Supporting Information

Enhanced photoelectrocatalysis in porous single crystalline rutile

titanium dioxide electrodes

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Figure S1. (a-b) XRD patterns of (020) KTP single crystal and PSC rutile (110) TiO₂. The insets are optical photographs, respectively.



Figure S2. (a-b) Element mapping of PSC rutile TiO₂ monolith. (c) EDS test of PSC rutile TiO₂ monolith.



Figure S3. The specific surface area of PSC Ti_nO_{2n-1} (n=9, 38) monoliths. (a) PSC $Ti_{38}O_{75}$. (b) PSC PSC Ti_9O_{17} .



Figure S4. Theoretical calculations of energy barrier for transformation from (010) KTP to rutile (110) TiO₂.



Figure S5. EPR spectra of PSC Ti₃₈O₇₅ and Ti₉O₁₇.



Figure S6. Density of states for rutile $\rm TiO_2$ and $\rm Ti_9O_{17}.$



Figure S7. Open circuit potential for PSC $Ti_{38}O_{75}$ and Ti_9O_{17} photoelectrodes under dark and illuminated conditions in 1 M NaOH electrolyte.



Figure S8. Impedance spectra of PSC $\rm Ti_9O_{17}$ and $\rm Ti_{38}O_{75}$ electrode in 1 M NaOH electrolyte.



Figure S9. (a) IPCE measurements for PSC rutile (110) TiO_2 at 1.23V in 1M NaOH. (b) ABPE curve for PSC rutile (110) TiO_2 monolith under 10 AM 1.5 G illumination.



Figure S10. XRD patterns of the PSC R-Ti $_9O_{17}$ catalyst after the stability test.

Catalyst	Electrolyte	Photocurrent density(mA cm ⁻²)	Photostability	Reference
		at 1.23 V VS. RHE	(min)	
TiO ₂ /Cu ₂ O/Al/Al ₂ O ₃	$0.1 \text{ M} \text{ Na}_2 \text{SO}_4$	4.52	166.67	1
WO _{3-x} @TiO _{2-x}	0.5 M No SO	2.2	260	2
Core-shell Nanosheets	$0.5 \text{ WI} \text{ Na}_2 \text{SO}_4$	5.2	300	
TiO ₂ NR @ NB	1 M NaOH	1.24	100	3
PSN TiO ₂	1 M NaOH	1.02	/	4
TiO2@CoNi-LDHs	0.1 M Na ₂ SO ₄	4.4	600	5
NTAs				
PSC Ti _n O _{2n-1}	1M NaOH	8	600	This work

Table S1. Comparing the performance of TiO₂ photoanodes with reported works

References

1. S. Zhang, Z. Liu, W.-G. Yan, Z. Guo and M. Ruan, Chinese Journal of Catalysis, 2020, 41, 1884-1893.

2. K. Yuan, Q. Cao, H.-L. Lu, M. Zhong, X. Zheng, H.-Y. Chen, T. Wang, J.-J. Delaunay, W. Luo, L. Zhang, Y.-Y.

Wang, Y. Deng, S.-J. Ding and D. W. Zhang, J. Mater. Chem. A, 2017, 5, 14697-14706.

3. W. Wang, J. Dong, X. Ye, Y. Li, Y. Ma and L. Qi, Small, 2016, 12, 1469-1478.

4. T. Butburee, Y. Bai, H. Wang, H. Chen, Z. Wang, G. Liu, J. Zou, P. Khemthong, G. Q. M. Lu and L. Wang, *Adv Mater*, 2018, **30**, e1705666.

5. W. Chen, T. Wang, J. Xue, S. Li, Z. Wang and S. Sun, Small, 2017, 13, 201602420.