

Supporting Information for

**Impact of Oxygen Vacancies on TiO₂ Charge Carrier Transfer for
Photoelectrochemical Water Splitting**

Xiaoqian Huang, Xiaoru Gao, Qihui Xue, Can Wang, Ruikang Zhang,* Yuanzhe Gao* and
Zhangang Han

*National Demonstration Center for Experimental Chemistry Education, Hebei Key Laboratory of
Organic Functional Molecules, College of Chemistry and Material Science, Hebei Normal
University, Shijiazhuang, Hebei 050024, People's Republic of China*

E-mail: zhangruikang@hebtu.edu.cn (R. Zhang); E-mail: yzgao2003@126.com (Y. Gao)

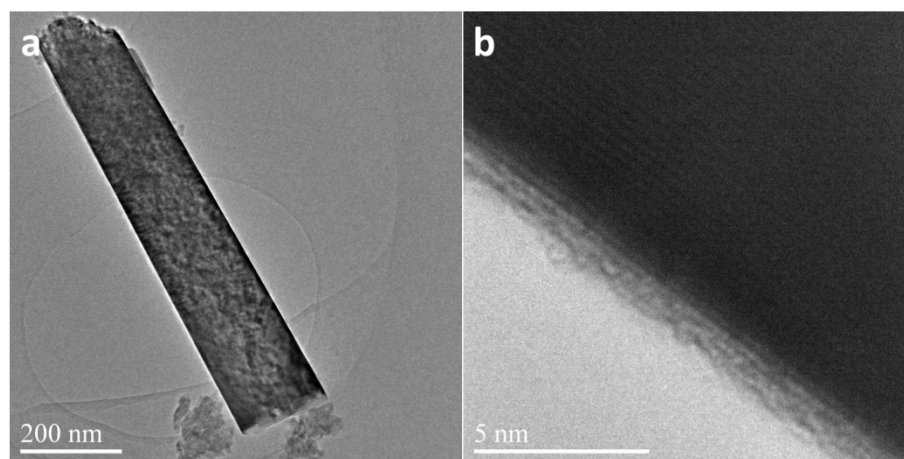


Figure S1 TEM images of pristine TiO₂ with a (a) low and (b) high magnification.

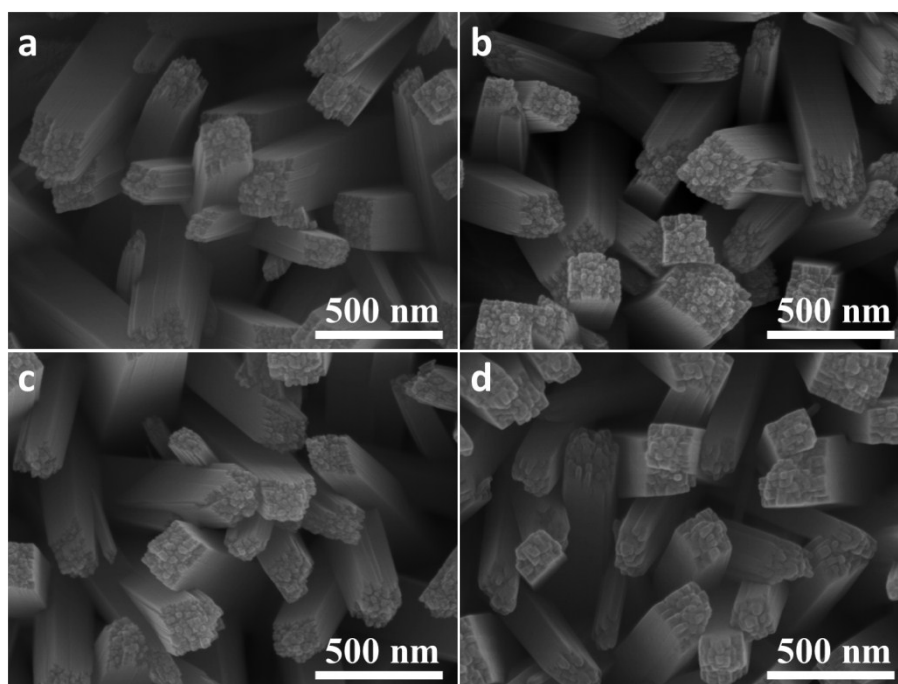


Figure S2 SEM images of (a) TiO₂-300, (b) TiO₂-400, (c) TiO₂-500 and (d) TiO₂-600 photoanodes, respectively.

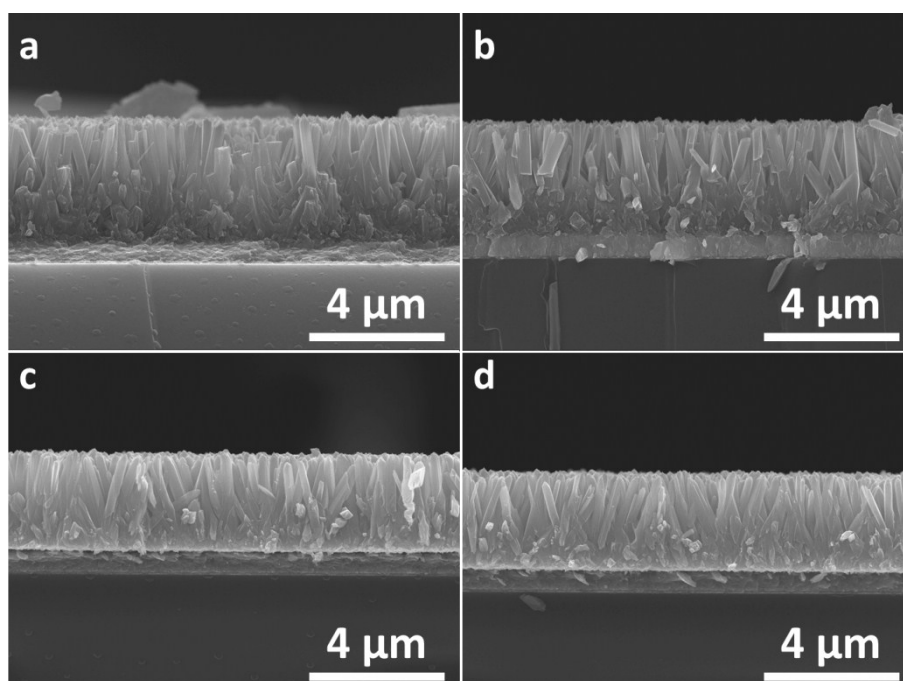


Figure S3 SEM images of (a) TiO₂-300, (b) TiO₂-400, (c) TiO₂-500 and (d) TiO₂-600 photoanodes in side view.

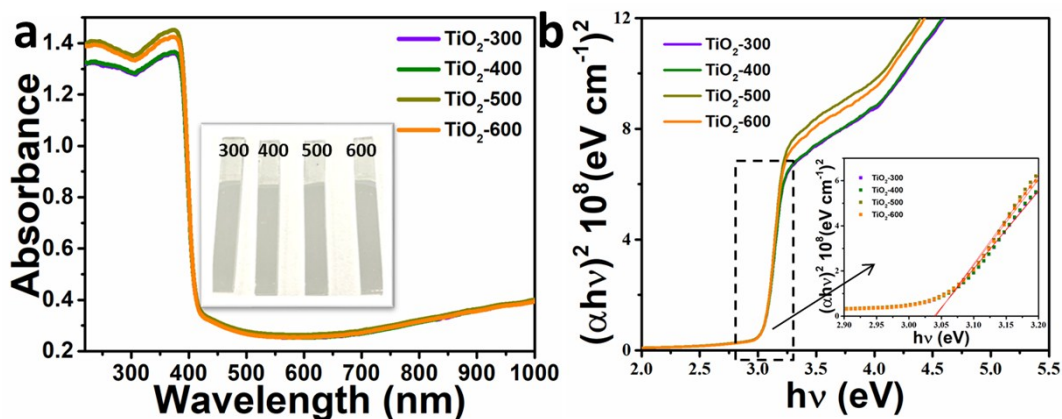


Figure S4 (a) UV-vis diffuse-reflectance spectra and (b) band gap energy of TiO₂-300, TiO₂-400, TiO₂-500 and TiO₂-600 photoanodes, respectively.

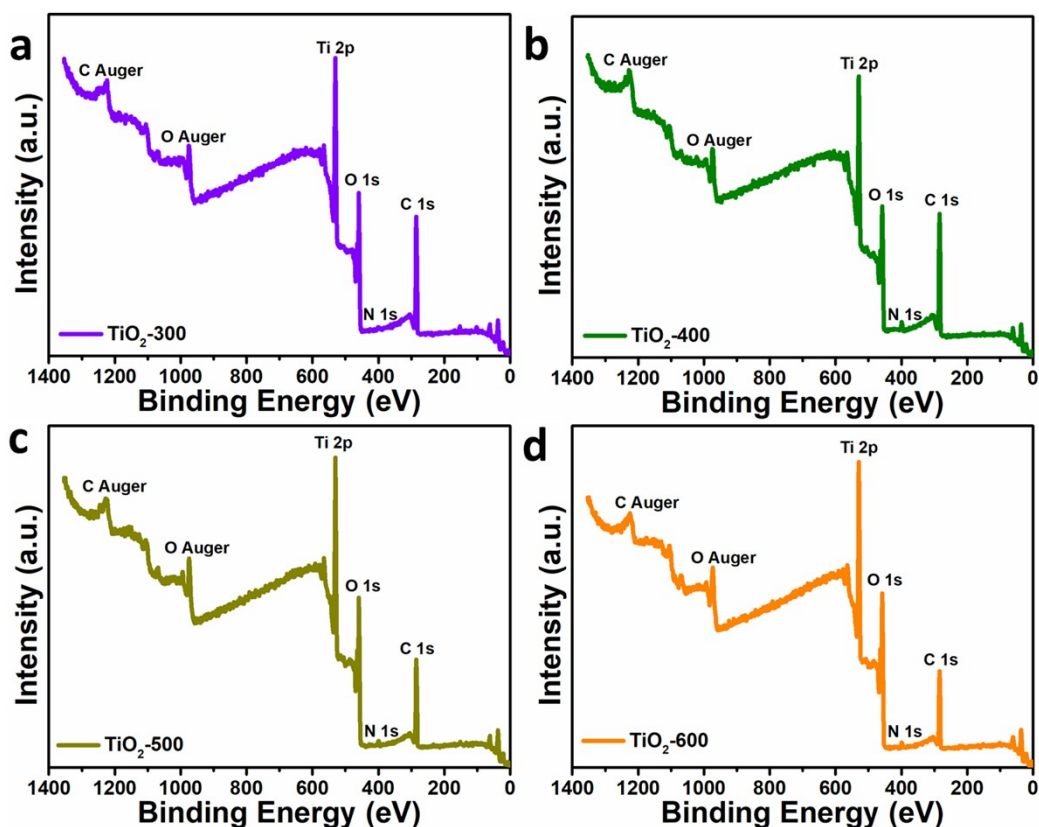


Figure S5 The full XPS spectra of (a) TiO₂-300, (b) TiO₂-400, (c) TiO₂-500 and (d) TiO₂-600 photoanodes, respectively.

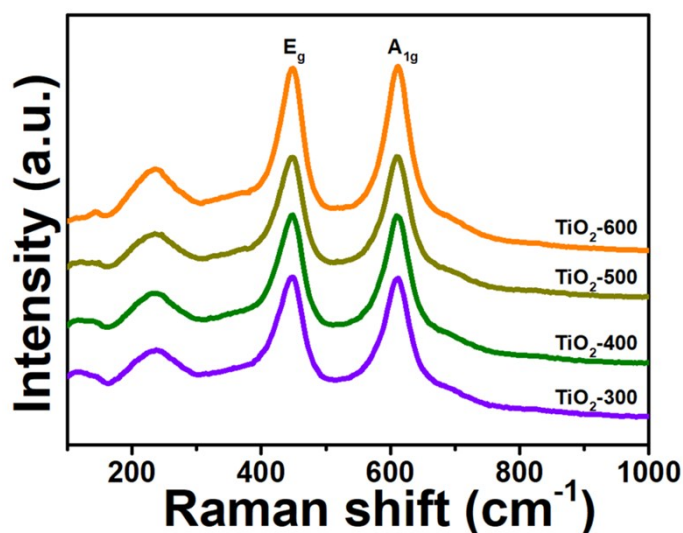


Figure S6 Raman spectra of TiO₂-300, TiO₂-400, TiO₂-500 and TiO₂-600 photoanodes.

Table S1 Comparison studies for various TiO₂ photoanodes and their PEC performances.

Samples	Applied bias	Electrolyte	J (mA cm ⁻²)	References
TiO ₂ fiber	1.23 V vs. RHE	1 M NaOH	~0.18	10
TiO ₂ nanorod	0.5 V vs. Ag/AgCl	1 M NaOH	~0.82	11
TiO ₂ nanotube	0.6 V vs. Ag/AgCl	1 M NaOH	~0.5	13
Anatase TiO ₂	0.6 V vs. Ag/AgCl	KOH with 10% Methanol	~1.02	38
Branched TiO ₂	1.23 V vs. RHE	0.1 M NaOH	~1.29	39
Ni/TiO ₂	0.6 vs. Ag/AgCl	1M KOH	~0.16	40
TiO ₂ -400	1.23 V vs. RHE	0.5 M Na ₂ SO ₄	~1.23	This work

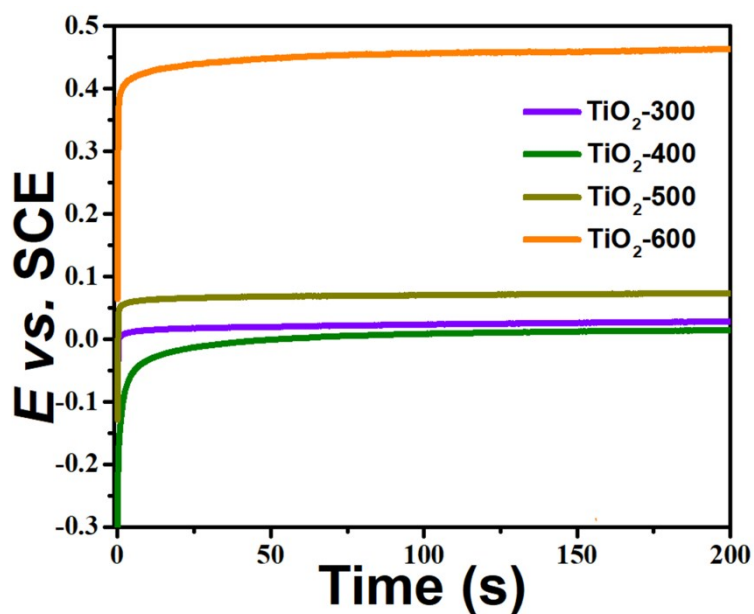


Figure S7 The measured Galvanostatic-Time curves at 0.2 mA cm⁻² for TiO₂-300, TiO₂-400, TiO₂-500 and TiO₂-600 photoanodes, respectively.

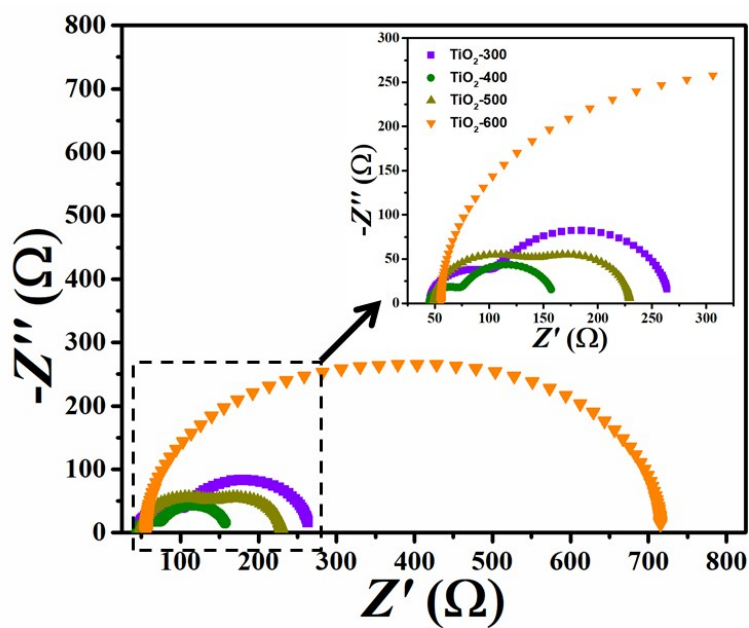


Figure S8 The fitting Nyquist plots of TiO₂-300, TiO₂-400, TiO₂-500 and TiO₂-600 photoanodes under illumination.

Table S2 Fitting EIS results of four TiO₂ photoanodes at $J= 0.2 \text{ mA cm}^{-2}$ under illumination.

pH= 7	TiO ₂ -300	TiO ₂ -400	TiO ₂ -500	TiO ₂ -600
R_1 (ohm)	60	30	90	310
C_1 (10^{-4} F)	0.12	0.35	0.10	0.04
R_2 (ohm)	160	85	90	350
C_2 (10^{-4} F)	1.0	3.5	1.0	0.14

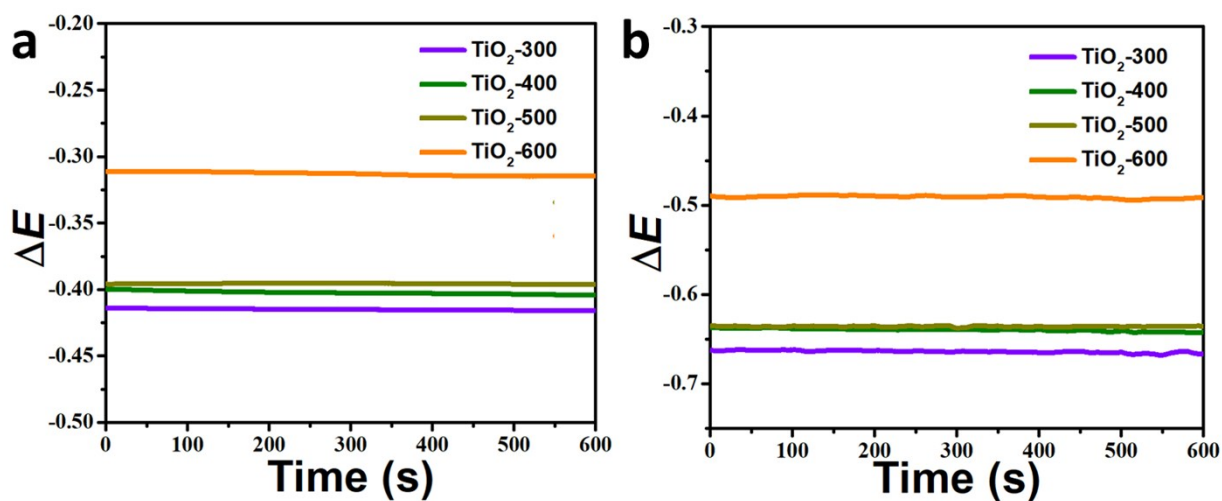


Figure S9 The measured open-circuit voltage of TiO₂-300, TiO₂-400, TiO₂-500 and TiO₂-600 photoanodes in (a) dark and in (b) light condition.