

Supporting Information

Defected ZnWO₄ decorated WO₃ nanorod arrays for efficient photoelectrochemical water splitting†

Ya Cui^{a,b}, Lun Pan^{a,b,*}, Ying Chen^{a,b}, Nisha Afzal^a, Sana Ullah^a, Danyang Liu^c, Li Wang^{a,b}, Xiangwen Zhang^{a,b}, Ji-Jun Zou^{a,b}

^a Key Laboratory for Green Chemical Technology of the Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

^b Collaborative Innovative Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

^c People's Public Security University of China, Beijing 100038, China.

* Corresponding author:

Tel and fax: 86-22-27892340

E-mail address: panlun76@tju.edu.cn (L. Pan).

Table S1. Lattice parameter and unit cell volume for pure WO₃ and WO₃@ZnWO₄ photoanodes.

		Lattice parameters						Cell volume (Å ³)
		a (Å)	b (Å)	c (Å)	α	β	γ	
	WO ₃	7.298	7.532	7.683	90.00	90.00	90.00	422.4
WZ-1	WO ₃	7.298	7.532	7.683	90.00	90.00	90.00	422.4
	ZnWO ₄	4.686	5.713	4.931	90.00	90.60	90.00	132.0
WZ-2	WO ₃	7.298	7.532	7.683	90.00	90.00	90.00	422.4
	ZnWO ₄	4.686	5.691	4.943	90.00	90.40	90.00	131.8
WZ-3	WO ₃	7.298	7.532	7.683	90.00	90.00	90.00	422.4
	ZnWO ₄	4.686	5.689	4.954	90.00	90.50	90.00	132.1
Standard WO ₃								
	JCPDS No. 43-1035	7.297	7.539	7.688	90.00	90.91	90.00	422.9
Standard ZnWO ₄								
	JCPDS No. 15-0774	4.691	5.720	4.925	90.00	90.64	90.00	132.1

Table S2. Comparison of different WO₃ based photoanodes system used for solar water splitting recently.

Photoanode material	Current density	preparation method	Morphology	References
WO ₃ nanorods /BiOI core/shell structure	0.79 mA/cm ²	hydrothermal and ionic layer adsorption reaction process.	WO ₃ nanorods/BiOI nanospheres	S1
WO ₃ @ZnWO ₄ @ZnO-ZnO	1.57 mA/cm ²	atomic layer deposition and hydrothermal process	nanosheets	S2
WO ₃ /BiVO ₄ heterojunction	0.8 mA/cm ²	solvothelmal deposition; spincoating	nanorod-array films	S3
WO ₃ /TiO ₂ photoanode	1.17 mA/cm ²	chemical bath deposition	WO ₃ nanoplates/TiO ₂ nanoprickle overlayers	S4
WO ₃ /g-C ₃ N ₄ heterojunction	0.73 mA/cm ²	hydrothermal growth and deposition-annealing process	nanosheet arrays	S5
WO ₃ @defected ZnWO ₄	1.87 mA/cm ²	solvothelmal method	nanorod arrays	This work

Table S3. Fitted values of R_s , R_{ct} for pure WO₃ and WO₃@ZnWO₄ under dark and AM 1.5 G simulated sunlight irradiation.

Device	R_s (Ω)	R_{ct} (Ω)
WO ₃	35.88	31347
WZ-1	34.47	33858
WZ-2	31.62	34638
WZ-3	27.86	35552
WO ₃ light	25.88	592
WZ-1 light	23.5	422.4
WZ-2 light	32.62	391.3
WZ-3 light	24.28	488.5

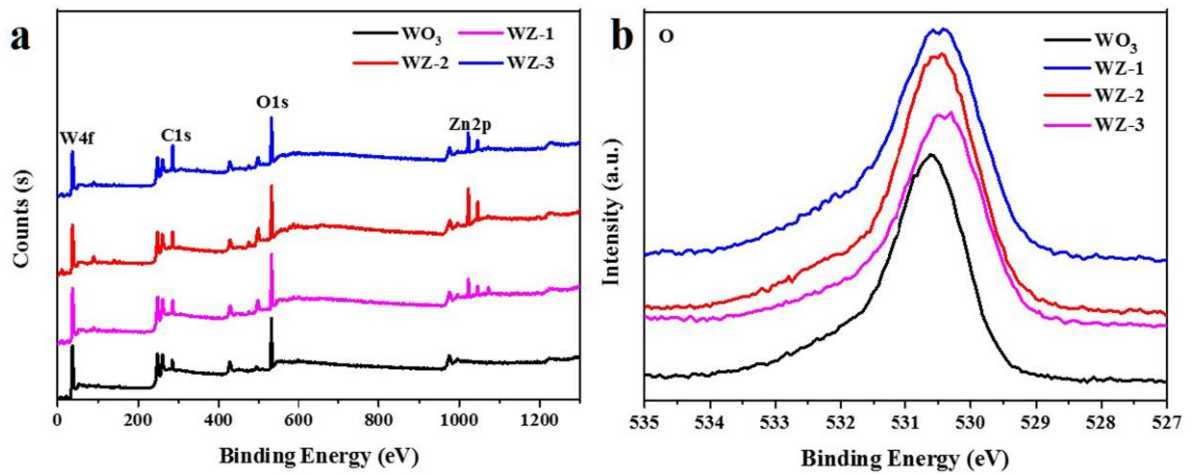


Fig. S1. The XPS spectra of WO₃ and WZ-x. (a) Survey spectra and (b) O 1s spectra.

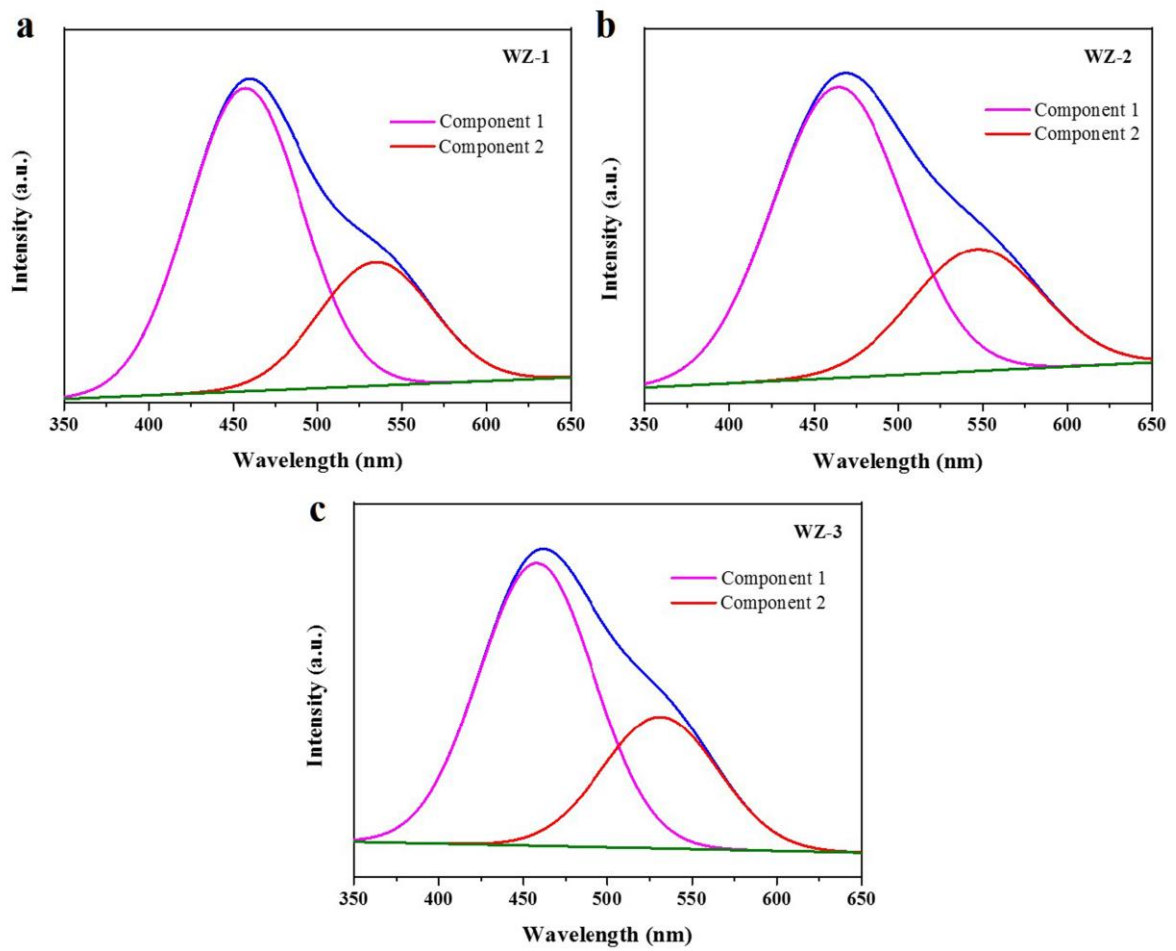


Fig. S2. Individual component, 1 (high intensity) and 2 (low intensity), of PL spectrum of WZ-x.

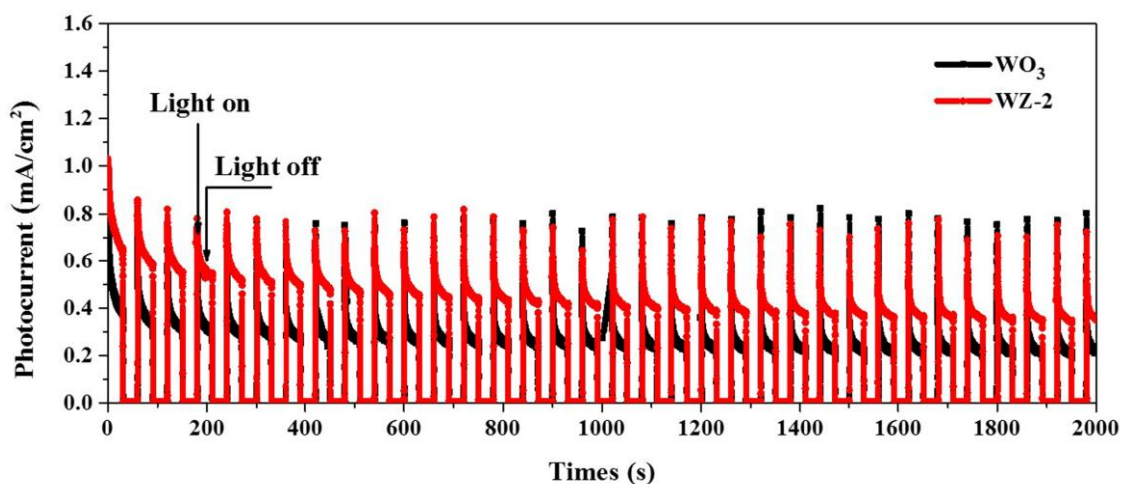


Fig. S3. PEC stability of WZ-2 under AM 1.5 G simulated sunlight irradiation at 0.4 V (vs. Ag/AgCl) via a 2000s continuous PEC water splitting experiment (60 s on-off cycle).

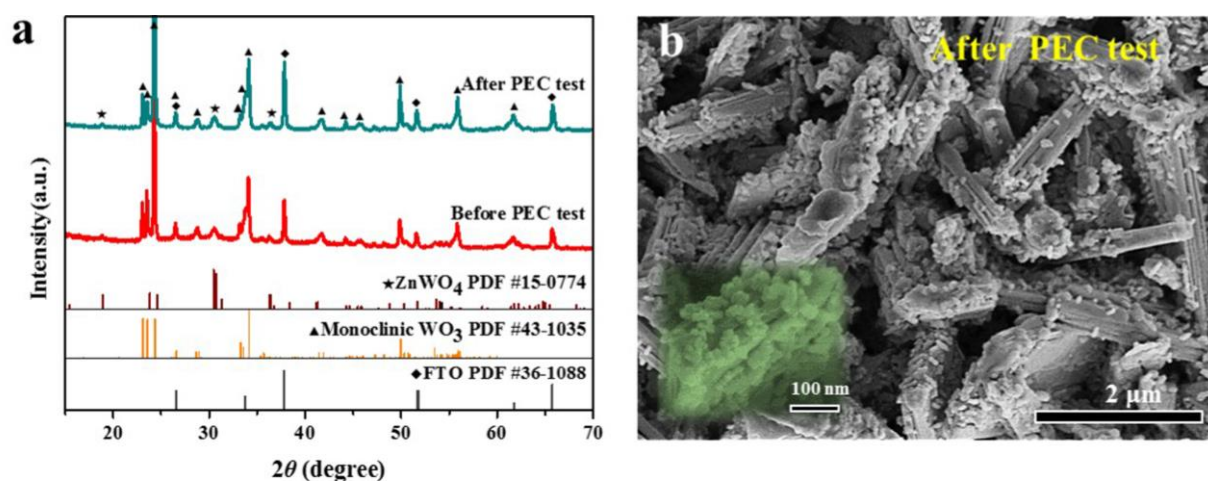


Fig. S4. (a) XRD patterns and (b) SEM images of WZ-2 before and after PEC water splitting reaction.

References:

- S1. H. Ma, J. Zhang and Z. Liu, *Appl. Surf. Sci.*, 2017, **423**, 63-70.
- S2. K. Yuan, Q. Cao, X. Li, H.-Y. Chen, Y. Deng, Y.-Y. Wang, W. Luo, H.-L. Lu and D. W. Zhang, *Nano Energy*, 2017, **41**, 543-551.
- S3. J. Su, L. Guo, N. Bao and C. A. Grimes, *Nano Lett.*, 2011, **11**, 1928-1933.
- S4. Q. Zeng, J. Bai, J. Li, B. Zhou and Y. Sun, *Nano Energy*, 2017, **41**, 225-232.
- S5. Y. Li, X. Wei, X. Yan, J. Cai, A. Zhou, M. Yang and K. Liu, *Phys. Chem. Chem. Phys.*, 2016, **18**, 10255.