Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers. This journal is © the Partner Organisations 2019

Supporting Information

Plasma Treated Bi₂WO₆ Ultrathin Nanosheets with Oxygen Vacancies for Improved Photocatalytic CO₂ reduction

Qidi Li,^a Xingwang Zhu,^a Jinman Yang,^a Qing Yu,^a Xianglin Zhu,^a Jinyu Chu,^{*,a}

Yansheng Du, *,a Chongtai Wang,^b Yingjie Hua,^b Huaming Li,^a Hui Xu*,a

^a School of the Environment and Safety Engineering, Institute for Energy Research,

Jiangsu University, Zhenjiang, Jiangsu 212013, People's Republic of China

^b School of Chemistry and Chemical Engineering, the Key Laboratory of Electrochemical Energy Storage and Energy Conversion of Hainan Province, Hainan

Normal University, Haikou, Hainan 571158, People's Republic of China

*E-mail: jychu@ujs.edu.cn (J. Chu)

*E-mail: <u>duys@ujs.edu.cn</u> (Y. Du)

*E-mail: <u>xh@ujs.edu.cn</u> (H. Xu)

Synthesis of Bi₂WO₆ ultrathin nanosheets

All chemicals were of analytical grade and used without any further purification. The Bi₂WO₆ ultrathin nanosheets was prepared by one-pot hydrothermal method. Typically experiment, 1 mmol Na₂WO₄·2H₂O, and 2 mmol Bi(NO₃)₃·5H₂O and 0.1 g Hexadecyl trimethyl ammonium Bromide (CTAB) were added in 80 ml deionized water. After 40 min stirring, the mixed solution was poured into a 100 ml Teflon-lined autoclave. Then the autoclave was then transferred to an oven and treated at 120 °C for 24 hours. Finally, the product was collected and washed several times with deionized water and absolute ethanol, then lyophilized to obtain Bi₂WO₆ ultrathin nanosheets (Bi₂WO₆).

Synthesis of Oxygen-vacancy Bi₂WO₆ ultrathin nanosheets

The as-prepared Bi₂WO₆ ultrathin nanosheets (50 mg) have been put into a quartz reactor, and a dielectric barrier discharge (DBD) plasma was used to treat the Bi₂WO₆ powder. Before the discharge, the quartz reactor was vacuumed and then Ar gas was introduced as the reaction gas to maintain the air flow rate of 300 mL min⁻¹. Afterwards, the DBD-plasma was initiated under 100W input power at room temperature. After treating for 15 min, the resulting products were denoted as Oxygen-vacancy Bi₂WO₆ ultrathin nanosheets (Vo-Bi₂WO₆).

Characterization of the photocatalysts

The phases structures of the as-prepared photocatalysts were characterized by a powder X-ray diffraction (XRD) using a Shimadzu XRD-6000 diffractometer with Cu K α (λ = 1.5418 Å) as source in the range of 2 θ =10~80° at a scan rate of

0.1167°s⁻¹.The field emission scanning electron microscopy (FE-SEM, JEOL-JSM-7001F, Japan) operating at an acceleration voltage of 10 kV and transmission electron microscopy operating at 200 kV were conducted to get the morphology of as-prepared photocatalysts. The thickness of the catalysts was detected by Atomic force microscopy (AFM, FM-Nanoview 6800). X-ray photoelectron spectroscopy (XPS) of the photocatalyst was obtained by using an ESCALab MKII spectrometer with 20 kV of MgKa radiation. Ultraviolet-visible (UV-vis) diffuse reflectance spectra (DRS) was employed to measure the optical properties of the as-prepared photocatalysts by using a UVvis spectrophotometer (Shimadzu UV-2450, Japan). Photoluminescence (PL) spectroscopy was investigated using a QuantaMaster & TimeMaster Spectrofluorometer. The electron paramagnetic resonance (EPR) was performed on a Bruker model ESR JES-FA200 spectrometer at a temperature of 77 K. The electrochemical measurements were carried out on an electrochemical workstation (CHI660B, Chenhua Instrument Company, Shanghai, China) using a three-electrode system. In situ FTIR spectra were obtained by using a Thermo Scientific Nicolet iS50. The specific surface area (SSA) and the pore size distribution (PSD) were determined by Micromeritics Instrument, respectively.

Photoelectrochemical test

Photocurrent and electrochemical impedance spectroscopy (EIS) measurements of samples were carried out on an electrochemical workstation (CHI660B, Chenhua Instrument Company, Shanghai, China) using a three-electrode system. In this system, a saturated calomel electrode (SCE) was used as the reference electrode and the platinum wire was the counter electrode, and the electrolyte solution was a 0.2 M Na₂SO₄ solution. Preparation of working electrode: 5 mg of photocatalyst powder was dispersed in 1 ml of ethanol solution, and then 20 μ L of the suspension was coated on 10 mm × 5 mm indium–tin oxide (ITO) glass and dried at 60 °C for 12 hours to remove Ethanol. A 300 W Xe lamp (PLS-SXE3, PerfectLight, Beijing) is used as the light source. There is no voltage applied between the electrodes, and the measurement is performed at room temperature.

Photocatalytic CO₂ reduction evaluation

Photocatalytic CO₂ reduction was performed on a photoreaction system (Labsolar-6A, PerfectLight, Beijing). 10 mg powder catalyst was dissolved under ultrasound for 10 min in the prepared solution including 4 mL of deionized water, 2 mL of TEOA, and 6 mL of MeCN in a 300 mL reactor with a quartz glass cover. After air in the reaction system was cleared away, high-purity CO₂ was introduced into the system until the pressure reached 70 KPa and circulated for 60 min to achieve uniform distribution of CO₂ gas. The temperature of photocatalytic CO₂ reduction was set at 10 °C by the cooling water circulation system which can promote the adsorption of CO₂. A 300 W Xe lamp (PLS-SXE3, PerfectLight, Beijing) was employed as the light source and light intensity is 258.05 mW/cm². A gas chromatograph (GC2002, KeChuang, Shanghai) equipped with thermal conductivity detector (TCD) and hydrogen flame ionized detector (FID) with a capillary column was used to determine the amount of the gas product.

DFT calculation details

DFT calculations were conducted using the Vienna ab initio simulation package (VASP), the projector augmented wave (PAW) potentials are used as pseudopotentials to describe the interactions between valence electrons and ions. The Perdew-Burke-Ernzerhof (PBE) functional of generalized gradient approximation (GGA) was used to describe the exchange-correlation of valence electrons. For density of states, two modes were calculated: Bi_2WO_6 and V_0 - Bi_2WO_6 . The plane wave cutoff energy as set to be 520 eV, and the k-point mesh was set as a $3 \times 3 \times 1$. The convergence threshold was set 1×10^{-4} eV in total energy and 0.05 eV Å⁻¹ in force on each atom. In the Bi_2WO_6 calculation, a $2 \times 1 \times 1$ supercell was created and a 10 Å vacuum layer was added to avoid inter-layer interaction. For the V_0 - Bi_2WO_6 simulation, one O atom was removed from each superlattice and all other parameters remained unchanged.



Fig. S1 XRD of Bi₂WO₆ and V₀-Bi₂WO₆.



Fig. S2 SEM of Bi₂WO₆.



Fig. S3 Nitrogen adsorption-desorption isotherms and the corresponding pore size distribution curves (inset) of (a) Bi₂WO₆ and (b) V₀-Bi₂WO₆.



Fig. S4 XPS survey spectra of (a) Bi_2WO_6 and (b) V_0 - Bi_2WO_6 .

Table S1. Comparison of the performances with other catalysts for

Light source	Catalyst	Reaction medium	Products	Activity	Reference
300 W Xe lamp	Bi2WO6	Liquid-solid, water and TEOA	CO	40.6 µmol g ⁻¹ h ⁻¹	This Work
visible light $(\lambda > 400 \text{ nm})$	BiOBr	Liquid-solid, water	СО	87.4 μmol g ⁻¹ h ⁻¹	[¹]
300 W Xe lamp	Bi12O17Cl2	Liquid-solid, water	СО	48.6 µmol g ⁻¹ h ⁻¹	[²]
300 W Xe lamp	Bi ₂ O ₂ (OH) (NO ₃)-Br	Gas-solid, water	СО	8.12 μmol g ⁻¹ h ⁻¹	[³]
300 W Xe lamp	BiOIO ₃	Gas-solid, water	СО	5.42 μ mol g ⁻¹ h ⁻¹	[⁴]
300 W Xe lamp	Bi ₃ O ₄ Br	Liquid-solid, water	СО	107.1 µmol g ⁻¹ h ⁻¹	[⁵]

photocatalytic CO₂ reduction



Fig. S5 wavelength dependence of quantum efficiency for V_O -Bi₂WO₆.



Fig. S6 XRD patterns of V_{O} -Bi₂WO₆ before and after the photocatalytic

CO₂ reduction reaction.



Fig. S7 schematic band structure of Bi_2WO_6 and V_0 - Bi_2WO_6 .



Fig. S8 band structure of (a) Bi_2WO_6 and (b) V_0 - Bi_2WO_6 .

References

- J. Wu, X. Li, W. Shi, P. Ling, Y. Sun, X. Jiao, S. Gao, L. Liang, J. Xu, W. Yan, C. Wang and Y. Xie, *Angew. Chem. Int. Ed.*, 2018, 57, 8719-8723.
- J. Di, C. Zhu, M. Ji, M. Duan, R. Long, C. Yan, K. Gu, J. Xiong, Y. She, J. Xia, H. Li and Z. Liu, *Angew. Chem. Int. Ed.*, 2018, 57, 14847-14851.
- 3. Y. Zhao, Y. Zhao, R. Shi, B. Wang, G. I. N. Waterhouse, L. Z. Wu, C. H. Tung and T. Zhang, *Adv. Mater.*, 2019, **31**, e1806482.
- 4. F. Chen, H. Huang, L. Ye, T. Zhang, Y. Zhang, X. Han and T. Ma, *Adv. Funct. Mater.*, 2018, **28**.
- J. Di, C. Chen, S. Z. Yang, S. Chen, M. Duan, J. Xiong, C. Zhu, R. Long, W. Hao, Z. Chi, H. Chen, Y. X. Weng, J. Xia, L. Song, S. Li, H. Li and Z. Liu, *Nat. Commun.*, 2019, 10, 2840.