Electronic Supporting Information

Oriented Bi₂WO₆ Photocatalyst induced by *In Situ* Bi Reduction towards Efficient Nitrogen Fixation

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1. Experimental

1.1 Synthesis of Bi/Bi₂WO₆ nano-disks.

Or-Bi/Bi₂WO₆ nano-disks were synthesized using a two-step method (micro-emulsion combining with ethylene glycol reduction).

Solution A: Na_2WO_4 was dissolved in 15 ml deionized water to give a WO_4^{2-} solution of 0.0005 M.

Solution B: $Bi(NO_3)_3 \cdot 5 H_2O$ and 1ml concentrated nitric acid was added into 7 ml deionized water to give a Bi^{3+} solution of 0.0005 M.

Firstly, 2ml solution A, 27 ml cyclohexane, 7.5 ml TX-10 (alkylphenol ethoxylates) and 7 ml hexyl alcohol were added into a 250 ml round-bottom flask to form a transparent reverse emulsion system. After continuously string for 10 min, 4 ml solution B was added into the mixture. The resulting mixture was aged at room temperature for 1 h. The precipitates were centrifugal separated and washed by deionized water and alcohol for several times. Finally, together with ethylene glycol (15 mL), the precursor was transferred into a 20 mL Teflon-lined stainless autoclave and reacted at 180 °C for 20 h under the autogenous pressure. The resultant product

was collected and washed by deionized water and alcohol for several times. Other catalyst samples were synthesized by varying the concentration of solution B.

1.2 Synthesis of pure Bi₂WO₆ sample.

Pure Bi₂WO₆ was synthesized by only hydrothermal method.

2 mmol Bi(NO₃)₃·5H₂O was dispersed in 15 mL deionized water by ultrasound. Subsequently, 1 mmol Na₂WO₄ was added into aforementioned solution under vigorous magnetic stirring. An hour later, the resulting precipitates together with 15 ml deionized water was transfered into a 20 mL Teflon-lined stainless steel autoclave to carry out hydrothermal process at 180 °C for 20 h.

1.3 Characterization

X-ray diffraction (XRD) patterns of as-prepared Bi₂WO₆ and Bi/Bi₂WO₆ samples were collected using a Rigaku D/max-2000 diffractometer with Cu-K α radiation (λ = 1.5406 Å). The morphology of the samples was observed by a HELIOS NanoLab 600i field emission field emission scanning electron microscope (FE-SEM). The size, morphology, and microstructure of the samples were investigated by using a FEI Tecnai G2 S-Twin transmission electron microscopy (TEM) with quantitative X-ray spectroscopy (EDX) capabilities. For X-ray photoelectron spectroscopy (XPS), a Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectrometer was used with a pass energy of 20.00 eV and with an Al-K α excitation source (1486.6 eV). Fourier transform infrared (FT-IR) spectra of the samples were measured with a FTIR spectrometer (Shimadzu) in the range of 600–4000 cm⁻¹ in the form of KBr pellets. UV-vis diffuse reflectance data were recorded on a UV–vis spectrophotometer (HITACHI UH4150) in the wavelength range of 200–800 nm, except for a white standard of BaSO₄ was used as a reference at room temperature. The photoluminescence (PL) measurement was performed under the ultraviolet excitation of 240 nm on a Fluoremax-4 fluorescence spectrometer. The Ion-liquid chromatography was carried out on a DIONEX INTEGRION HPIC.

1.4 Electrochemical Measurements

The Mott–Schottky plots, electrochemical impedance spectroscopy and photocurrent measurements were performed on a AUT 86258 electrochemical work station (Metrohm, Switzerland) with a three electrode cell, comprising a platinum foil counter electrode, a saturated Ag/AgCl reference electrode, a photocatalyst-coated ITO as the working electrode, and 0.5 M Na₂SO₄ solution was used as the electrolyte. Specifically, 0.05g as-prepared catalyst sample was dispersed in 500 \Box 1 Alpha-Terpineol to form a solution, and then 0.15 mL of the suspension was dip-coated on the conductive surface of the glass slide. The prepared working electrode was allowed to dry overnight at 140 °C.

1.5 Nitrogen Photofixation Reaction

The N₂ photofixation reaction was performed in a quartz photochemical reactor with water circulation to maintain at 20 °C. 100 ml deionized water containing 0.05g asprepared catalyst sample was carried out about 5 min ultrasonic process. The mixture was then followed by bubbling with a constant high-purity N₂ flow (60 mL·min⁻¹) and magnetic stirring for 30 min in dark to remove dissolved air in the solution and achieve adsorption-desorption equilibrium between photocatalysts and N₂. The light source was produced by a 300 W Xenon lamp (Trusttech PLS-SXE 300, Beijing). The high-purity N₂ was bubbled all the time and 3.0 mL reaction solution (after centrifugation) was taken out and transferred into a tube every 20 min. Ultimately, ammonia products were analysed by the Nessler's reagent method and the absolute calibration was achieved using ammonium sulfate solutions of known concentration as standards. (Fig. S9)



Fig. S1. (a) XRD pattern and (b) SEM image of precursor.



Fig. S2. FITR spectrum of unwashed precursor.

Fig. S2 shows the FITR spectrum of unwashed precursor. The infrared absorption peak of the C-O bond was observed at 1309 cm⁻¹, which originated from the surfactant molecules adsorbed on the surface of precursor. This suggested that during microemulsion step, the precipitation reaction was occurred in the micelles thus can maintain the precursors particles in nanoscale.



Fig. S3. TEM images of precursor.



Fig. S4. (a) XRD pattern and (b) SEM image of Bi_2WO_6 .



Fig. S5. SEM images for Or-Bi/BWO sample.



Fig. S6. TEM images for Or-Bi/BWO nano-disks.



Fig. S7. HRTEM images shows preferred orientation of Or-Bi/BWO nano-disks.



Fig. S8. EDX line scanning profile for Or-Bi/BWO.



Fig. S9. XPS spectra of Or-Bi/BWO and BWO.



Fig. S10. EPR spectra for Or-Bi/BWO sample.



Fig. S11. PL spectra of Or-Bi/BWO and BWO.



Fig. S12. EIS spectra of Or-Bi/BWO and BWO.



Fig. S13. The calibration curve of Nessler's reagent colorimetry (left) and photos of yellow complex obtained during the ammonia synthesis reaction (right).



Fig. S14. ATR-FTIR spectra recorded during the photocatalytic N_2 fixation over Or-

Bi/BWO.



Fig. S15. N_2 adsorption-desorption isotherms of BWO and Or-Bi/BWO samples.



Fig. S16. The comparison for photocatalytic nitrogen fixation performance normalized by the specific surface area of BWO and Or-Bi/BWO samples.



Fig. S17. SEM images for series of catalysts.



Fig. S18. XRD patterns for series of catalysts.



Fig. S19. (a) XRD pattern and (b) SEM image of BWO-MS.



Fig. S20. Time-resolved photo-luminescence (TRPL) decay for the three samples.



Fig. 21. Transient photocurrent responses with constant potential for the three samples.



Fig. S22. Blank experiments under different reaction conditions.



Fig. S23. Band structure schematic of $Or-Bi/Bi_2WO_6$ and possibly occurring reaction

mechanism of nitrogen photofixation on surface.

Catalyst	Sacrificial agent	Wavelength	NH3 yield (μmol·g ⁻¹ ·h ⁻¹)	Ref.
Ultrathin TiO ₂ nanosheets	None	UV–vis	78.9	<i>Adv. Mater.</i> 2019, 1806482.
Defect-rich SUC Bi ₃ O ₄ Br	None	-	50.8	<i>Adv. Mater.</i> 2019, 1807576.
Bi ₂ MoO ₆ /OV- BiOBr	None	Full spectra	90.7	Nanoscale, 2019, 11 10439-10445.
Au/P25	None	UV-vis/Vsible	430/140	Nanoscale, 2019, 11, 10072–10079
c-PAN- decorated Bi ₂ WO ₆	None	Ful spectra	140	ACS Sustainable Chem. Eng. 2018, 6, 11190–11195
Ag-δ-Bi ₂ O ₃	None	\geq 400 nm	1.7	<i>J. colloid Interface</i> <i>Sci.</i> , 2019, 533: 649-657.
Au/TiO ₂ -OV	CH₃OH	\ge 420 nm	78.6	J. Am. Chem. Soc. 2018, 140, 8497–8508
BiO	None	Full spectra	72.5 (PH=3.8)	J. Mater. Chem. A, 2017, 5, 201–209
Or-Bi/Bi ₂ WO ₆	None	Full spectra	86	This work

Table 1. Nitrogen Photofixation performance for other reported nanomaterials.