Supplementary Information

Tree-like Nanoporous WO_3 Photoanode with Enhanced Charge Transport Efficiency for Photoelectrochemical Water Oxidation

*Sun Shin[a,d,1], Hyun Soo Han[a,b,1], Ju Seong Kim[a], Ik Jae Park[a], Myeong Hwan Lee[a], Kug Sun Hong[a] and In Sun Cho[c,]**

[a]Department of Materials Science and Engineering, Seoul National University, Seoul 151-744, Korea
[b]Department of Mechanical Engineering, Stanford University, Stanford, CA 94306, United States
[c]Department of Materials Science and Engineering & Energy Systems Research, Ajou University, Suwon 443-749, Korea
[d]Engineering Research Institute, Ajou University, Suwon 443-749, Korea

Corresponding Author:
E-mail: insuncho@ajou.ac.kr

[1] These authors contributed equally to this work.

Table S1. Calculated nanocrystals sizes in the WO_3 photoanodes synthesized at various oxygen partial pressures (W-100: 100 mTorr, W-300: 300mTorr, and W-600: 600 mTorr), which is estimated from Scherrer equation using (002) reflection peak.

	λ (nm)	**β (rad)**	**θ_B**	**Size (nm)**
W-100	0.154	$2.48\ 10^{-3}$	12.1848	**57.2**
W-300	0.154	$2.83\ 10^{-3}$	12.1848	**53.3**
W-600	0.154	$2.412\ 10^{-3}$	12.1848	**58.7**

$$\tau = \frac{0.9\lambda}{\beta \cos \theta_B},$$

τ is the mean size of the crystallite;

λ is the X-ray wavelength;

β_B is the line broadening at half the maximum intensity in radian

θ is the Bragg angle

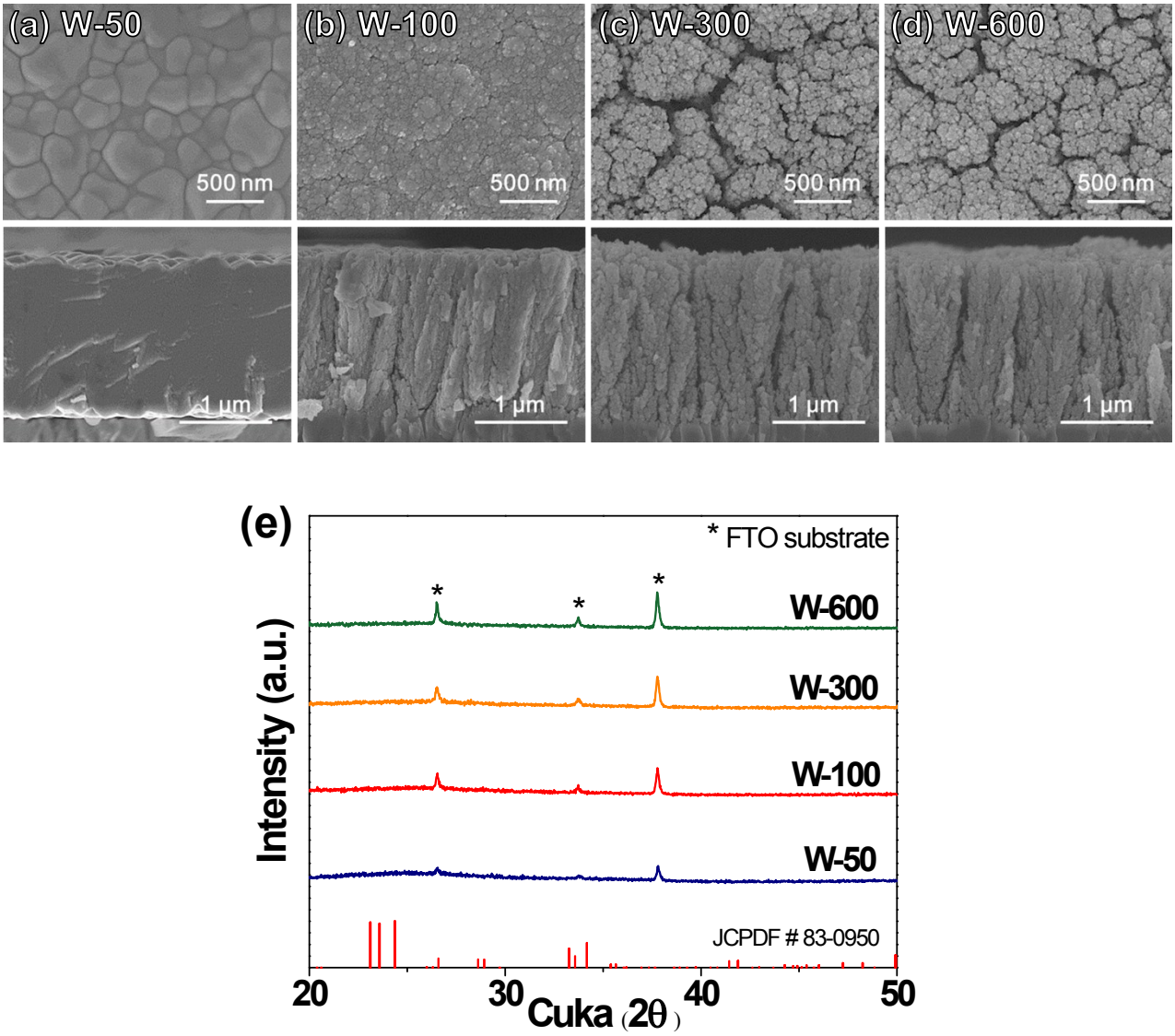


Figure S1. (a-d) Top and cross-sectional view SEM images and (e) XRD patterns of as-prepared WO_3 photoanodes deposited at oxygen working pressure of (a) 50 mTorr (deposition time=45min), (b) 100 mTorr (deposition time=30min), (c) 300 mTorr (deposition time=15min), and (d) 600 mTorr (deposition time=10min). The growth time was adjusted to tune the film thickness (1.8μm).

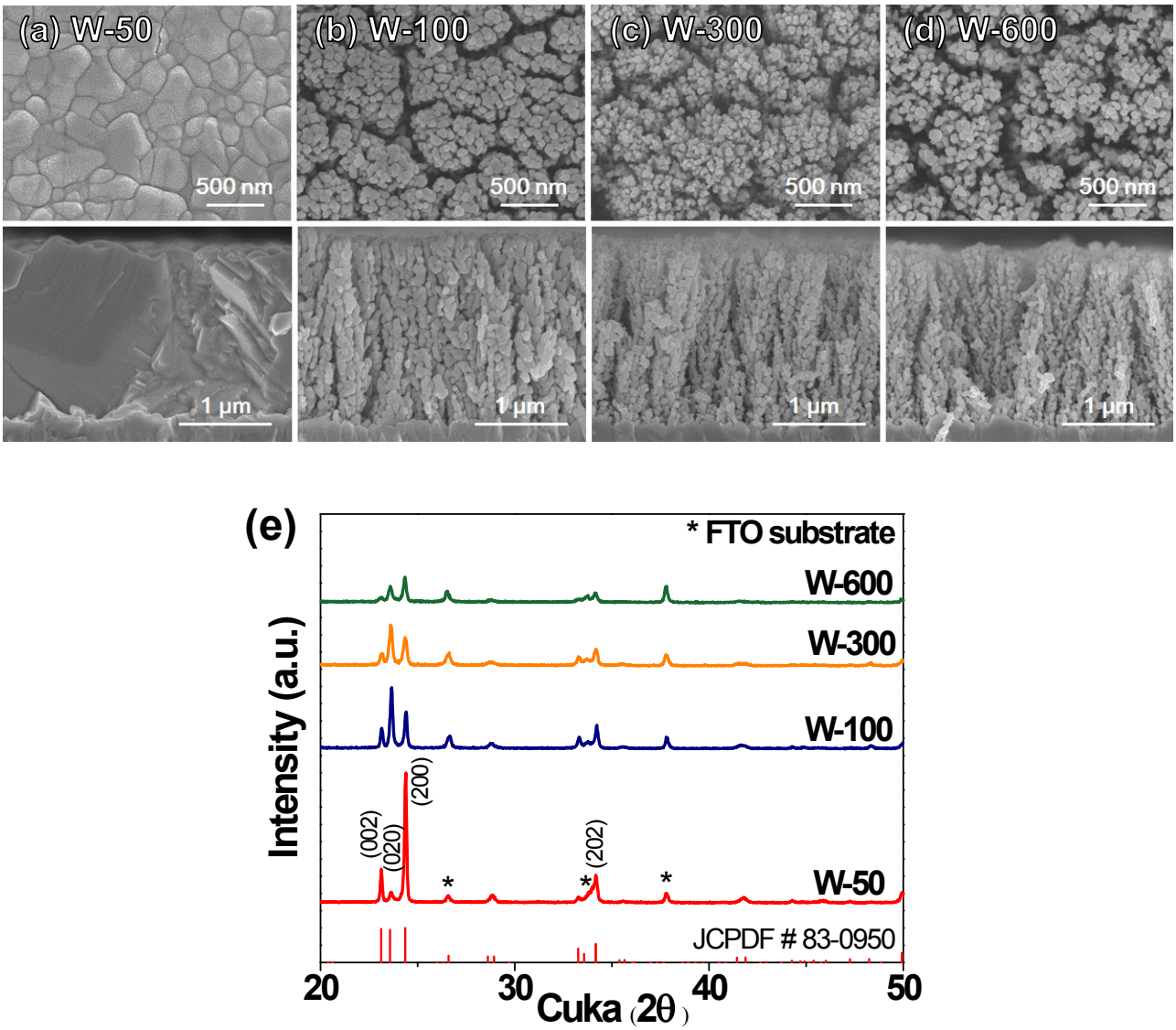


Figure S2. (a-d) Top and cross-sectional view SEM images, and (e) XRD patterns of WO_3 photoanodes after thermal annealing at 550 °C/2h, which are deposited at various oxygen working pressures. (a) 50 mTorr (deposition time=45min), (b) 100 mTorr (deposition time=30min), (c) 300 mTorr (deposition time=15min), and (d) 600 mTorr (deposition time=10min). *The samples prepared at 300 and 600 mTorr are showing weak adhesion with FTO substrate so that those films are often detached or cursched during PEC measurements.

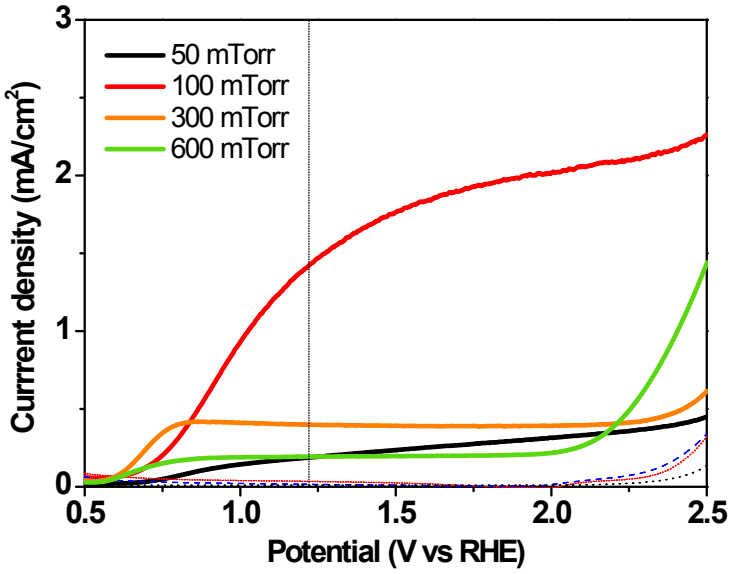


Figure S3. Photocurrent-potential (J-V) curves of WO_3 photoanodes (thickness=1.8 μm, after thermal annealing at 550 °C/2h). Most of samples synthesized at higher O_2 pressure, *i.e.*, 300mT and 600mT are detached or crushed during PEC measurements. Therefore, the much lower photocurrent densities of these samples may be attributed to the poor contact with FTO substrate.

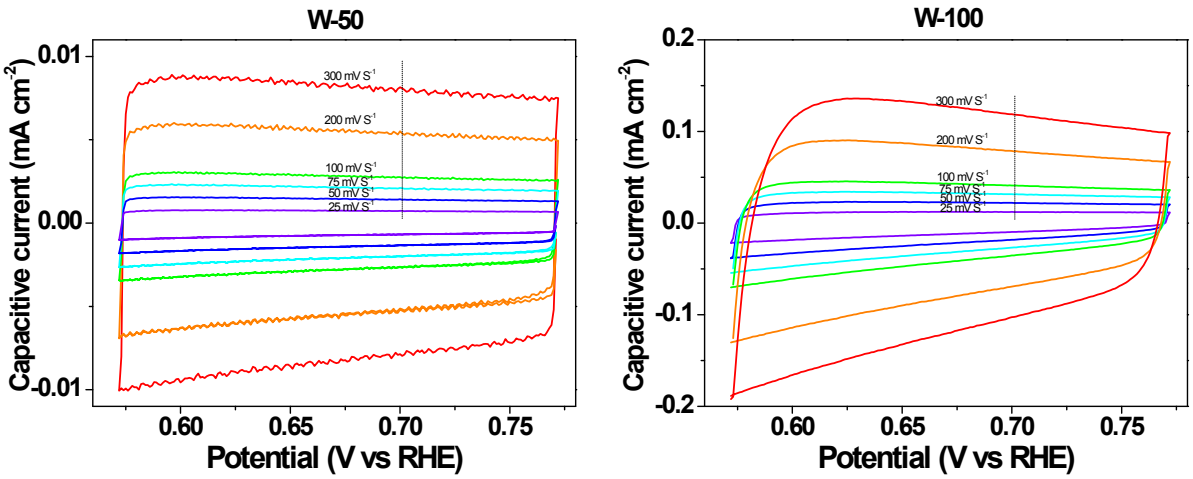
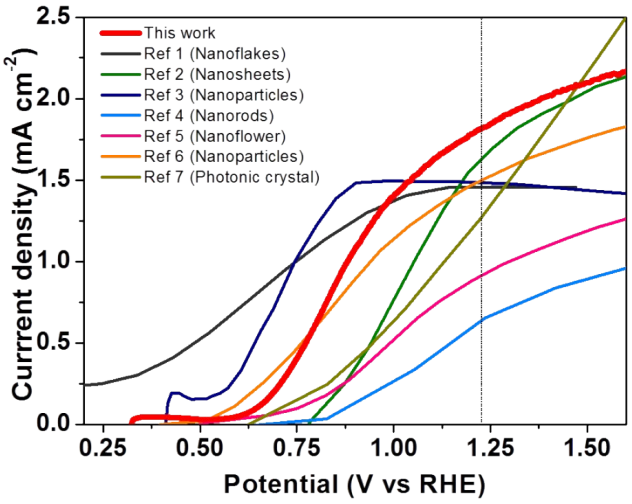
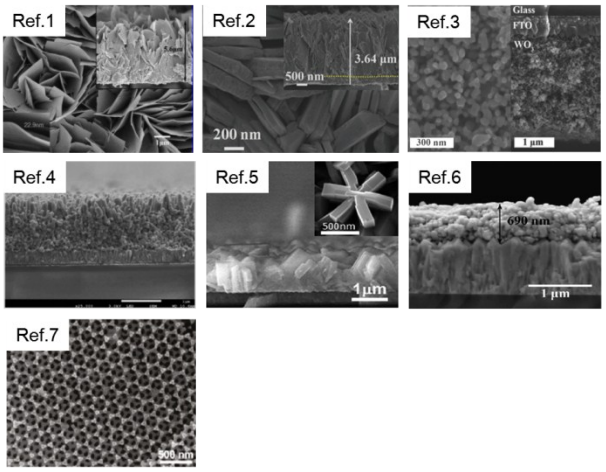


Figure S4. Cyclic voltammograms of WO_3 photoanodes (W-50 and W-100) measured at different scan rates (25-300 mV/sec). The sweep potential range, *i.e.*, (-0.05 - 0.15 V vs. Ag/AgCl → 0.57 - 0.77 V vs. RHE) was selected based on the previous report.[1] In this range, all current is only attributed to capacitive charging due to the absence of any redox features in the dark condition. Even though it is not possible to obtain a value of the true electrochemical surface area per projected geometric area without an atomically flat WO_3 reference standard and detailed knowledge of the electronically accessible surface sites, we adopted this method and determined the relative electrochemical surface area by assuming that the intrinsic specific surface capacitance of all WO_3 films is approximately the same.[2]





Refs	Morphology of WO_3 (Thickness, μm)	PEC measurement conditions			Jph @1.23V_{RHE} (mA/cm^2)
		Electrolyte (pH)*	Light source	Electrodes system	
Ref. 1[3]	Nanoflakes (5.6)	0.1M Na_2SO_4 (pH 3.0-7.0)	Solar simulator (1sun, 100mW/cm^2)	Two electrodes (Pt counter)	1.45
Ref. 2[4]	Nanosheets (3.64)	0.1M Na_2SO_4 (pH 3.0-7.0)	Solar simulator (1sun, 100mW/cm^2)	Three electrodes (Pt counter, Ag/AgCl ref.)	1.63
Ref. 3[5]	Nanoparticles (2.3)	1 M H_2SO_4 (pH ~0.0)	Solar simulator (1sun, 100mW/cm^2)	Three electrodes (Pt counter, Hg/Hg_2SO_4 saturated K_2SO_4 ref.)	1.48
Ref. 4[6]	Nanorods (1.58)	0.5 M Na_2SO_4 (pH 3.0-7.0)	Solar simulator (1sun, 100mW/cm^2)	Three electrodes (Pt counter, SCE ref.)	0.66
Ref. 5[7]	Nanoflowers (0.6)	1 M H_2SO_4 (pH ~0.0)	Solar simulator (1sun, 100mW/cm^2)	Three electrodes (Pt counter, SCE ref.)	0.91
Ref. 6[8]	Nanoparticles (0.69)	0.5 M H_2SO_4 (pH ~0.0)	Solar simulator (1sun, 100mW/cm^2)	Three electrodes (Pt counter, Ag/AgCl ref.)	1.50
Ref. 7[9]	Inverse opal (2.6)	0.1 M Na_2SO_4 (pH 3.0-7.0)	500W Xenon Lamp (250mW/cm^2, 300-800nm)	Three electrodes (Pt counter, SCE ref.)	1.28
This work	Tree-like nanoporous (3.2)	Phosphate buffer (pH 7.0)	Solar simulator (1sun, 100mW/cm^2)	Three electrodes (Pt counter, Ag/AgCl ref.)	1.82

Figure S5. Comparison of PEC performance with previous works. Photocurrent-potential (J-V) curves of WO_3 photoanodes and corresponding SEM images. Table summarizes WO_3 morphology and measurement conditions. *Since all the reference papers doesn't mention the pH values, the pH values are referred from other papers.

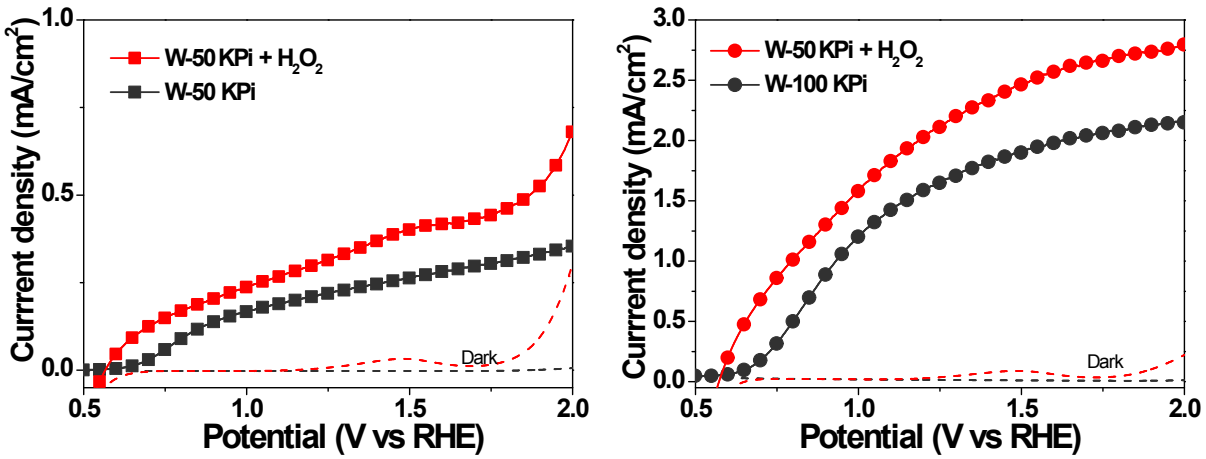


Figure S6. Photocurrent-potential (J-V) curves of W-50 and W-100 samples before and after addition of H_2O_2 (5 vol.%). Na_2SO_3 also gives similar results. The charge transport and transfer efficiencies were estimated as functions of applied potential by using H_2O_2 or Na_2SO_3 as hole scavenger under AM1.5G simulated solar light illumination. The key assumption for this approach is that the oxidation kinetics of H_2O_2 or Na_2SO_3 is very fast and its charge transfer efficiency is 100%, so the ratio of photocurrent density measured in H_2O and H_2O_2 (or H_2O and Na_2SO_3) give the charge transfer efficiency ($\eta_{transfer}$) for H_2O. (Eq. 1) The charge transport efficiency ($\eta_{transport}$) was further calculated by dividing photocurrent density in H_2O_2 (or Na_2SO_3) by the total light absorption efficiency (η_{e^-/h^+}) which is obtained from integration of light absorption (Figure 3c) with respect to the AM1.5G solar light spectrum (Eq. 2).

$$\eta_{transfer} = \frac{J_{ph,\,H_2O}}{J_{ph,\,H_2O_2}} \qquad (1)$$

$$\eta_{transport} = \frac{J_{ph,\,H_2O_2}}{\eta_{e^-/h^+}} \qquad (2)$$

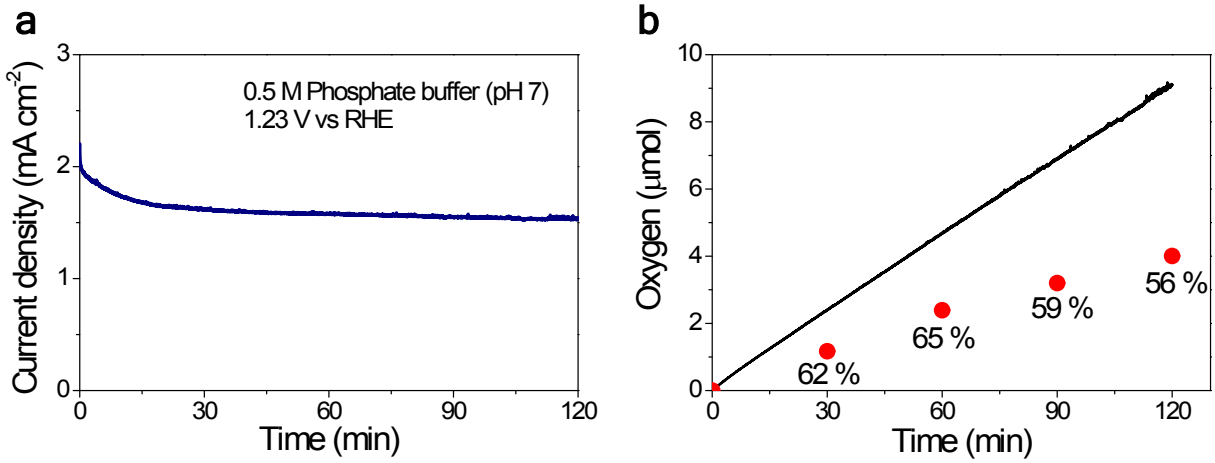


Figure S7. (a) Photocurrent-time (J-t) curves of W-100 photoanode measured at 1.23 V versus RHE in 0.5 M phosphate buffer solution under simulated solar light illumination (100mW/cm^2). (b) Expected amounts of O_2 calculated from the photocurrent assuming 100% Faradaic efficiency (Black line) and actual amounts of O_2 produced (red circle). The numbers show calculated faradaic efficiencies at the given time.

References

1. N. Wang, J. Zhu, X. Zheng, F. Xiong, B. Huang, J. Shi and C. Li, *Faraday Discussions*, 2014.
2. B. A. Pinaud, P. C. Vesborg and T. F. Jaramillo, *The Journal of Physical Chemistry C*, 2012, **116**, 15918-15924.
3. J. Su, X. Feng, J. D. Sloppy, L. Guo and C. A. Grimes, *Nano Letters*, 2011, **11**, 203-208.
4. D.-D. Qin, C.-L. Tao, S. A. Friesen, T.-H. Wang, O. K. Varghese, N.-Z. Bao, Z.-Y. Yang, T. E. Mallouk and C. A. Grimes, *Chemical Communications*, 2012, **48**, 729-731.
5. S. Hilaire, M. J. Suess, N. Kranzlin, K. Bienkowski, R. Solarska, J. Augustynski and M. Niederberger, *Journal of Materials Chemistry A*, 2014, **2**, 20530-20537.
6. Y. Liu, L. Zhao, J. Su, M. Li and L. Guo, *ACS Applied Materials & Interfaces*, 2015, **7**, 3532-3538.
7. N. Wang, D. Wang, M. Li, J. Shi and C. Li, *Nanoscale*, 2014, **6**, 2061-2066.
8. R. H. Gonçalves, L. D. T. Leite and E. R. Leite, *ChemSusChem*, 2012, **5**, 2341-2347.
9. X. Chen, J. Ye, S. Ouyang, T. Kako, Z. Li and Z. Zou, *ACS Nano*, 2011, **5**, 4310-4318.