆, Raman spectra analysis is performed using a WITec alpha-300R instrument with a 532 nm excitation wavelength laser at 9 mW laser intensity, and a spectral scan rate of once every 6 seconds. To minimize testing errors, the exposure time is set to 6 seconds and results are accumulated 5 times. Single crystal silicon is used to calibrate the Raman frequency for each experiment. An electrochemical workstation (Gamry Interface) is used to control the potential. Catalyst ink is dropped onto the glassy carbon electrode as the working electrode, with the sample plane kept perpendicular to the incident laser. Platinum wire and an Ag/AgCl electrode (saturated KCl) are used as the counter and reference electrodes, respectively, with a mixed solution of 0.05 M H₂SO₄ and 200 ppm KNO₃ as the electrolyte.

Table S1 Comparisons of NitrRR performance of Bi₂WO₆ with recently reported electrocatalysts.

Electrocatalyst	Potential (V vs. RHE)	FE (%)	Ref.
Bi ₂ WO ₆	-0.3 V	62%	this work
BiNCs	-0.6 V	66%	[1]
FC	-0.65 V	20%	[2]
MO ₂ CT _x	-0.4 V	41%	[3]
Ni/NCNS	-0.52 V	77.8%	[4]
Co ₃ O ₄ @MoS ₂	-0.64 V	52.7%	[5]
NDC-800	-1.4 V	17.8%	[6]
Cu _{0.43} Ni _{0.57} /NC	-1.3 V	50%	[7]
Fe(20%)@N-C	-1.0	25%	[8]
re-Cu NRs	-1.0 V	44.3%	[9]

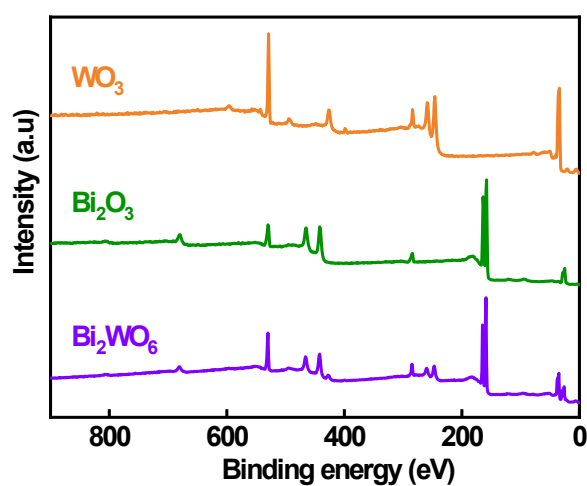


Figure S1 XPS survey scan of Bi₂O₃, WO₃ and Bi₂WO₆.

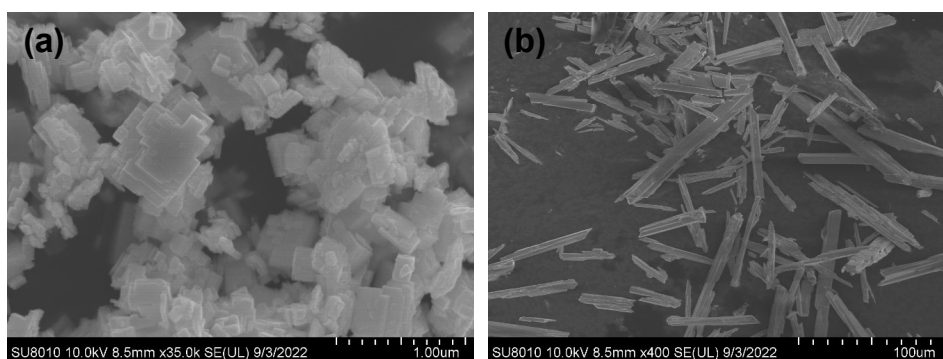


Figure S2 SEM images of WO₃ (a) and Bi₂O₃ (b).

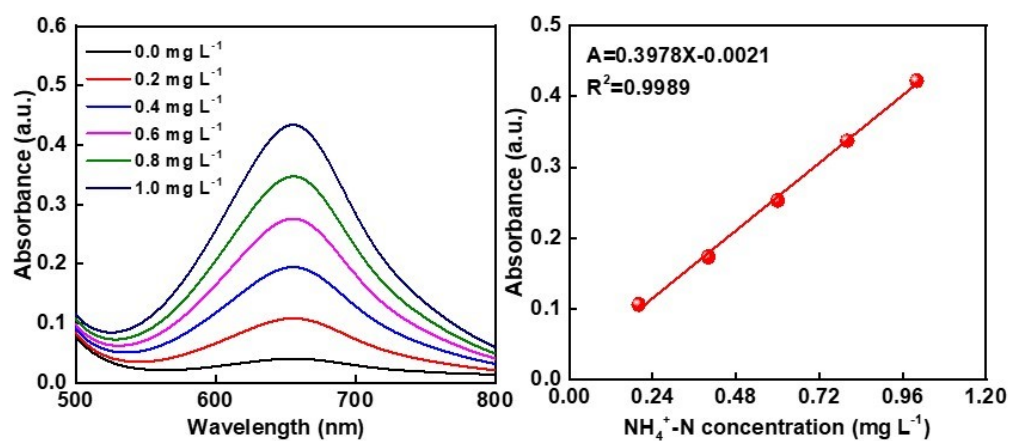


Figure S3 (a) UV-vis spectroscopies of standard NH₄⁺ concentrations. (b) Plots of intensity vs. NH₄⁺ concentration.

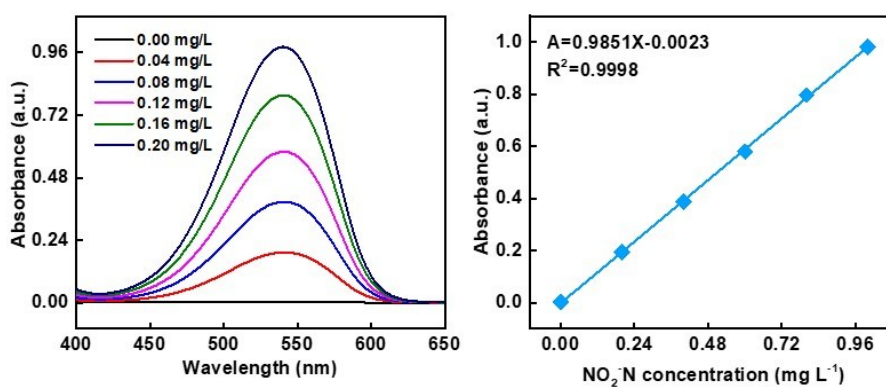


Figure S4 (a) UV-vis spectroscopies of standard NO₂⁻ concentrations. (b) Plots of intensity vs. NO₂⁻ concentration.

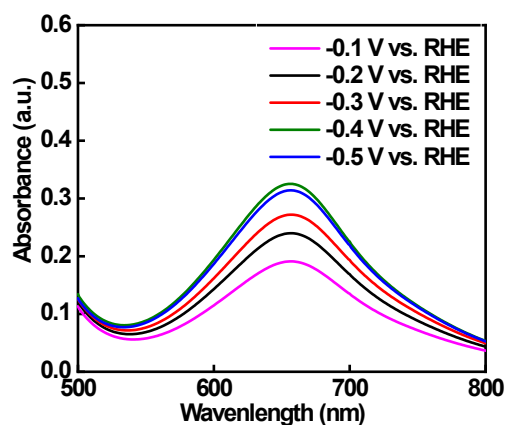


Figure S5 UV-vis spectroscopies from 500-800 nm of electrolytes after 2 h long term electrocatalysis by Bi_2WO_6 under various potentials.

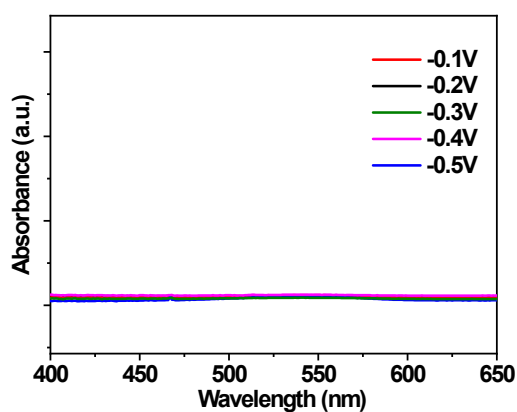


Figure S6 UV-vis spectroscopies from 400-650 nm of electrolytes after 2 h long term electrocatalysis by Bi_2WO_6 under various potentials.

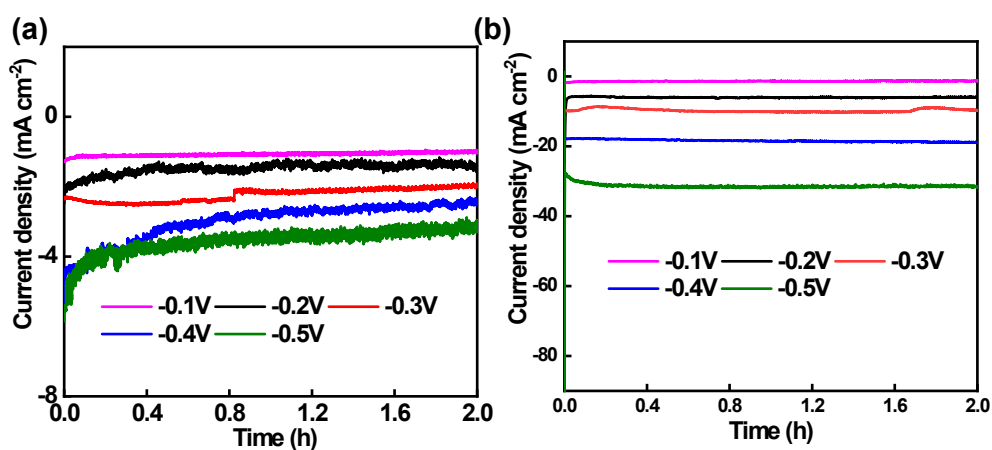


Figure S7 i-t tests of Bi_2O_3 (a) and WO_3 (b).

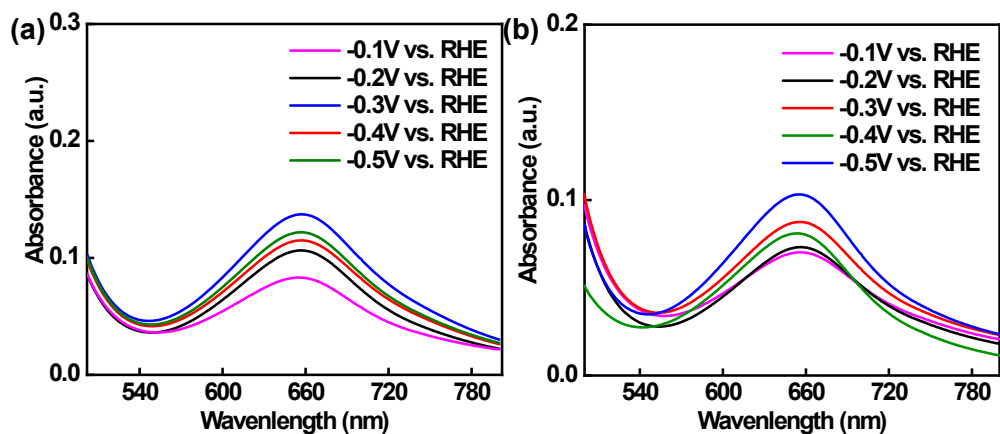


Figure S8 UV-vis spectroscopies of Bi_2O_3 (a) and WO_3 (b) under various potentials.

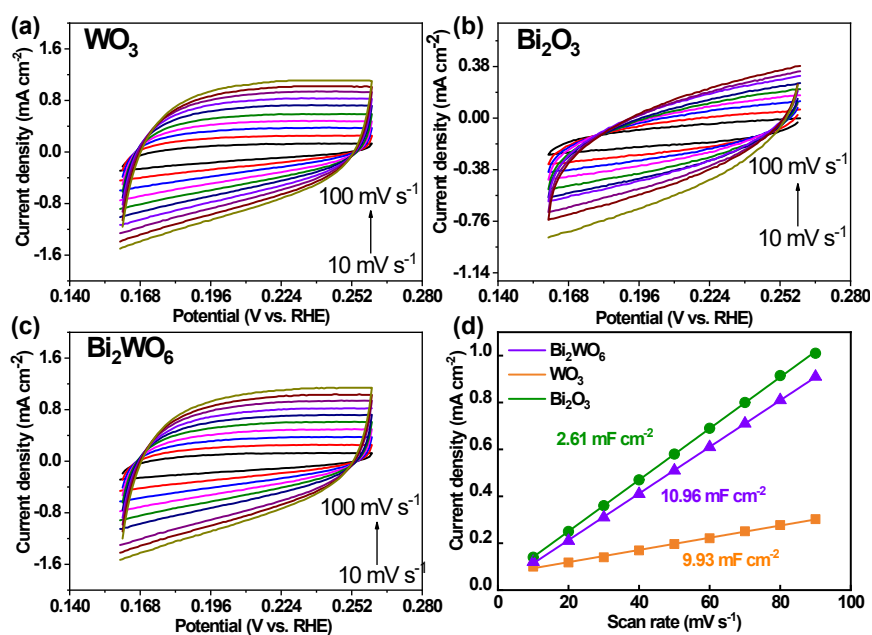


Figure S9 Cyclic voltammetry curves of WO_3 (a), Bi_2O_3 (b) and Bi_2WO_6 (c) at various scan rates. (d) C_{dl} of WO_3 , Bi_2O_3 and Bi_2WO_6 .

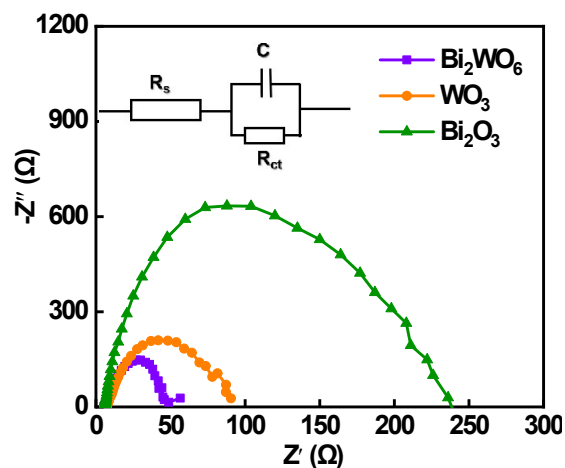


Figure S10 Electrochemical impedance spectroscopies of Bi_2O_3 , WO_3 and Bi_2WO_6 .

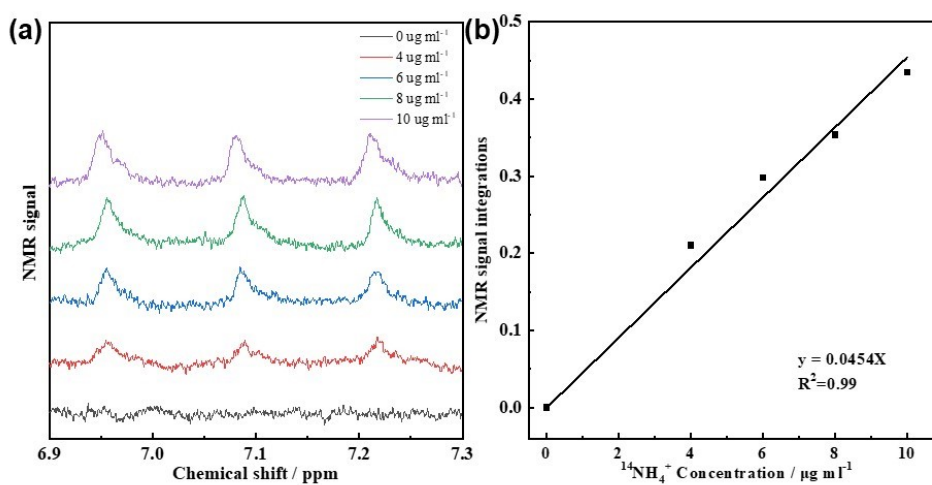


Figure S11 NMR spectra of standard NH_4^+ concentrations. (b) Plots of intensity vs. NH_4^+ concentration.

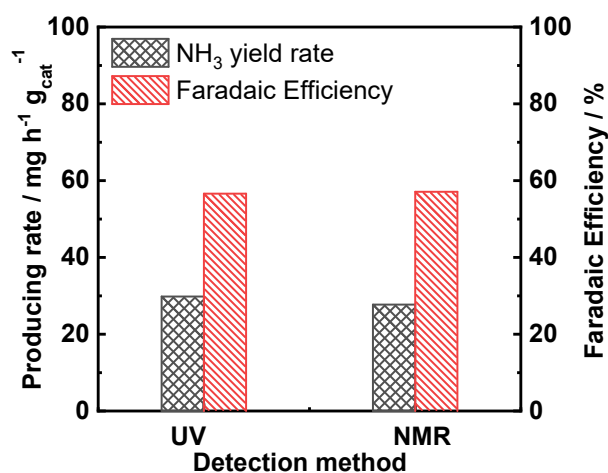


Figure S12 Comparison of ammonia Faradaic efficiency and yielding rate calculated from UV and NMR methods.

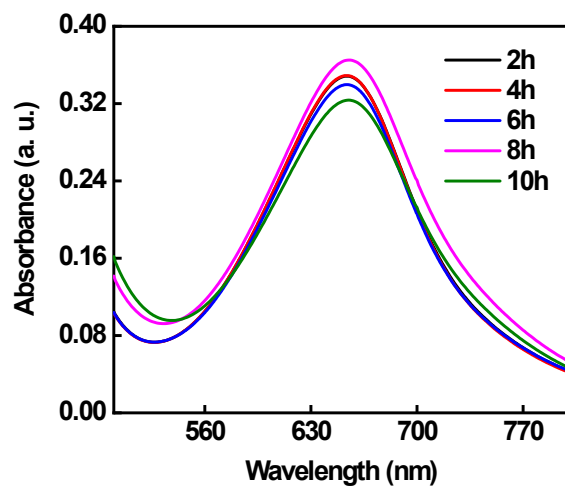


Figure S13 UV-vis spectroscopies of Bi_2WO_6 after long term electrocatalysis.

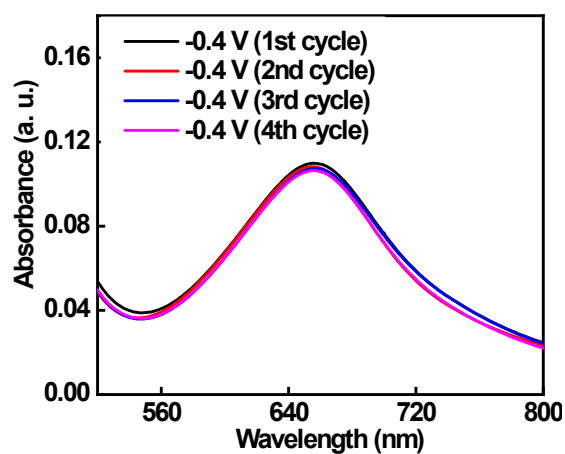


Figure S14 UV-vis spectroscopies of Bi_2WO_6 tested 4 times.

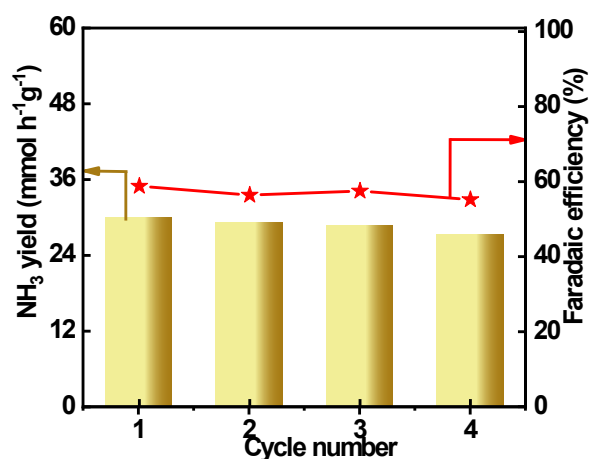


Figure S15 Faradaic efficiency and ammonia yielding rate of Bi_2WO_6 tested 4 times.

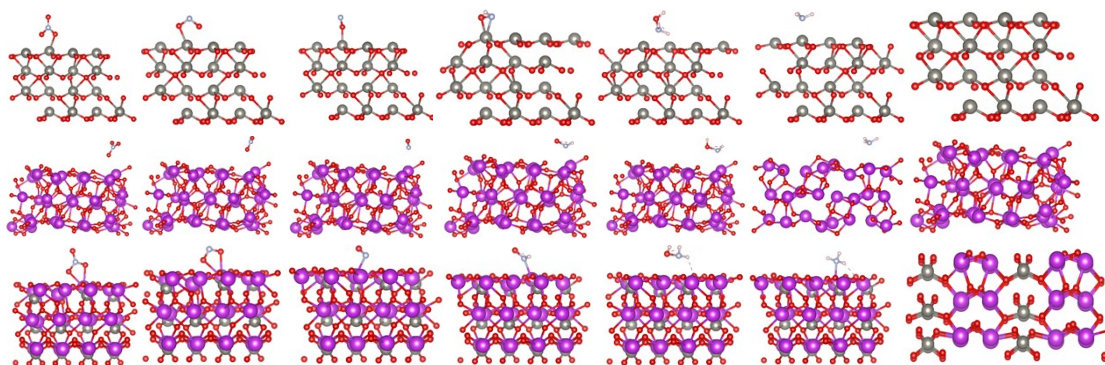


Figure S16 Reaction intermediates on WO_3 , Bi_2O_3 and Bi_2WO_6 .

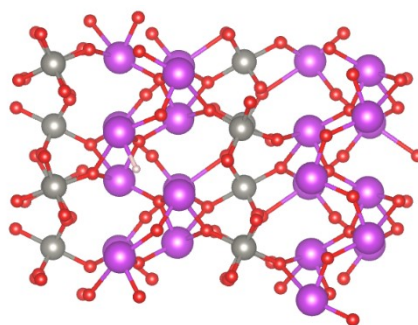


Figure S17 Chemical structure of hydrogen atom on Bi_2WO_6 .

References

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