Supporting Information

Constructing asymmetric active sites on defective Ru/$W_{18}O_{49}$ for photocatalytic nitrogen fixation

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10 pages, 9 figures, 1 table

CONTENTS

1. Characterization

X-ray diffraction (XRD) patterns were recorded with a Rigaku Dmax-3C operated at 40 kV and 30 mA. Transmission electron microscopy (TEM) images and high-resolution transmission electron microscopy (HRTEM) were obtained on the JEOL-2010FEF at 200 kV. Electron paramagnetic resonance (EPR) spectra were recorded on an EMX PLUS spectrometer (Bruker). X-ray photoelectron spectroscopy (XPS) data were obtained on Perkin-Elmer PHI 5000. UV/Vis Diffuse Reflectance Spectra (DRS) were measured using a MC-2530 instrument spectrometer. Raman spectra were obtained by a confocal microprobe spectrometer (Thermo DXR Microscope). Fourier transform infrared spectroscopy (FTIR) spectra were performed using a Nicolet iS10 spectrometer. Photoelectrochemical measurements were performed on CHI660E workstation using three-electrode cell with a photocatalyst samples as working electrode, a Pt foil as counter electrode and a standard Ag/AgCl reference electrode, respectively. The N_2 adsorption performances were charactered by a temperature-programmed desorption instrument (TPD, TriStar II 3020). Photoluminescence (PL) spectra were performed on FLS1000 fluorescence spectrophotometer (Edinburgh Instruments).

2. Photocatalytic nitrogen fixation

The photocatalytic N_2 reduction experiments were performed at ambient conditions. Typically, 0.02g of catalyst was added into 80 mL deionized water. After the formation of a uniform catalyst suspension by ultrasonic treatment, the high-purity nitrogen was bubbled through the suspension to obtain a N_2-saturated environment. A Xe lamp (300 W) was used as simulated solar light source, and the light source was turned on to start the reaction. Conditions: nitrogen was injected into the reaction system at a flow rate of 10 mL/min. The overall reaction time was 4 h, and samples were taken in 1 h. The

concentrations of NH_4^+ were determined by Nessler's reagent method. The quantification of hydrazine (N_2H_4) was measured by the method of Watt and Chrisp.

3. Supplementary figures and text

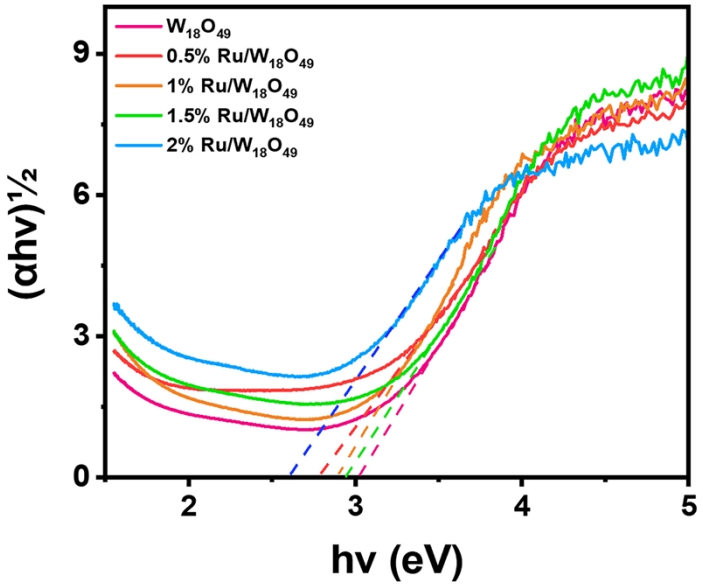

Figure S1. Plots of $(ahv)^{1/2}$ versus photon energy for calculation of bandgap.

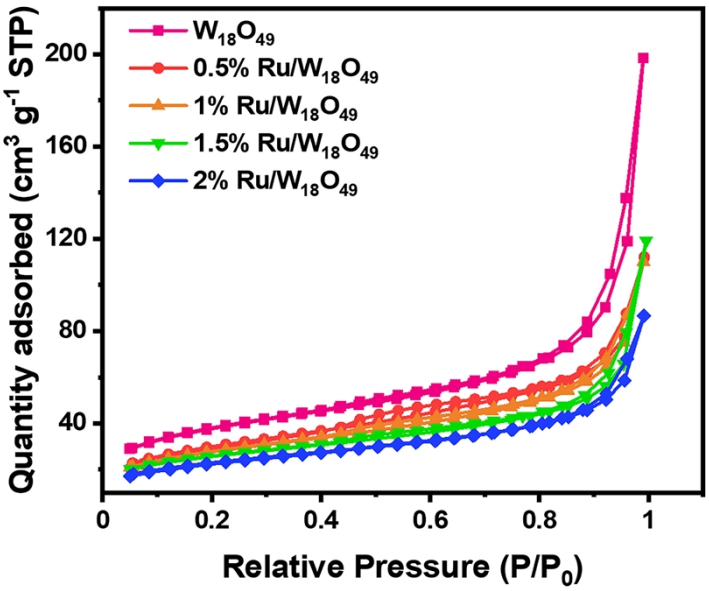

Figure S2. BET of prepared samples.

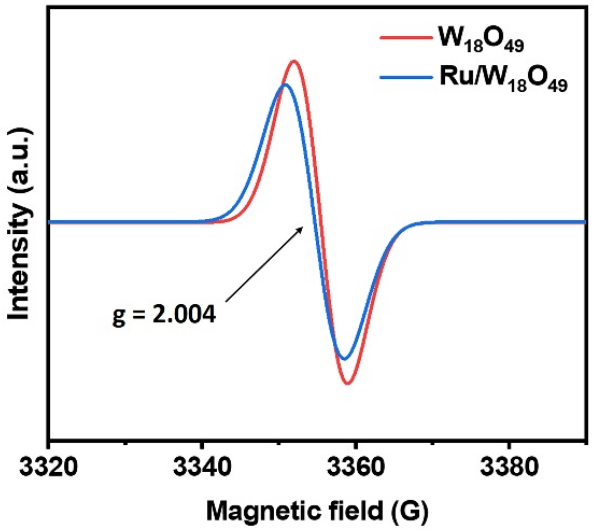

Figure S3. EPR spectra of $W_{18}O_{49}$ and 1.5 % $Ru/W_{18}O_{49}$ at 150 K.

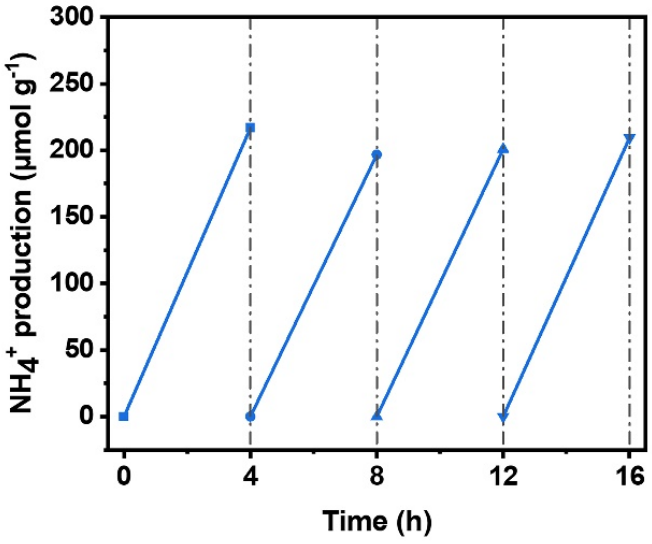

Figure S4. Photocatalytic ammonia production in the cyclic tests of $Ru/W_{18}O_{49}$.

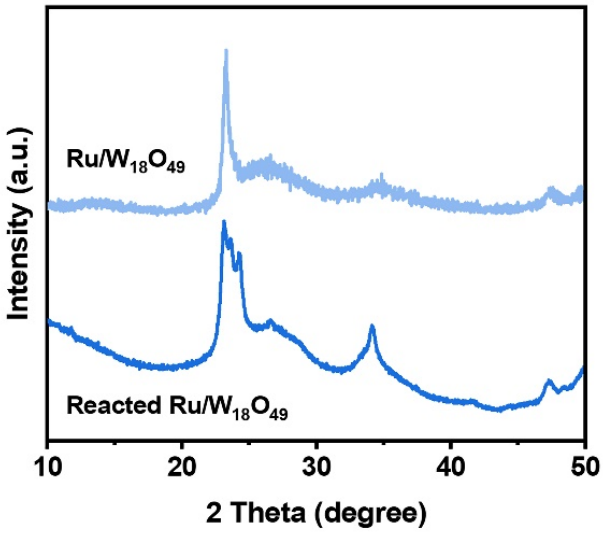

Figure S5. XRD patterns of $Ru/W_{18}O_{49}$ and reacted $Ru/W_{18}O_{49}$.

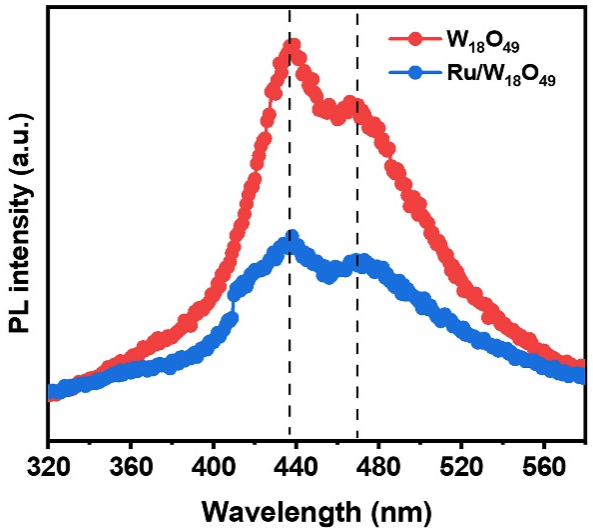

Figure S6. Room-temperature steady-state PL spectra of $W_{18}O_{49}$ and $Ru/W_{18}O_{49}$ with an excitation light of 300 nm.

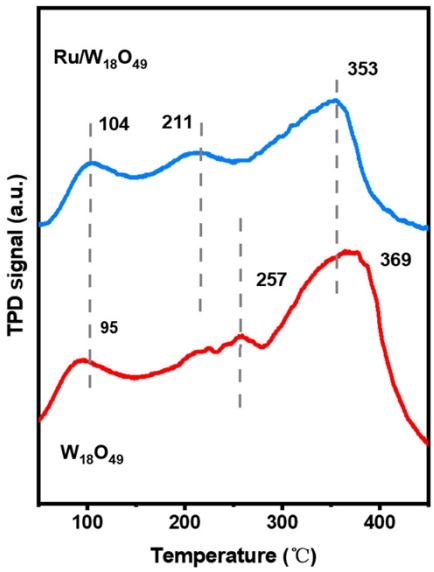

Figure S7. N_2-TPD profiles of $W_{18}O_{49}$ and Ru/$W_{18}O_{49}$.

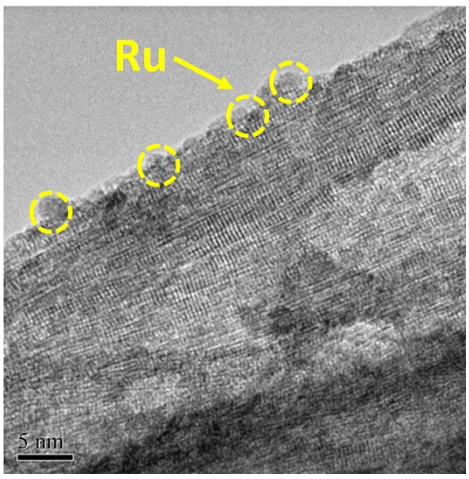

Figure S8. TEM image of 1.5% Ru/WO_3.

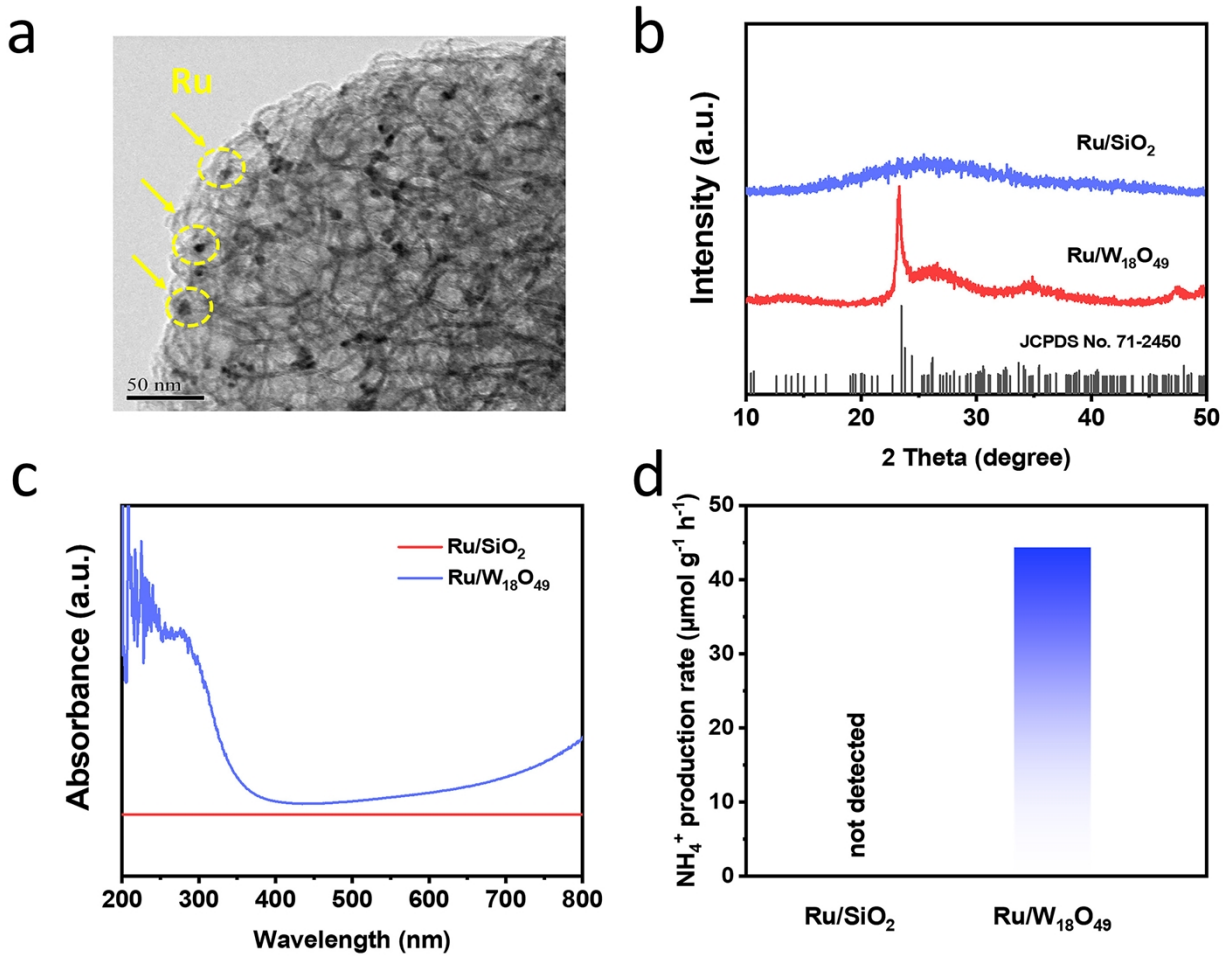

Figure S9. (a) TEM image. (b) XRD patterns. (c) UV/Vis absorption spectra. (d) Photocatalytic ammonia production rate on Ru/SiO_2 (1.5%) and $Ru/W_{18}O_{49}$ (1.5%).

Table S1 BET of samples

Samples	BET (m^2/g)
$W_{18}O_{49}$	129.8
0.5% Ru/$W_{18}O_{49}$	104.3
1.0% Ru/$W_{18}O_{49}$	95.9
1.5% Ru/$W_{18}O_{49}$	87.4
2% Ru/$W_{18}O_{49}$	84.7