

## Supporting Information

### Construction of 2D@0D InVO<sub>4</sub>@MnWO<sub>4</sub> S-scheme for Efficient

### Photocatalytic Reduction CO<sub>2</sub> to CO

*Wenzhuo Xiang<sup>a</sup>, Guoyu Xu<sup>a</sup>, Lujiang Xiao<sup>a</sup>, Zizhong Zhang<sup>a</sup>, Tao Ji<sup>b</sup>, Wenyue Su<sup>a,\*</sup>*

<sup>a</sup>State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry,

Fuzhou University, Fuzhou 350116, China.

<sup>b</sup> College of Civil Engineering, Fuzhou University, Fuzhou 350116, China.

\* Corresponding author. E-mail: suweny@fzu.edu.cn.

## Contents list

### Experimental Section

**Fig. S1** XRD patterns  $\text{MnWO}_4$ ,  $\text{InVO}_4$ , and a%  $\text{InVO}_4@ \text{MnWO}_4$  composites.

**Fig. S2** XPS spectra of samples: (a) survey spectra, (b) In 3d, (c) Mn 2p

**Fig. S3** XRD patterns of  $\text{InVO}_4@ \text{MnWO}_4$  composite before and after activity cycling test.

**Fig. S4** The AQE wavelength-dependence of  $\text{InVO}_4@ \text{MnWO}_4$  for the photocatalytic  $\text{CO}_2$  reduction.

**Fig. S5** (a) UV-vis DRS spectra of samples, (b) Tauc plots of  $\text{MnWO}_4$  and  $\text{InVO}_4$ .

**Fig. S6** TEM images of  $\text{InVO}_4@ \text{MnWO}_4$  photodeposited with Pt (a, b) nanoparticles and  $\text{PbO}_2$  (c, d) nanoparticles.

**Fig. S7** SEM images of  $\text{InVO}_4@ \text{MnWO}_4$  (a) before reaction, (b) after reaction.

**Fig. S8** XPS survey spectrum of (a)  $\text{InVO}_4@ \text{MnWO}_4$  before and after cycling tests; the high resolution XPS spectra of (b) V 2p, (c) W 4f, (d) O 1s, (e) In 3d and (f) Mn 2p.

**Table S1.** The W content in a%  $\text{InVO}_4@ \text{MnWO}_4$  composites.

**Table S2.** Photocatalytic  $\text{CO}_2$  reduction performance data of  $\text{InVO}_4$ -based photocatalysts.

**Table S3.** The physical adsorption capacity of samples.

**Table S4.** Exponential function fitted parameters of the TRPL decay spectra for  $\text{MnWO}_4$ ,  $\text{InVO}_4$  and  $\text{InVO}_4@ \text{MnWO}_4$  composite.

### Reference

## Experimental Section

### Characterization

Powder X-ray diffraction (XRD) patterns are obtained using a Bruker D8 Advance diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 0.15406$  nm) and a  $0.02^\circ$  step size. UV-vis diffuse reflectance spectra (DRS) are measured on a Varian Cary 5000 spectrophotometer, using BaSO<sub>4</sub> as a reference. A Hitachi SU 8010 FE-SEM observes sample morphology and size. Samples for SEM are ultrasonically dispersed in deionized water, dropped onto a conductive silicon wafer, dried, and coated with gold to enhance conductivity. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images are captured with a FEI TECNAI G2F20 instrument. TEM samples are prepared by dispersing in ethanol, and dropping 3-5 droplets of the supernatant onto a TEM microgrid membrane to dry. SEM and TEM are conducted at 5 kV and 200 kV, respectively. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) are performed using a Thermo ESCALAB-250 spectrometer, calibrated with 284.8 eV contaminated carbon as the standard. Low temperature N<sub>2</sub> and CO<sub>2</sub> adsorption isotherms are measured using Micromeritics ASAP 2020. Room temperature photoluminescence (PL) spectra and transient PL lifetime are measured on an Edinburgh Instrument FLS-980 spectrophotometer at 480 and 357 nm excitation wavelengths. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is performed on an Avio 200 instrument. Electron paramagnetic resonance (EPR) data are collected using a Bruker A300 spectrometer. Work functions (WF) are determined with a Kelvin probe (SKP5050, KP Technology Ltd.) using an Au-coated silicon cantilever ( $WF_{Au} = 5.1$  eV).

The transmission path of photogenerated charges in the prepared sample are explored by photoinduced redox probe experiment. Typically, using methanol and NaIO<sub>3</sub> as hole and electron sacrificial reagents, 1 wt.% Pt and 5 wt.% PbO<sub>2</sub> are photodeposited on InVO<sub>4</sub>@MnWO<sub>4</sub> with H<sub>2</sub>PtCl<sub>6</sub> and Pb(NO<sub>3</sub>)<sub>2</sub> as precursors, respectively.

### Electrochemical measurement

PEC measurement is performed using a PAR VMP3 workstation. To prepare PEC samples, 10 mg of powder is dispersed in 450  $\mu\text{L}$  DMF and 50  $\mu\text{L}$  Nafion with ultrasonic dispersion. Then, 20  $\mu\text{L}$  of this suspension is dropped onto a 0.28  $\text{cm}^2$  area on an FTO sheet and left to dry. The FTO with the sample acts as the working electrode, with Pt wire and Ag/AgCl serving as the counter and reference electrodes, respectively. Electrochemical impedance spectroscopy (EIS) is measured using a CHI-660E workstation over a frequency range of 0.1 to 100,000 Hz in a 0.5 M KCl solution containing 0.01 M  $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$  (1:1). linear sweep voltammetry (LSV) curves for OER are obtained in 0.5 M KOH (pH = 13.69) at a scan rate of 10  $\text{mV s}^{-1}$ . The photocurrent measurement is recorded in 0.2 M  $\text{Na}_2\text{SO}_4$  (pH = 6.8) using a 300 W Xe lamp with a UV-CUT filter ( $\lambda \geq 400 \text{ nm}$ ).

#### **Photocatalytic $\text{H}_2\text{O}$ oxidation half-reaction Test:**

The photocatalytic  $\text{H}_2\text{O}$  oxidation half-reaction is carried out in a Pyrex top-irradiation reaction vessel connected to a glass closed gas system by dispersing 50 mg of photocatalysts powder into 100 mL ultrapure water contained 0.01 M  $\text{AgNO}_3$  as the sacrificial agent and 0.2 g  $\text{La}_2\text{O}_3$  as a pH buffer agent under the irradiation of a 300 W Xe lamp with an ultraviolet cutoff filter ( $\lambda > 400 \text{ nm}$ ). The reactor is sealed and evacuated several times to eliminate the air before irradiation.

#### **Photocatalytic $\text{CO}_2$ reduction half-reaction Test:**

The photocatalytic  $\text{CO}_2$  reduction half-reaction is carried out in a cylindrical glass reactor (volume,  $\sim 100 \text{ mL}$ ) by dispersing 10 mg of photocatalysts powder into 10 mL acetonitrile contained 0.5 mL triethanolamine (TEOA) as sacrificial agent under the irradiation of a 300 W Xe lamp with an ultraviolet cutoff filter ( $\lambda > 400 \text{ nm}$ ). The reaction vessel is sealed and filled with  $\text{CO}_2$  before irradiation.

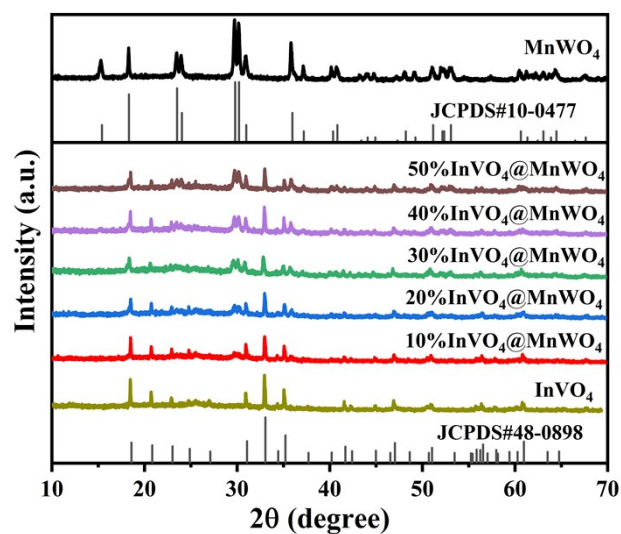


Fig. S1 XRD patterns  $\text{MnWO}_4$ ,  $\text{InVO}_4$ , and a%  $\text{InVO}_4@ \text{MnWO}_4$  composites.

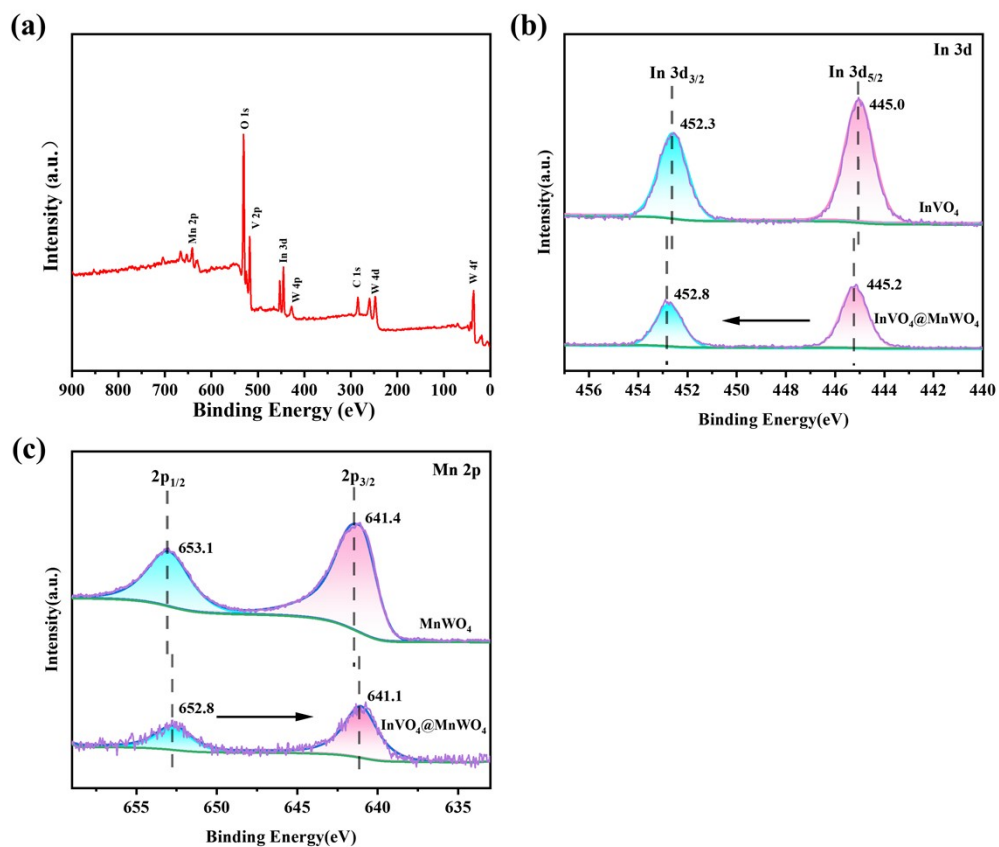


Fig. S2 XPS spectra of samples: (a) survey spectra, (b) In 3d, (c) Mn 2p.

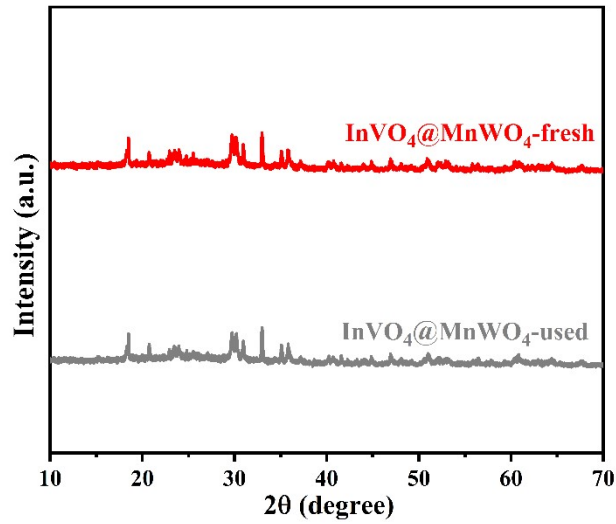


Fig. S3 XRD patterns of InVO<sub>4</sub>@MnWO<sub>4</sub> composite before and after activity cycling test.

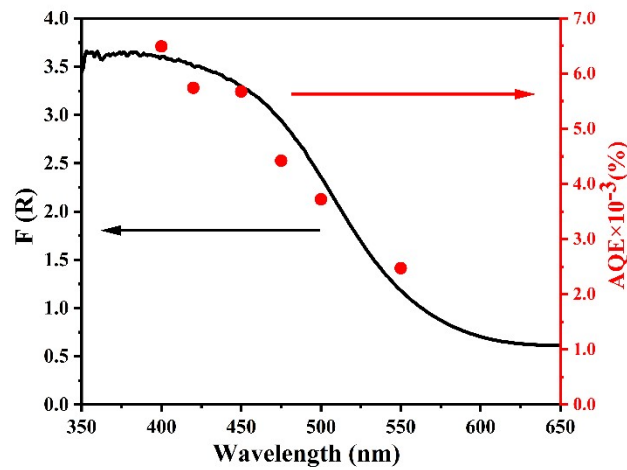


Fig. S4 The AQE wavelength-dependence of InVO<sub>4</sub>@MnWO<sub>4</sub> for the photocatalytic CO<sub>2</sub> reduction.

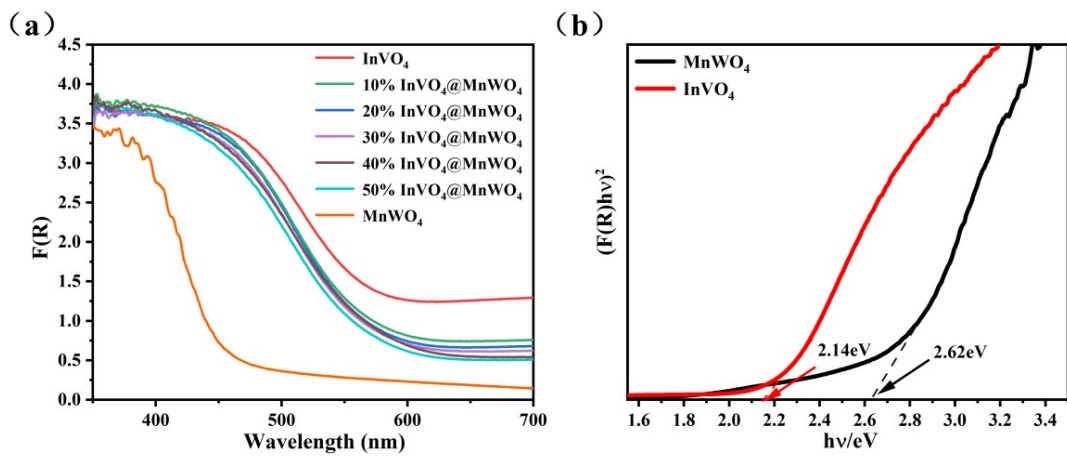
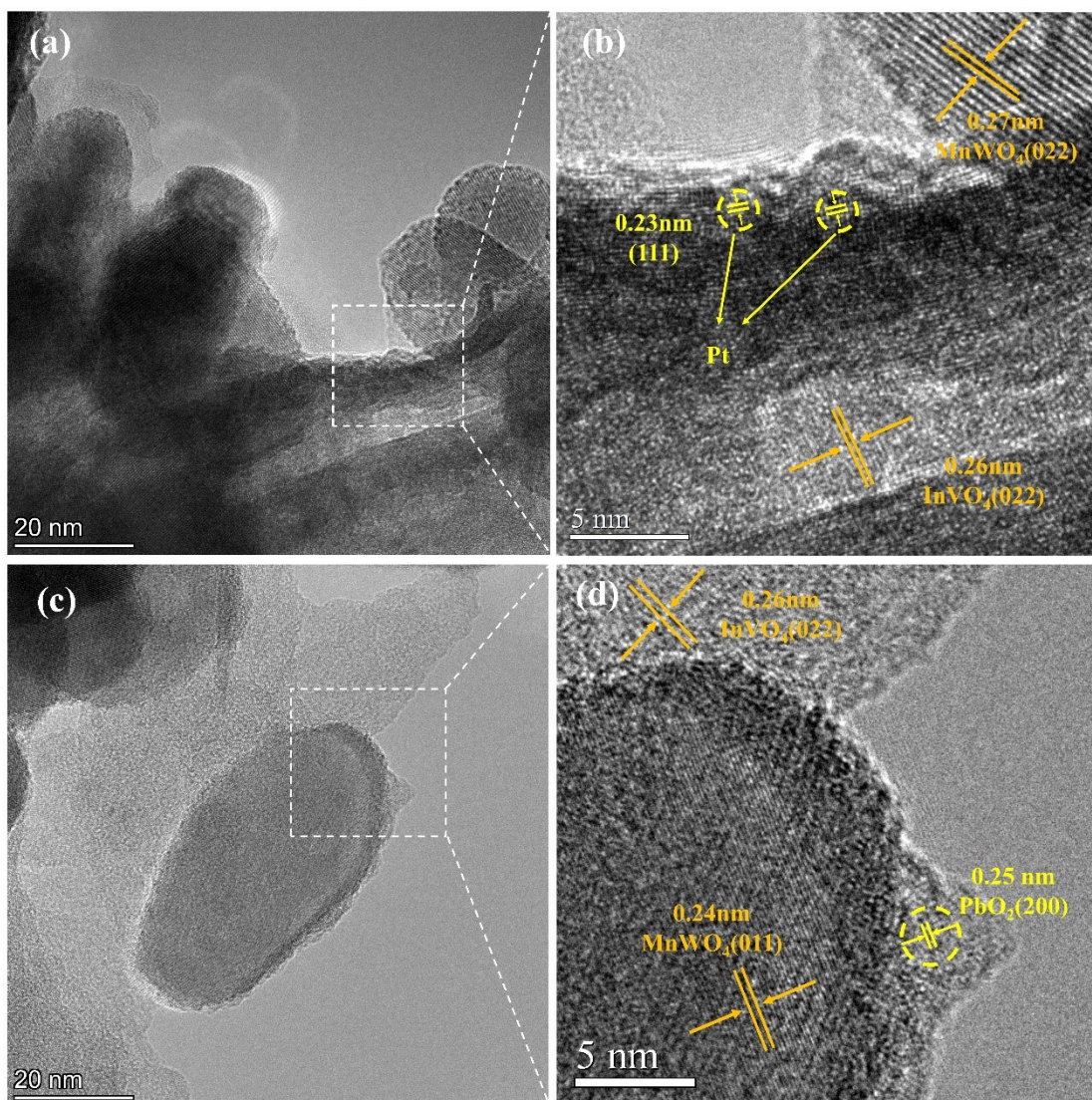


Fig. S5 (a) UV-vis DRS spectra of samples, (b) Tauc plots of MnWO<sub>4</sub> and InVO<sub>4</sub>.



**Fig. S6** TEM images of  $\text{InVO}_4@ \text{MnWO}_4$  photodeposited with Pt (a, b) nanoparticles and  $\text{PbO}_2$  (c, d) nanoparticles.

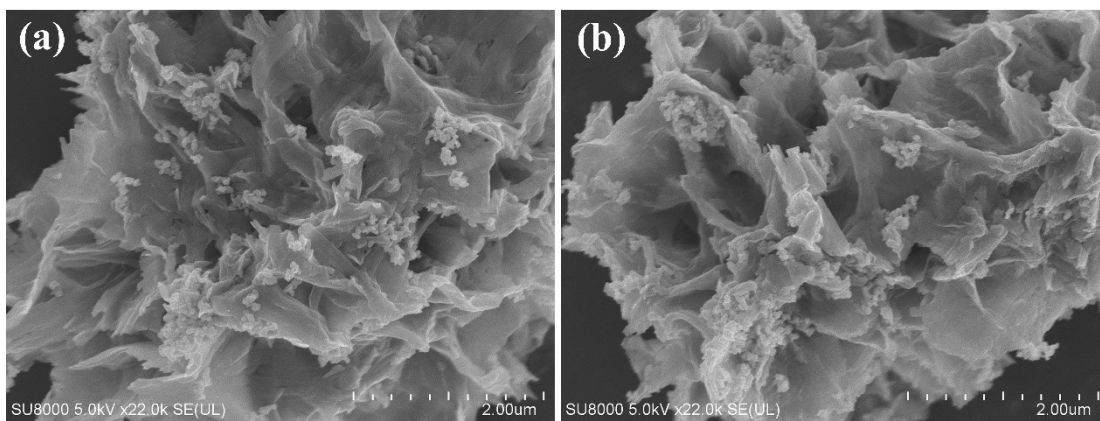


Fig. S7 SEM images of InVO<sub>4</sub>@MnWO<sub>4</sub> (a) before reaction, (b) after reaction.

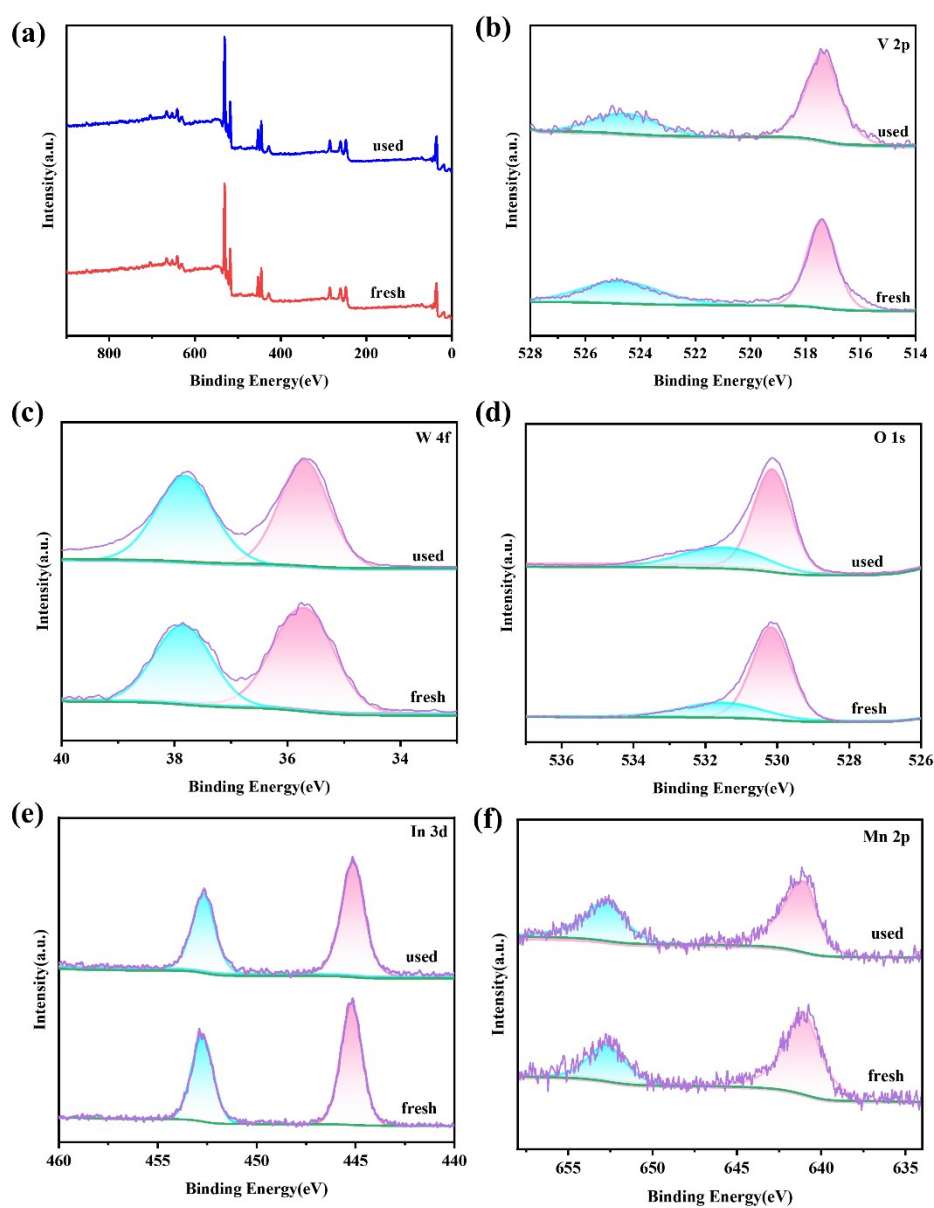


Fig. S8 XPS survey spectrum of (a) InVO<sub>4</sub>@MnWO<sub>4</sub> before and after cycling tests; the high resolution XPS spectra of (b) V 2p, (c) W 4f, (d) O 1s, (e) In 3d and (f) Mn 2p.



**Table S1.** The W content in a% InVO<sub>4</sub>@MnWO<sub>4</sub> composites.

Samples	W content (wt %)	
	Added value	Measured value
10%InVO <sub>4</sub> @MnWO <sub>4</sub>	6.07	5.14
20%InVO <sub>4</sub> @MnWO <sub>4</sub>	12.14	11.42
30%InVO <sub>4</sub> @MnWO <sub>4</sub>	18.21	17.63
40%InVO <sub>4</sub> @MnWO <sub>4</sub>	24.28	23.87
50%InVO <sub>4</sub> @MnWO <sub>4</sub>	30.35	29.94

**Table S2.** Photocatalytic CO<sub>2</sub> reduction performance data of InVO<sub>4</sub>-based photocatalysts.

Photocatalyst	CH <sub>4</sub> evolution (μmol g <sup>-1</sup> h <sup>-1</sup> )	CO evolution (μmol g <sup>-1</sup> h <sup>-1</sup> )	AQE (λ=400nm)	Reference
InVO <sub>4</sub> @MnWO <sub>4</sub>	-	6.20	0.0065%	This work
Bi <sub>2</sub> WO <sub>6</sub> /InVO <sub>4</sub>	1.13	17.97	-	1
InVO <sub>4</sub> /β-AgVO <sub>3</sub>	1.62	12.61	0.49%	2
p-C <sub>3</sub> N <sub>4</sub> /InVO <sub>4</sub>	1.88	14.05	-	3
InVO <sub>4</sub> /Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	0.09	13.83	0.0041%	4
InVO <sub>4</sub> /La <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>	-	11.7	0.002%	5

**Table S3.** The physical adsorption capacity of samples.

Samples	S <sub>BET</sub> (m <sup>2</sup> /g)	Q <sub>CO<sub>2</sub></sub> (cm <sup>3</sup> /g)	Q <sub>CO<sub>2</sub></sub> /S <sub>BET</sub> (cm <sup>3</sup> /m <sup>2</sup> )
InVO <sub>4</sub>	15.6	4.6	0.29
MnWO <sub>4</sub>	20.3	6.5	0.32
InVO <sub>4</sub> @MnWO <sub>4</sub>	16.9	5.6	0.33

**Table S4.** Exponential function fitted parameters of the TRPL decay spectra for MnWO<sub>4</sub>, InVO<sub>4</sub> and InVO<sub>4</sub>@MnWO<sub>4</sub> composite.

Samples	τ <sub>1</sub>		τ <sub>2</sub>		τ <sub>a</sub>
	value (ns)	A <sub>1</sub> %	value (ns)	A <sub>2</sub> %	value (ns)
InVO <sub>4</sub>	0.09	98.12	3.02	1.88	0.13
MnWO <sub>4</sub>	0.12	99.23	3.24	0.77	0.16
InVO <sub>4</sub> @MnWO <sub>4</sub>	0.26	97.78	3.38	2.22	0.36

For TRPL, the decay curves can be well fitted by the following biexponential equations:

$$I(t) = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$

The average carrier life of the each sample can be calculated by the following formula <sup>6</sup>:

$$\tau_a = (A_1 \tau_1^2 + A_2 \tau_2^2) / (A_1 \tau_1 + A_2 \tau_2)$$

where the  $I_0$  represents the baseline correction value,  $A_1$  and  $A_2$  are the pre-exponential factors, and  $\tau_1$ ,  $\tau_2$  and  $\tau$  represent the lifetime (ns) in different processes and average lifetime.

## Reference

1. J. Li, W. Feng, Z. Xiu, X. Han, Direct Z-scheme charge transfer of Bi<sub>2</sub>WO<sub>6</sub>/InVO<sub>4</sub> interface for efficient photocatalytic CO<sub>2</sub> reduction, *Chem. Eng. J.*, 2022, 446, 137129.
2. J. Yang, J. Hao, S. Xu, Q. Wang, J. Dai, A. Zhang, X. Pang, InVO<sub>4</sub>/β-AgVO<sub>3</sub> Nanocomposites as a Direct Z-Scheme Photocatalyst toward Efficient and Selective Visible-Light-Driven CO<sub>2</sub> Reduction, *ACS Appl. Mater. Interfaces*, 2019, 11, 32025–32037.
3. L. Wang, D. Chen, S. Miao, F. Chen, C. Guo, P. Ye, J. Ning, Y. Zhong, Y. Hu, Nitric acid-assisted growth of InVO<sub>4</sub> nanobelts on protonated ultrathin C<sub>3</sub>N<sub>4</sub> nanosheets as an S-scheme photocatalyst with tunable oxygen vacancies for boosting CO<sub>2</sub> conversion, *Chem. Eng. J.*, 2022, 434, 133867.
4. L. Li, Y. Yang, L. Yang, X. Wang, Y. Zhou, Z. Zou, 3D Hydrangea-like InVO<sub>4</sub>/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> Hierarchical Heterosystem Collaborating with 2D/2D Interface Interaction for Enhanced Photocatalytic CO<sub>2</sub> Reduction, *ChemNanoMat*, 2021, 7, 815–823.
5. L. Xiao, L. Lin, J. Song, Z. Zhang, X. Wang, W. Su, Construction of a direct Z-scheme InVO<sub>4</sub>/La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> photocatalyst toward efficient and selective CO<sub>2</sub> reduction to CO, *J. Alloys Compd.*, 2023, 935, 168086.
6. L. Yuan, Y. Li, Z. Tang, J. Gong, Y. Xu, Defect-Promoted Visible Light-Driven C-C Coupling Reactions Pairing with CO<sub>2</sub> Reduction, *J. Catal.*, 2020, 390, 244-250.