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Supporting information

Surface electron modulation of plasmonic semiconductor for enhanced CO_2 photoreduction

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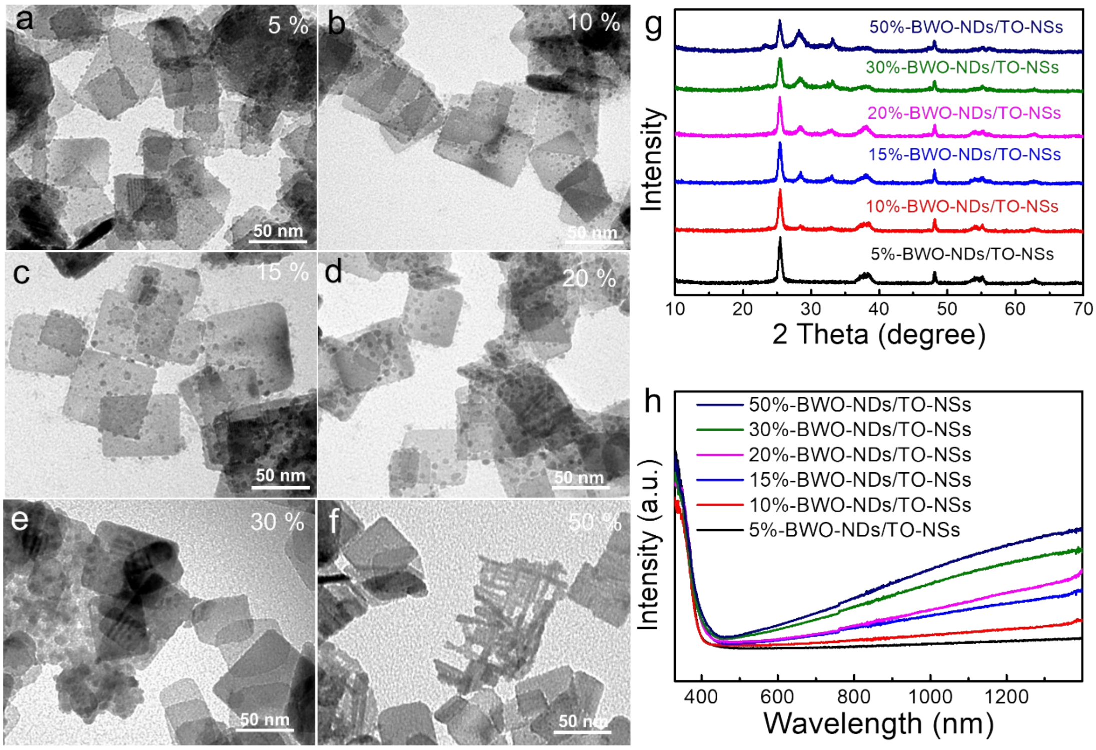

Fig. S1. TEM images of plasmonic heterostructure BWO-NDs/TO-NSs with different amount of Bi_2WO_6: 5 (a), 10 (b), 15 (c), 20 (d), 30 (e) and 50% (f), respectively. Their XRD patterns (g) and UV-vis-NIR DRS (h).

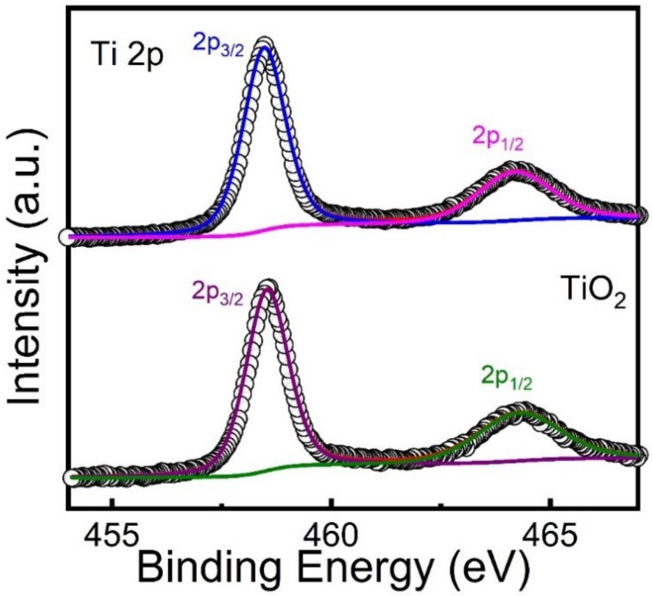

Fig. S2. Ti 2p XPS spectra on TiO_2 before and after light irradiation.

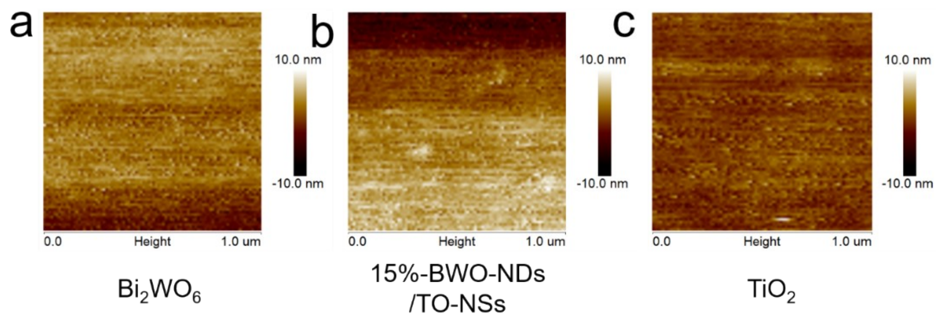

Fig. S3. The AFM images of plasmonic Bi_2WO_6 films, 15%-BWO-NDs/TO-NSs film and TiO_2 films.

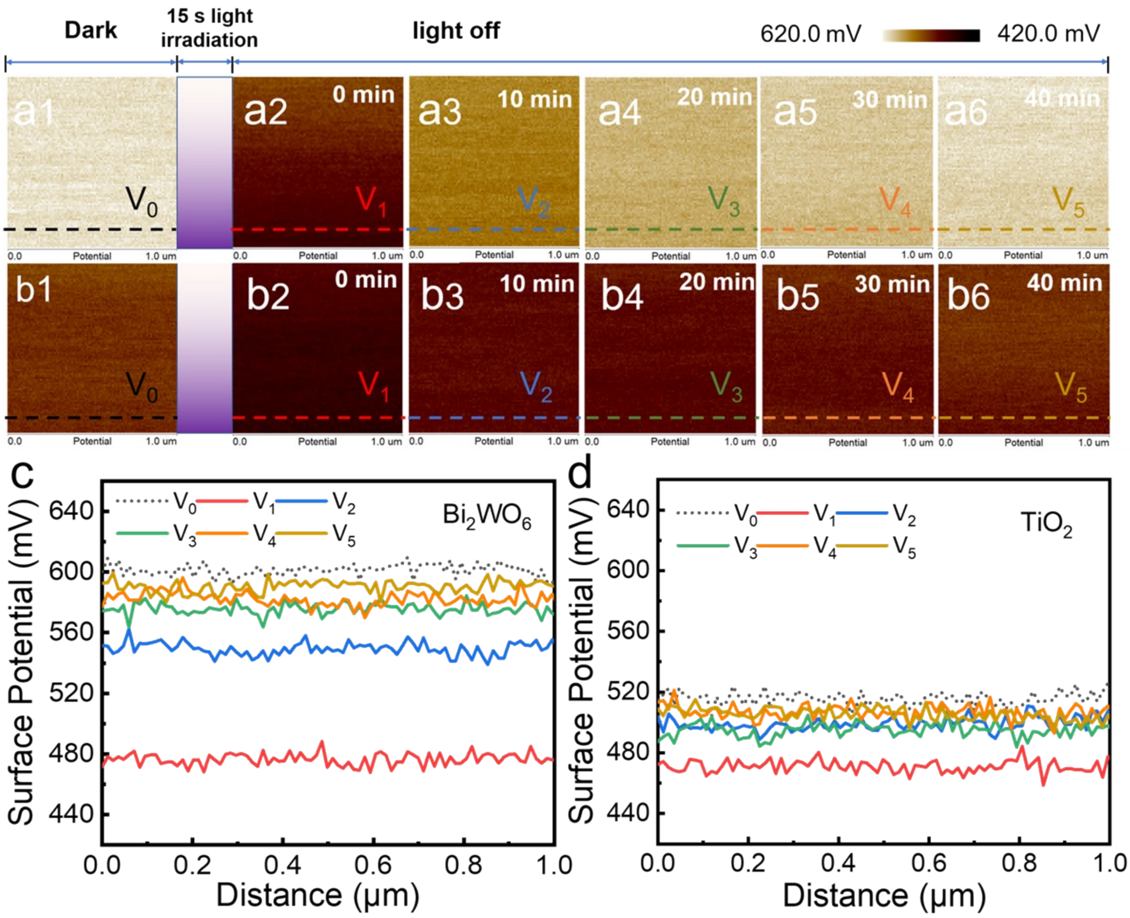

Fig. S4. The surface potential images of Bi_2WO_6 before and after 15 s light irradiation with time (a1-a6), The surface potential images of TiO_2 before and after 15 s light irradiation with time (b1-b6), Surface potentials (c,d) along the lines marked in (a,b).

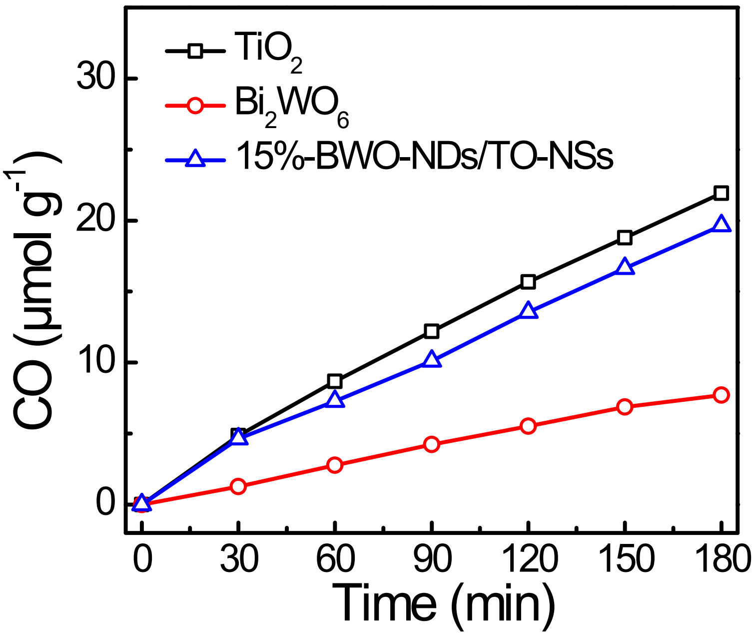

Fig. S5. CO generation over TiO_2, Bi_2WO_6, and 15%-BWO-NDs/TO-NSs as photocatalysts during CO_2-RR, respectively, under UV-visible light irradiation.

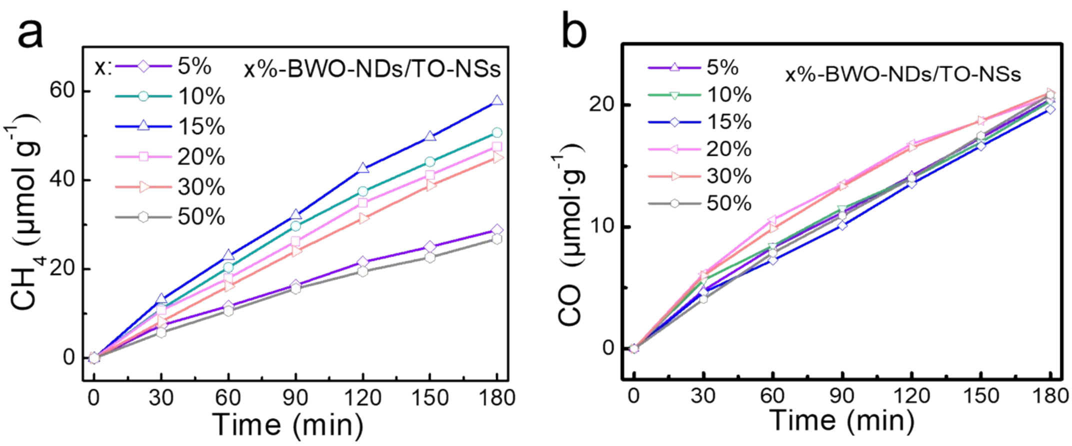

Fig. S6. CH_4 (a) and CO (b) generation over BWO-NDs/TO-NSs hybrids with 5, 10, 15, 20, 30 and 50 wt% Bi_2WO_6 in composition, respectively. Light source, 300 W Xenon lamp, light density of 200 mW cm^{-2}.

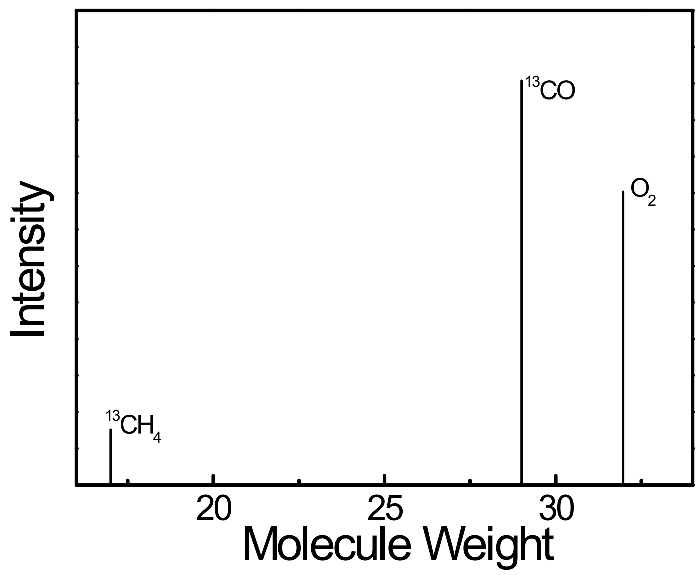

Fig. S7. Mass spectrometry (MS) spectra of products during CO_2-RR by using ^{13}C-isotope labeled $^{13}CO_2$ as reactants.

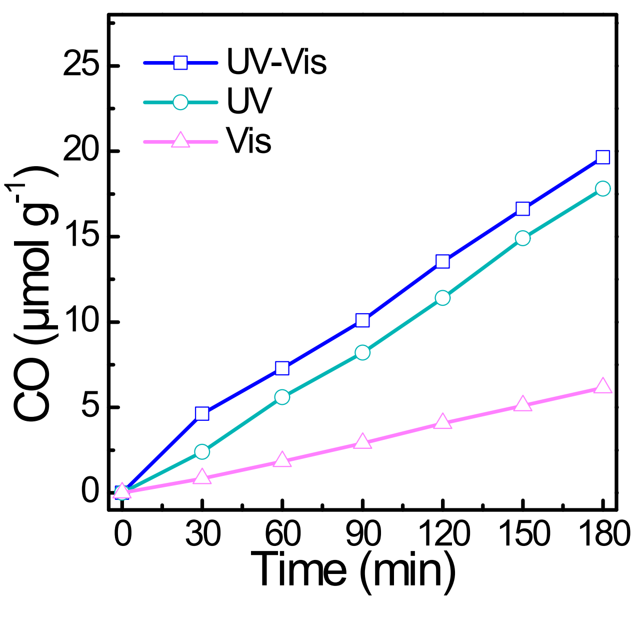

Fig. S8. CO generation rates over 15%-BWO-NDs/TO-NSs under visible (Vis, >420 nm), UV and UV-visible (UV-Vis) light irradiation, respectively.

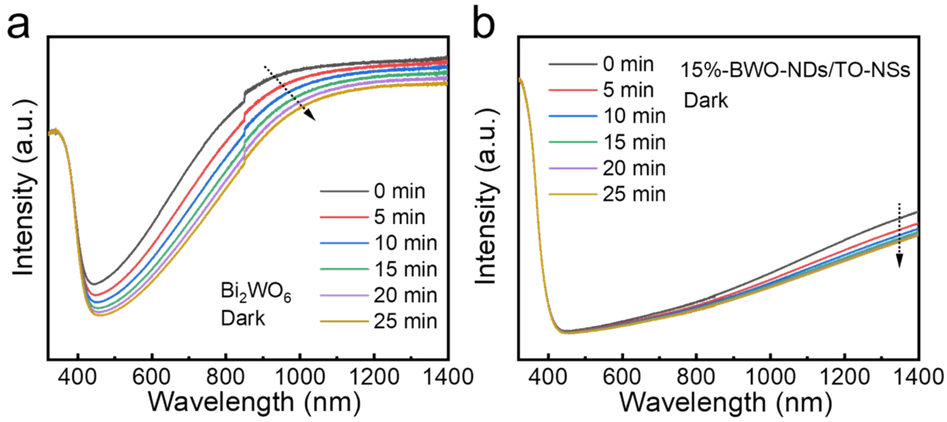

Fig. S9. UV-vis-NIR DRS changes of plasmonic Bi_2WO_6 (a) and 15%-BWO-NDs/TO-NSs heterostructures (b) after stopping light irradiation.

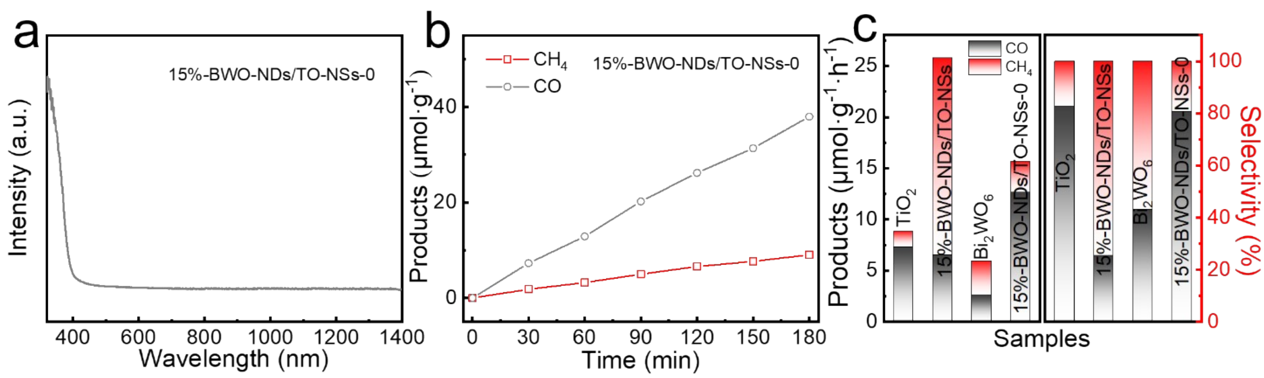

Fig. S10. DRS (a) of sample 15%-BWO-NDs/TO-NSs-0. Its products during CO_2-RR under UV–vis light irradiation (b). Products generation rates and selectivity (c) over o TiO_2, Bi_2WO_6, 15%-BWO-NDs/TO-NSs and 15%-BWO-NDs/TO-NSs-0.

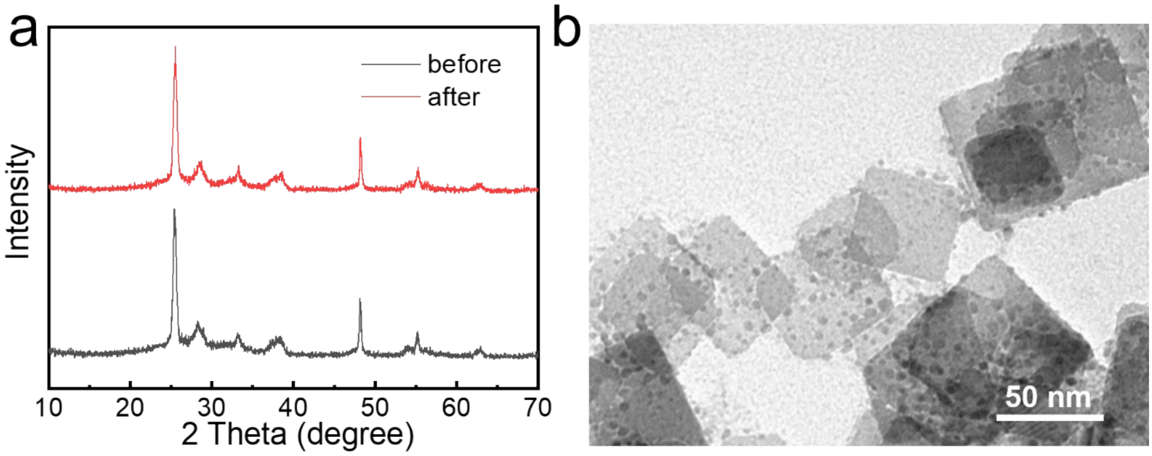

Fig. S11. XRD patterns (a) and TEM image (b) of 15%-BWO-NDs/TO-NSs samples after three photoreaction cycles.

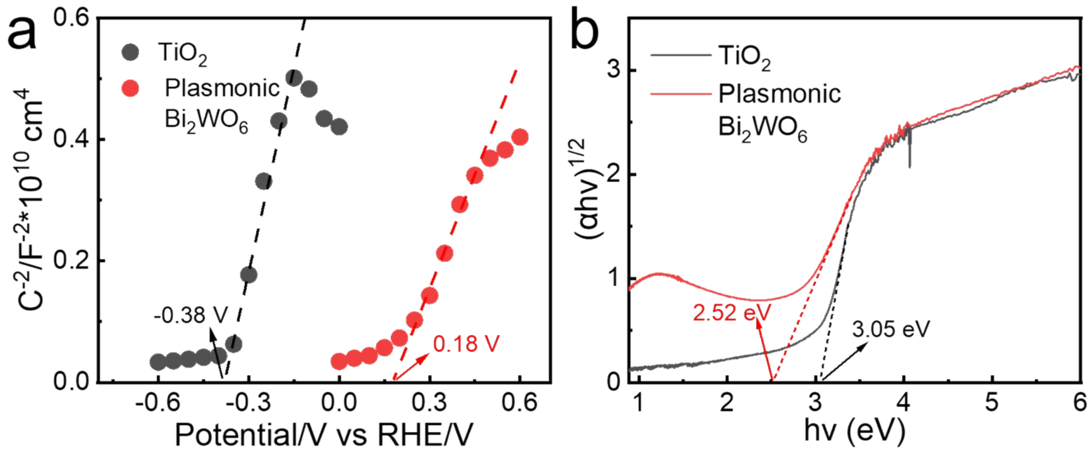

Fig. S12. Mott-Schottky plots (a) of TiO_2 and plasmonic Bi_2WO_6 measured in a NaOH (1 M; pH 13.6) electrolyte at frequencies 100 Hz. Plots (b) of the transformed Kubelka–Munk functions vs the energy of light.

Photocatalysts	**Light source**	**Reaction medium**	**Main products and highest yield**	**Selectivity of CH_4**
Ti_3C_2/Bi_2WO_6	300 W Xe-lamp	Gas-solid, CO_2/H_2O vapor	1.78 (CH_4)/ 0.44 (CH_3OH) μmol g^{-1} h^{-1}	80.2% [1]
20BWO/IVO	300 W Xe-lamp (λ > 420 nm)	Liquid-solid water (5 mL H_2O)	1.13 (CH_4)/ 17.97 (CO) μmol g^{-1} h^{-1}	3.7% [2]
Bi_2WO_6-TiO_2	300 W Xe-lamp (320 nm < λ < 780 nm)	Liquid-solid water (5 mL H_2O)	5.3 (CH_4)/~6.3 (CO) μmol g^{-1} h^{-1}	45.6 % [3]
Bi_2WO_6-OV/BiOI	500 W Xe-lamp (λ > 400 nm)	Gas-solid, CO_2/H_2O vapor	2.29 (CH_4) / 40.02 (CO) μmol g^{-1} h^{-1}	5.4 % [4]
2D/2D $CsPbBr_3/Bi_2WO_6$	150 W Xe lamp (AM 1.5G filter、150 mW cm^{-2})	Liquid-solid 8 ml EA, 2 ml IPA	14.33 (CH_4) / 9.38 (CO)/1.82(H_2) μmol g^{-1} h^{-1}	56.1% [5]
Ultrathin ZnPc/$BiVO_4$ nanosheet	300 W Xe lamp (420 nm cut-off filter)	CO_2/H_2O vapor	0.15 (CH_4) / 0.97 (CO) μmol g^{-1} h^{-1}	13.4% [6]
Bi_2MoO_6-OVs	300 W Xe lamp (λ > 420 nm)	Gas-solid, CO_2/H_2O vapor	2.10 (CH_4) / 0.27 (CO) μmol g^{-1} h^{-1}	88.6% [7]
Bi_2WO_6 nanosheets	300 W Xe lamp (AM 1.5G filter)	CO_2/H_2O vapor	0.63 (CH_4) / 7.12 (CO)/4.6 (O_2) μmol g^{-1} h^{-1}	5.1% [8]
TiO2@PDA	350 W Xe lamp (AM 1.5G filter)	Liquid-solid, water (2 ml H_2O)	1.5 (CH_4)/0.26 (CH_3OH) μmol g^{-1} h^{-1}	85% [9]
Au-TiO_2(O)	300 W Xe lamp (420 nm < λ < 780)	Liquid-solid, water (CO_2/H_2O solution)	0.2 (CH_4) / 1.2 (CO) μmol g^{-1} h^{-1}	14.3 % [10]
This work	300 W Xe lamp (420 nm < λ < 780)	Gas-solid, CO_2/H_2O vapor	19.2 (CH_4)/6.6 (CO) μmol g^{-1} h^{-1}	75%

Table S1 Photocatalytic CO_2 reduction performance of 15%-BWO-NDs/TO-NSs compared to other up-to-date catalysts.

References

1. S. Cao, B. Shen, T. Tong, J. Fu, J. Yu, 2D/2D Heterojunction of Ultrathin MXene/Bi_2WO_6 Nanosheets for Improved Photocatalytic CO_2 Reduction, Adv. Funct. Mater. 2018, **28**, 1800136.
2. J. Li, F. Wei, Z. Xiu and X. Han, *Chem. Eng. J.*, 2022, **446**, 137129.
3. L. Yuan, K. Q. Lu, F. Zhang, X. Fu and Y. J. Xu, *Appl. Catal. B-Environ.*, 2018, **237**, 424-431.
4. X. Y. Kong, W. Q. Lee, A. R. Mohamed and S. P. Chai, *Chem. Eng. J.*, 2019, **372**, 1183-1193.
5. Y. Jiang, H. Y. Chen, J. Y. Li, J. F. Liao, H. H. Zhang, X. D. Wang and D. B. Kuang, *Adv. Funct. Mater.*, 2020, **30**, 2004293.
6. J. Bian, J. Feng, Z. Zhang, Z. Li, Y. Zhang, Y. Liu, S. Ali, Y. Qu, L. Bai, J. Xie, D. Tang, X. Li, F. Bai, J. Tang and L. Jing, *Angew. Chem. Int. Ed.*, 2019, **131**, 10989-10994.
7. X. Yang, S. Wang, N. Yang, W. Zhou, P. Wang, K. Jiang, S. Li, H. Song, X. Ding, H. Chen and J. Ye, *Appl. Catal. B-Environ.*, 2019, **259** 118088.
8. Y. Liu, D. Shen, Q. Zhang, Y. Lin and F. Peng, *Appl. Catal. B-Environ.*, 2021, **283**, 119630.
9. A. Meng, B. Cheng, H. Tan, J. Fan, C. Su and J. Yu, *Appl. Catal. B-Environ.*, 2021, **289**, 120039.
10. A. Wang, S. Wu, J. Dong, R. Wang, J. Wang, J. Zhang, S. Zhong and S. Bai, *Chem. Eng. J.*, 2021, **404**, 127145.