Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Materials

Photogenerated-Carrier Separation along Edge Dislocation of WO_3 Single Crystal Nanoflower Photoanode

Yuyu Bu[a], Jun Ren[d], Huawei Zhang[e], Dongjiang Yang[c*], Zhuoyuan Chen[b*] and Jin-Ping Ao[a*]

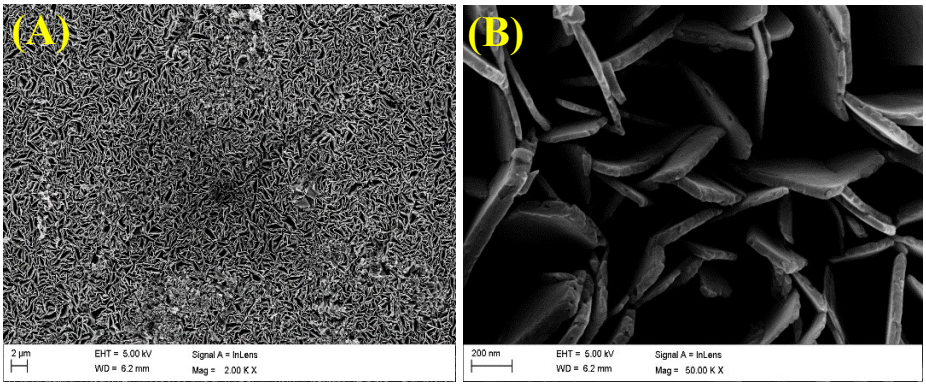


Fig. S1. Vertical growth WO_3 nanosheet on polished Ti substrate. (A) low resolution; (B) high resolution.

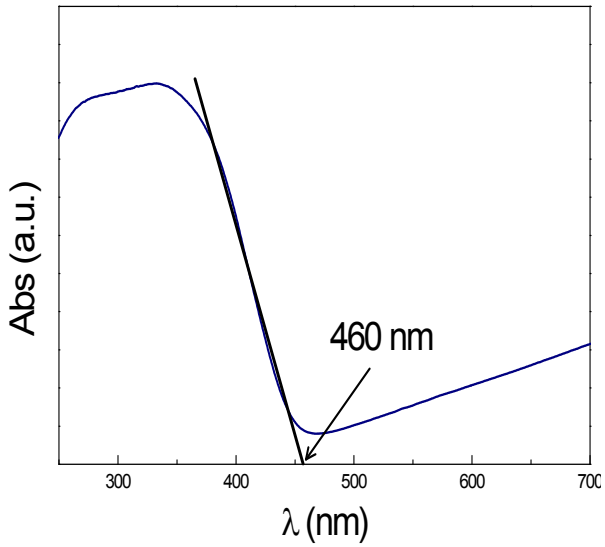


Fig. S2. The UV/Vis diffuse reflectance spectra of WO_3-E8-2h.

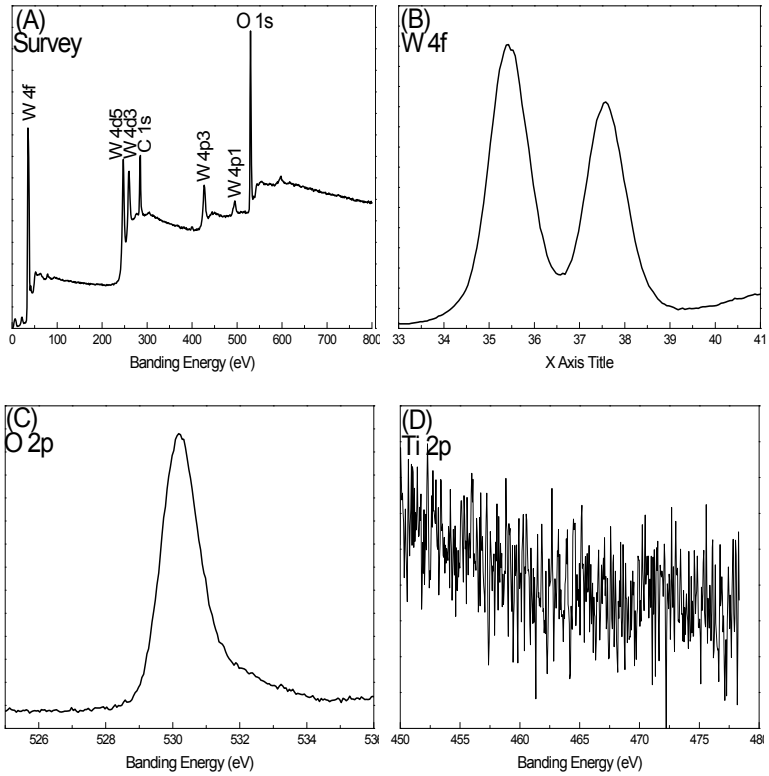
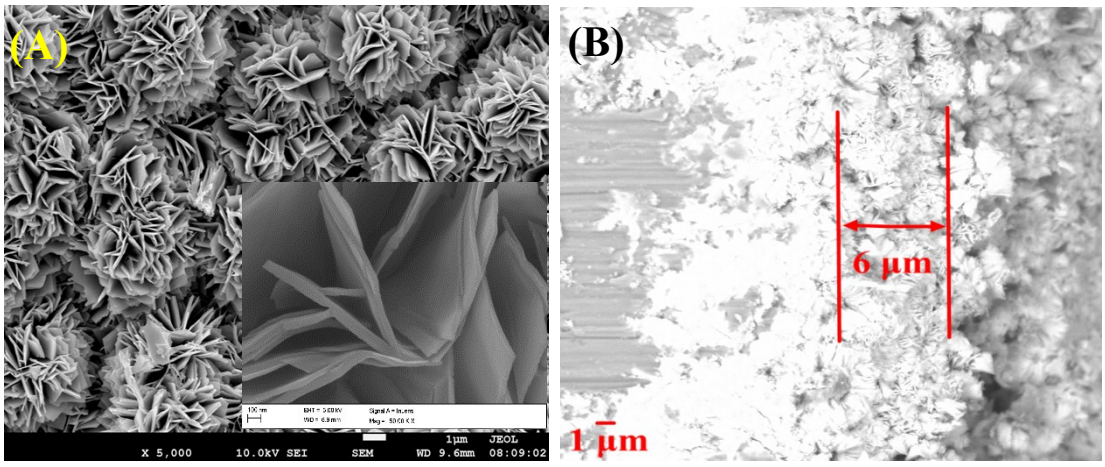


Fig. S3. The XPS spectra of the WO_3-E8-2h. (A) the total XPS survey spectrum; (B) the W4f core level XPS spectrum; (C) the O2p core level XPS spectrum; (D) the Ti2p core level XPS spectrum.



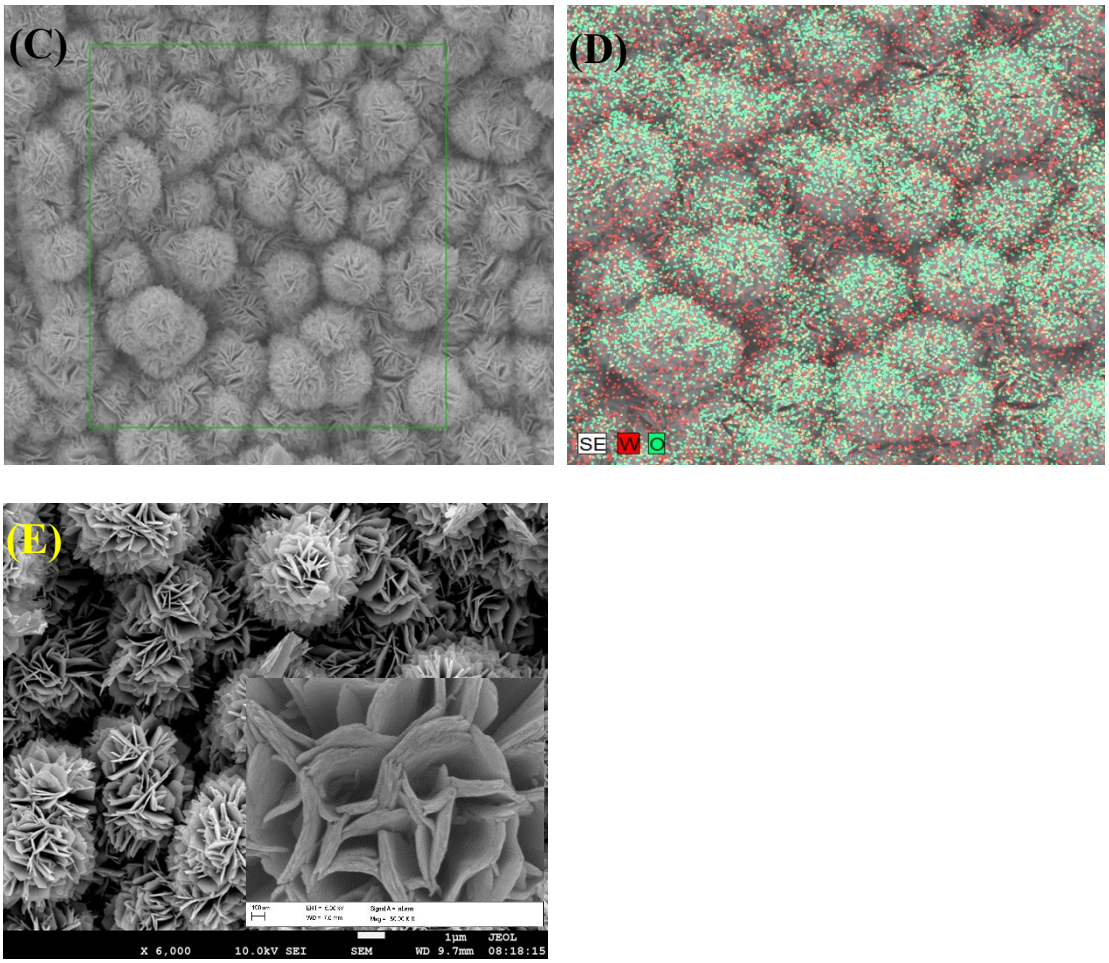


Fig. S4. (A) Top SEM image of WO_3-E8-2h, insert is the high-resolution SEM of it; (B) Cross-section SEM image of WO_3-E8-2h; (C) Selected area of the SEM image on the top of WO_3-E8-2h; (D) distribution of the O and W elements in the selected area. (E) Top SEM image of WO_3-E8-12h, insert is the high-resolution SEM of it.

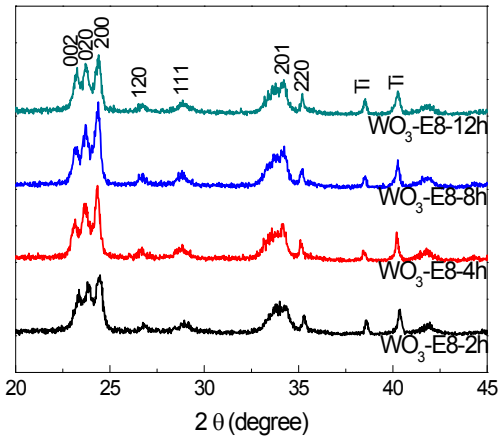


Fig. S5. XRD results of WO_3-E8 with different annealing time (2, 4, 8, 12 hours) at 500 °C.

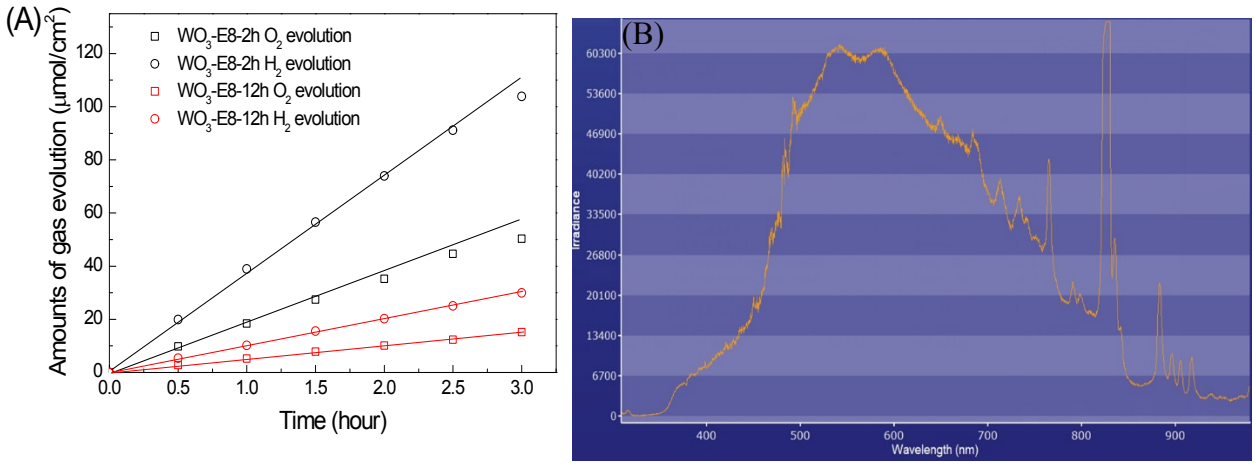


Fig. S6. (A) PEC Water splitting for O_2 and H_2 evolution properties of WO_3-E8-2h and WO_3-E8-12h (bias potential 1.5 V vs Ag/AgCl); (B) Spectral energy distribution curve of the Xe light used in this study.

The Faradic efficiency can be described as follows:

$$\text{Faradic efficiency} = \frac{m \cdot n \cdot F}{i \cdot t} \times 100\% \quad (1)$$

In which Equ., the m is the mole value for O_2 at a time. n is the electrons exchange number for one O_2 molecular production. F is the faraday constant. i is the photocurrent density. t is the reaction time.

Because of the photocurrent density of WO_3-E8-2h photoanode just can keep at near 2.1 mA cm^{-2} in the initial one hour, so we calculated the Faradic efficiency in this term. Combination the information in Fig. 5C and Fig. S6A, the Faradic efficiency =

$$\frac{18.4\times10^{-6}\times4\times96487}{2.1\times10^{-3}\times3600}\times100\% \approx 93.93\%$$

So, in the initial one hour, the WO_3-E8-2h photoanode shows higher than 90% Faradic efficiency. The losing Faradic efficiency may contributed to the photoanode corrosion.

Tab. S1. Comparison of the photoelectrochemical performance of the typical WO_3 photoelectrodes reported in literature and in the present study.

WO_3 with different structure	Light intensity ($mW \cdot cm^{-2}$)	Bias potential (V)	Electrolyte	Photoinduced current density ($mA \cdot cm^{-2}$)	Ref.
WO_3 Flake wall	100 (AM 1.5)	1.0 V (vs Ag/AgCl)	Na_2SO_4 (0.1 M)	1.4	[1]
Molecular iron modified WO_3	100 (AM 1.5)	1.0 V (vs Ag/AgCl)	Na_2SO_4 (0.1 M)	1.1	[2]
WO_3 planar film	100 (AM 1.5)	1.0 V (vs Ag/AgCl)	Na_2SO_4 (0.5 M)	1.0	[3]

WO_3 planar film	100 (AM 1.5)	1.0 V (vs Ag/AgCl)	Na_2SO_4 (0.5 M)	0.5	[4]
WO_3 Nanorod array	100 (AM 1.5)	1.0 V (vs Ag/AgCl)	Na_2SO_4 (0.5 M)	0.25	[5]
WO_3 Nanoflower	100 (AM 1.5)	1.0 V (vs Ag/AgCl)	Na_2SO_4 (0.1 M)	1.8	Present study

Tab. S1 shows the photoelectrochemical performance of WO_3 with different morphologies prepared in recent years and compared them with this work. According to the reports from the literatures, the best photoelectrochemical performance was obtained by WO_3 with flake wall like structure in Na_2SO_4 solution under the illumination of AM 1.5 (100 $mW \cdot cm^{-2}$) and at the bias potential of 1 V (vs Ag/AgCl), and the photoinduced current density of WO_3 with this structure could reach 1.4 $mA \cdot cm^{-2}$. In the present work, for the nanoflower-structured WO_3 thin-film photoelectrode with 8 h of hydrothermal reaction, a photoinduced current density of 1.8 $mA \cdot cm^{-2}$ was obtained under the same test condition as in the compared references, which is significantly enhanced compared with that in the previous reports.

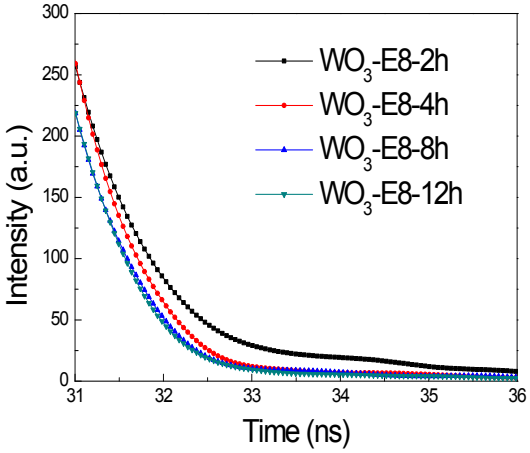


Fig. S7. Time-resolved photoluminescence (TR-PL) spectrum of WO_3 photoanodes with different annealing times (2 h to 12 h) at the emission wavelength of 440 nm.

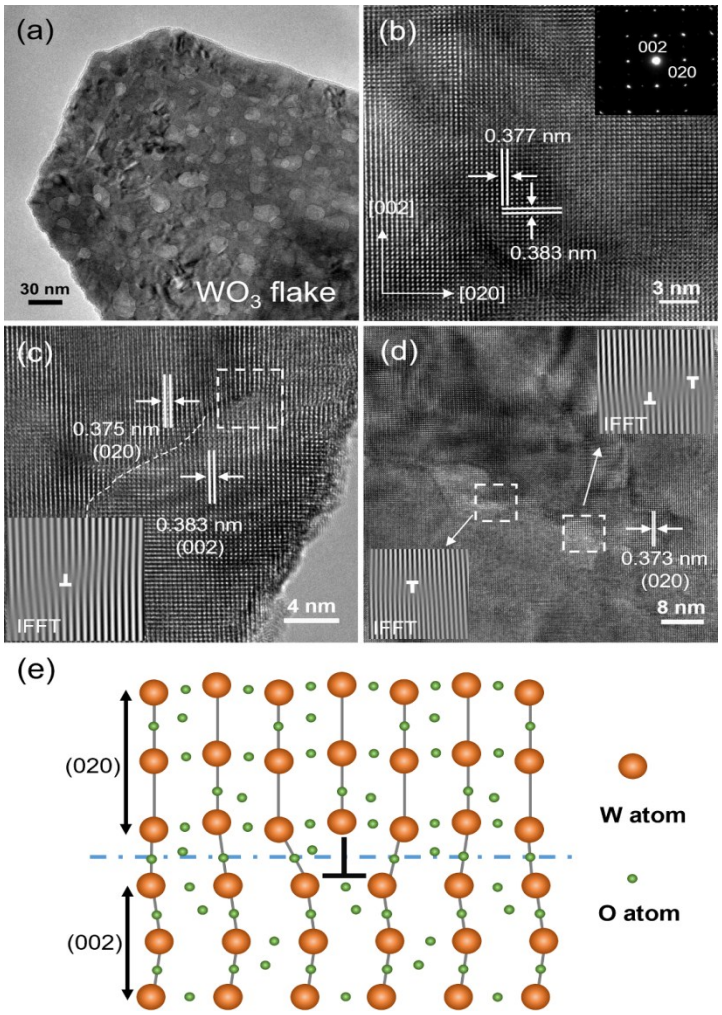


Fig. S8. TEM images of WO_3-E8-2h thin film. (A) low and (B-D) high resolution; Selected area electron diffraction (SAED) pattern for this sample is inserted in (B); and the corresponding IFFT images insert in (C) and (D).

Reference

[1] F. Amano, D. Li, B. Ohtani, B. *Chem. Commun*. **2010**, *46*, 2769.

[2] B. M. Klepser, B. M. Bartlett, *J. Am. Chem. Soc*. **2014**, *136*, 1694.

[3] K. Zhang, X. J. Shi, J. K. Kim, J. H. Park, *Chem. Chem. Phys*. **2012**, *14*, 11119.

[4] J. Su, L. Guo, N. Bao, C. A. Grimes, C. *Nano Lett*. **2011**, *11*, 1928.

[5] Y. Pihosh, I. Turkevych, K. Mawatari, T. Asai, T. Hisatomi, J. Uemura, M. Tosa, K. Shimamura, J. Kubota, K. Domen, T. Kitamori, *Small* **2014**, *10,* 3692.