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Supplementary Information for

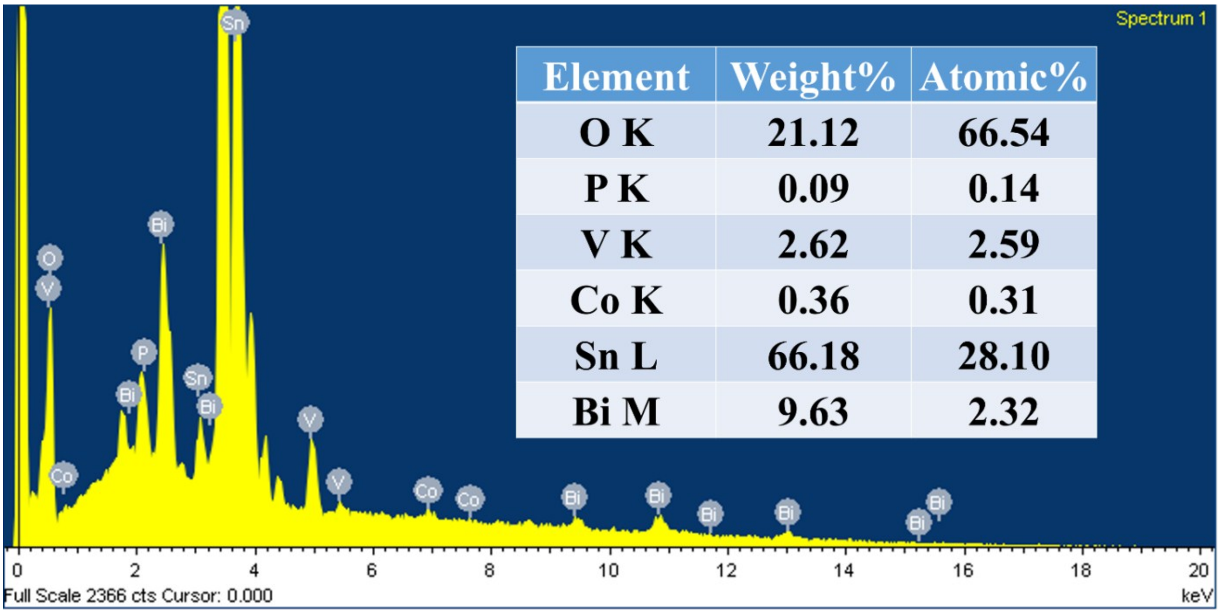
Directed Synthesis of SnO_2@$BiVO_4$/Co-Pi Photoanode for Highly Efficient Photoelectrochemical Water Splitting and Urea Oxidation

Jingchao Liu [a], Jianming Li [b], Mingfei Shao*[a] and Min Wei [a]

[a] *State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China*

[b] *Petroleum Geology Research and Laboratory Center, Research Institute of Petroleum Exploration & Development (RIPED), PetroChina, Beijing 100083, China*

**Corresponding author. E-mail: shaomf@mail.buct.edu.cn*



Element	Weight%	Atomic%
O K	21.12	66.54
P K	0.09	0.14
V K	2.62	2.59
Co K	0.36	0.31
Sn L	66.18	28.10
Bi M	9.63	2.32

Fig. S1 EDX spectra and corresponding elemental contents of SnO_2@$BiVO_4$/Co-Pi NRAs.

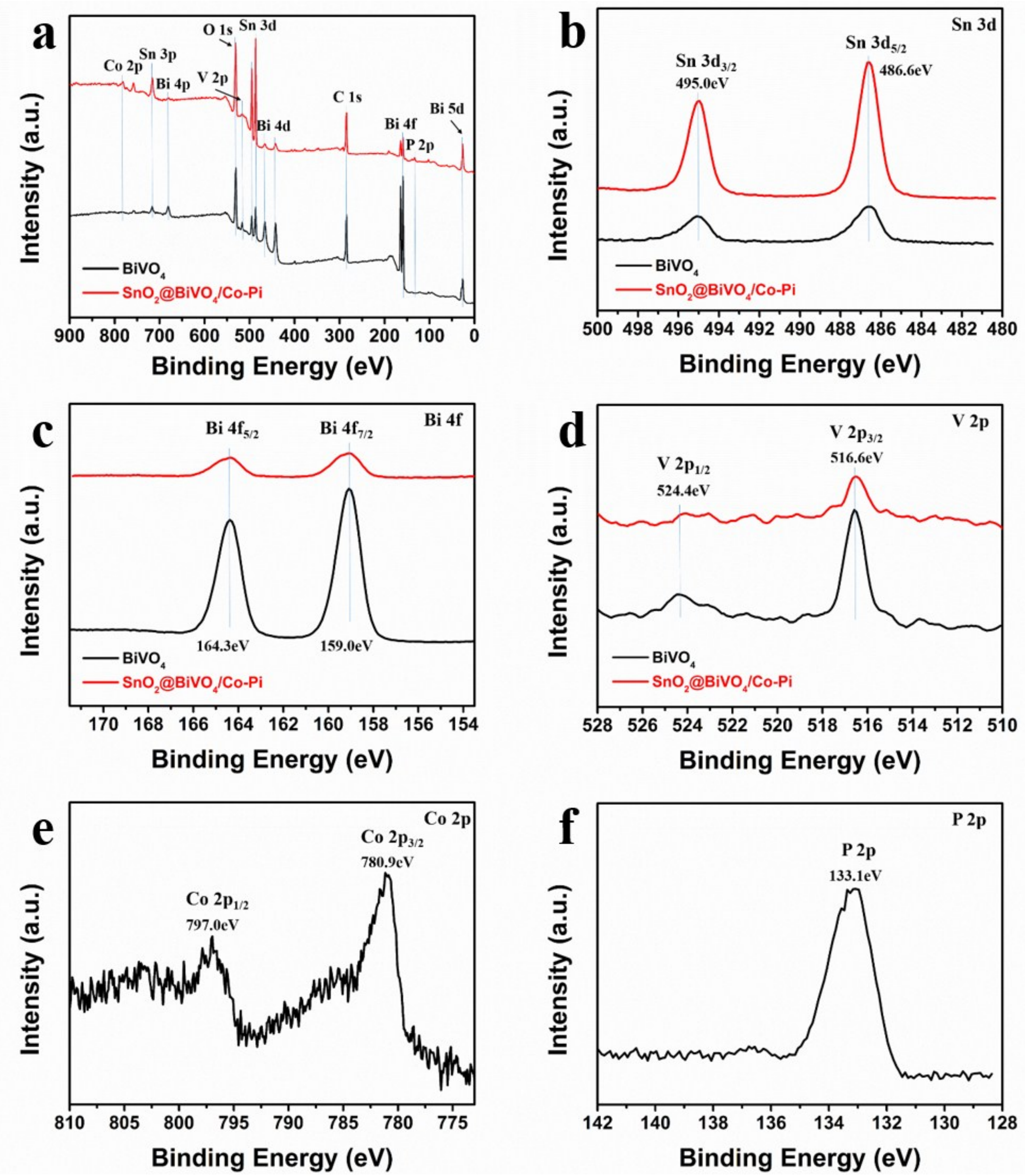


Fig. S2 XPS spectra of $BiVO_4$ and SnO_2@$BiVO_4$/Co-Pi photoanode: the survey spectrum (a) and high resolution XPS spectrum of Sn 3d (b), Bi 4f (c), V 2p (d). XPS spectra of SnO_2@$BiVO_4$/Co-Pi Photoanode: Co 2p (e) and P 2p (f).

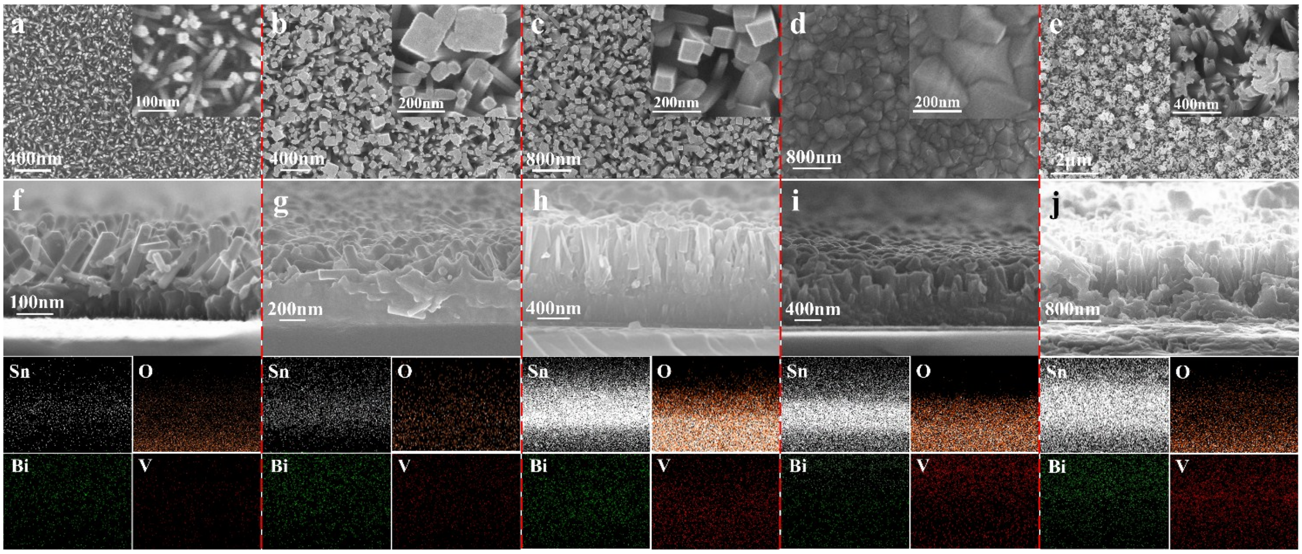


Fig. S3 Top-view SEM images of (a) 25-SnO_2, (b) 50-SnO_2, (c) 100-SnO_2, (d) 100*-SnO_2 and (e) 150-SnO_2, respectively. Cross-sectional SEM images and EDX mappings of (f) 25-SnO_2@$BiVO_4$, (g) 50-SnO_2@$BiVO_4$, (h) 100-SnO_2@$BiVO_4$, (i) 100*-SnO_2@$BiVO_4$ and (j) 150-SnO_2@$BiVO_4$, respectively.

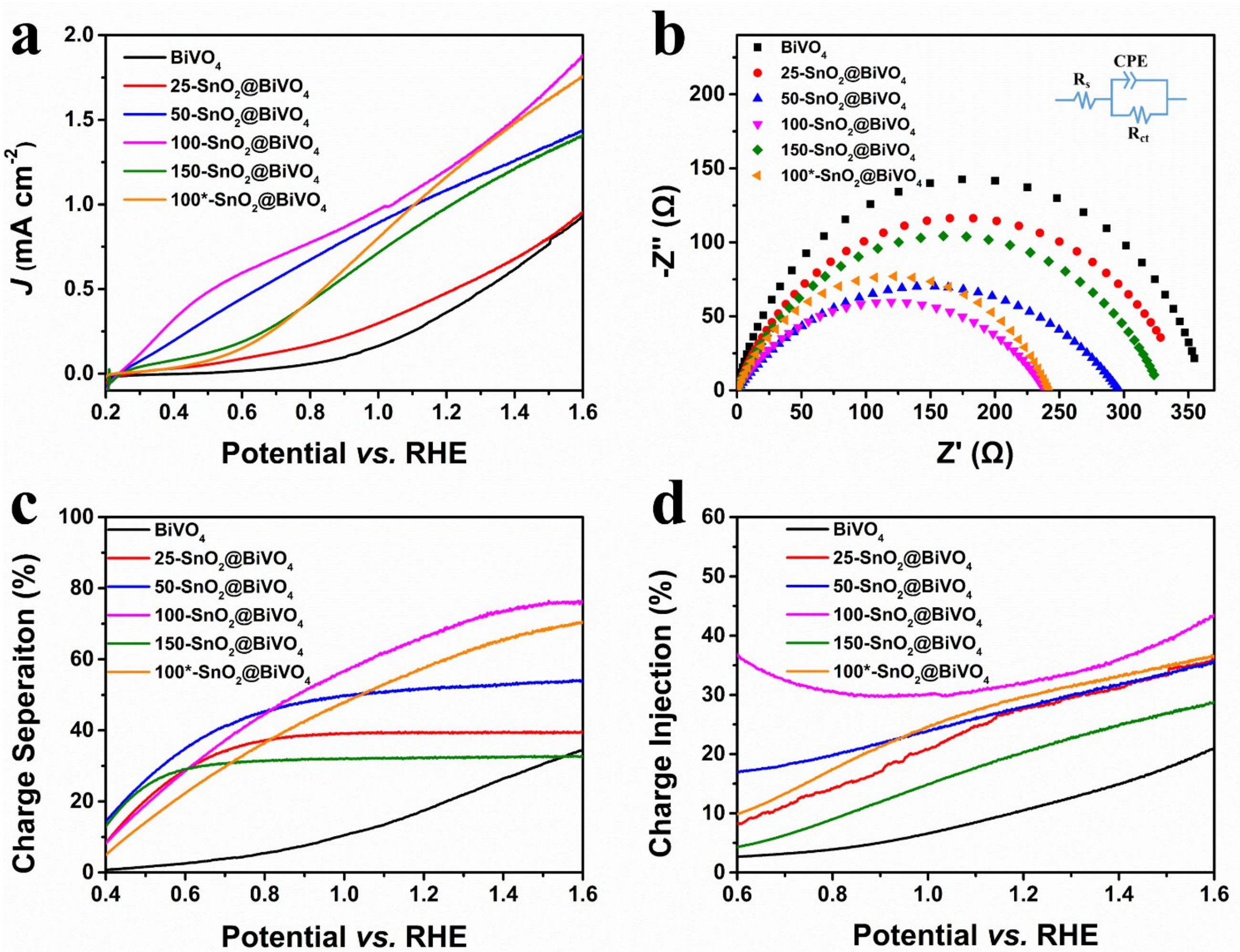


Fig. S4 (a) Current–potential curves of the photoanodes under AM 1.5 G illumination in 0.1M PBS. (b) EIS measured at 1.23 V *vs.* RHE under illumination. Inset: Corresponding equivalent circuit. R_{ct} is the charge-transfer resistance across the electrode/electrolyte interface, R_s is the solution resistance, and CPE is the constant phase component. (c) Charge separation efficiency and (d) Charge injection efficiency *vs.* potential curves for the samples of $BiVO_4$, 25-SnO_2@$BiVO_4$, 50-SnO_2@$BiVO_4$, 100-SnO_2@$BiVO_4$, 150-SnO_2@$BiVO_4$ and 100*-SnO_2@$BiVO_4$, respectively.

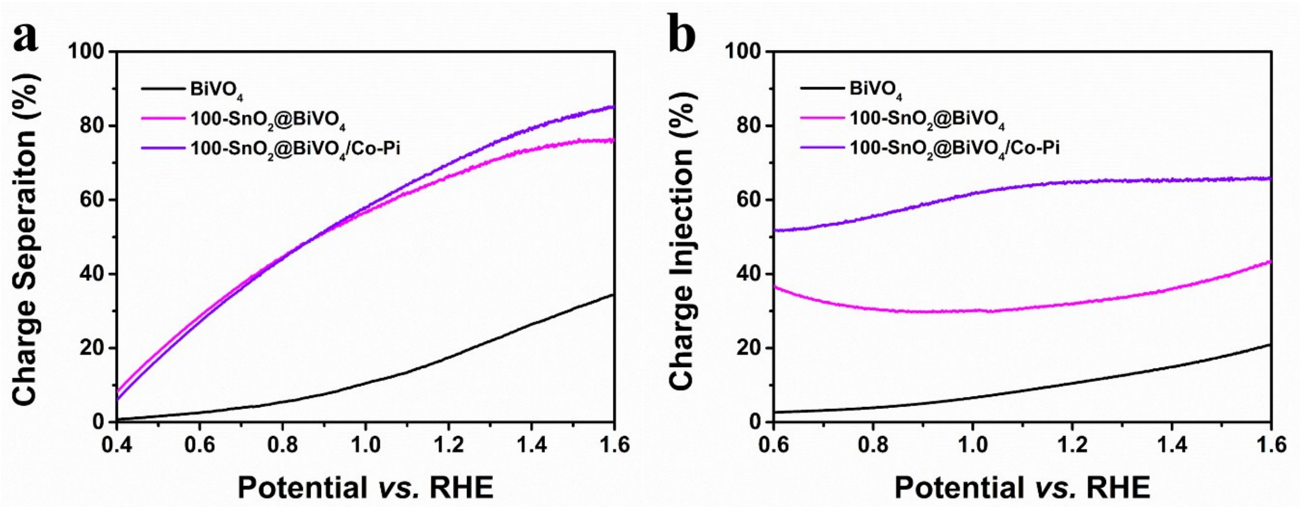


Fig. S5 (a) Charge separation efficiency and (b) Charge injection efficiency *vs.* potential curves for the samples of $BiVO_4$, 100-SnO_2@$BiVO_4$ and 100-SnO_2@$BiVO_4$/Co-Pi, respectively.

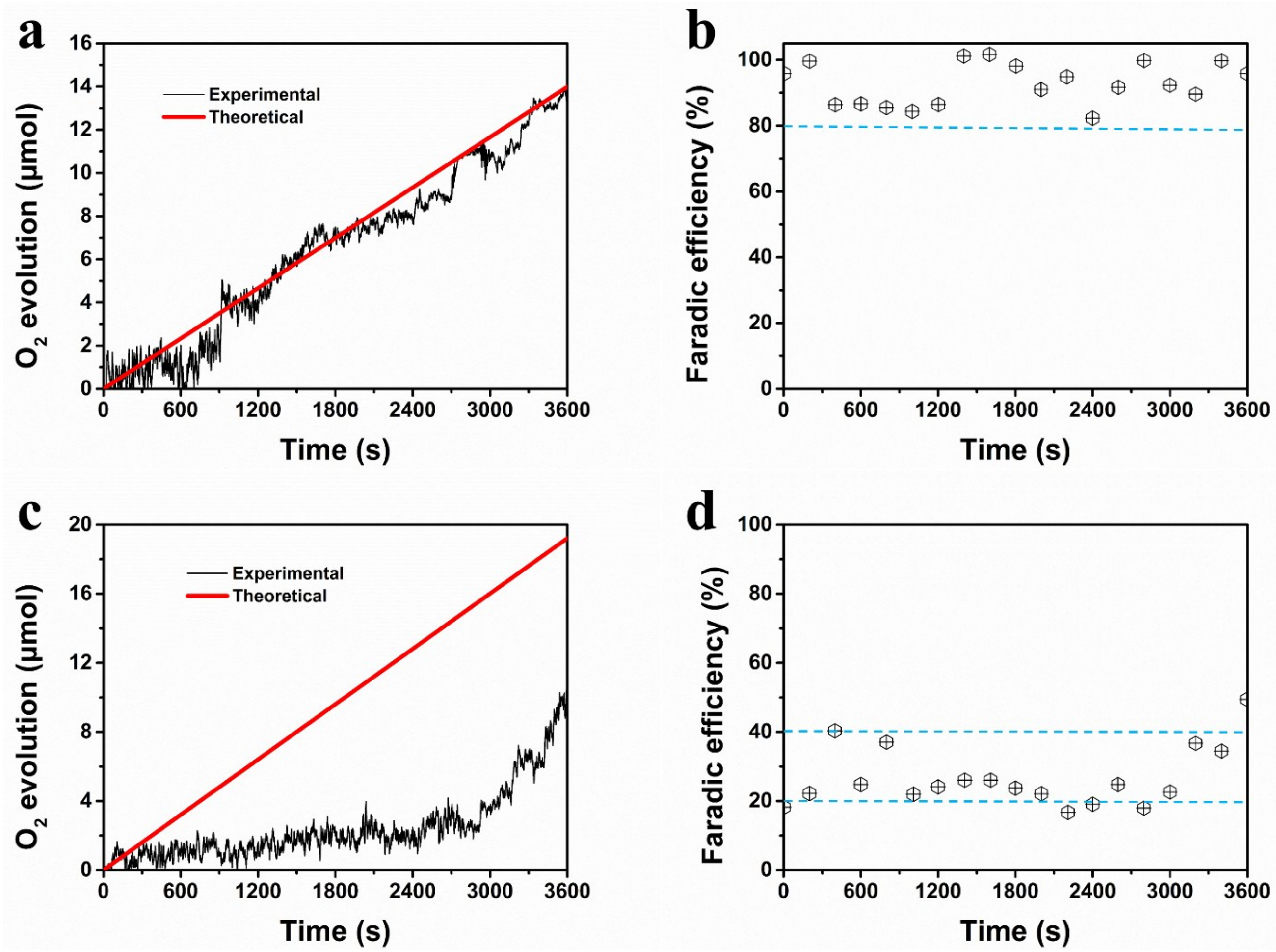


Fig. S6 (a) O_2 evolution (black curve) on SnO_2@$BiVO_4$/Co-Pi photoanode at bias of 1.23 V vs. RHE. Red line is the theoretical result based on the number of transferred electrons. (b) Faradaic efficiency of the triadic photoanode for water oxidation. Symbols represent the data calculated from the experimental results. Solution, 0.1 M PBS (pH 7); scan rate, 20 mV s^{-1}; and AM1.5G (intensity: 100 mW cm^{-2}), back-side illumination. (c) and (d) are obtained in 0.1M PBS + 2% urea.

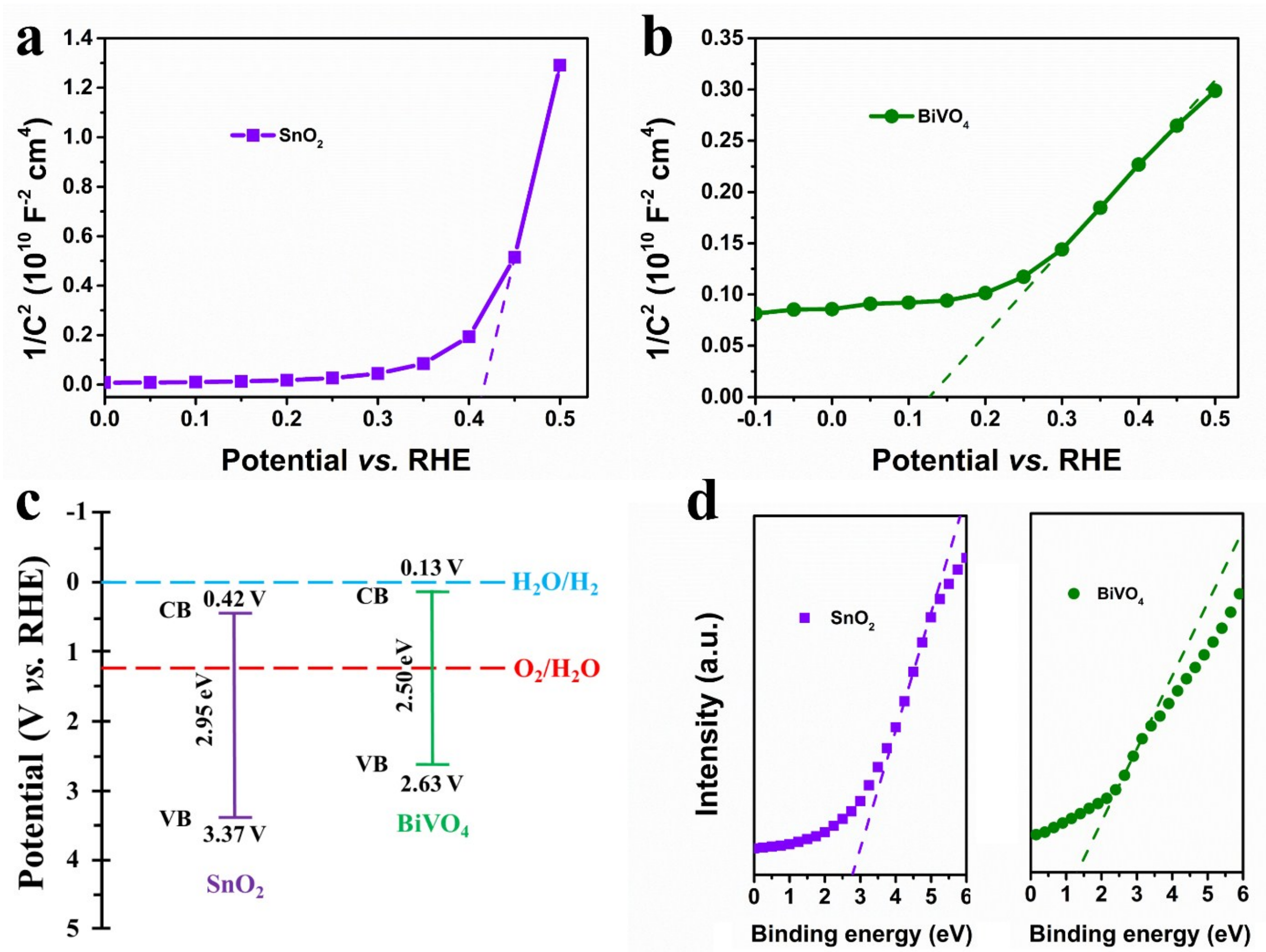


Fig. S7 Mott-Schottky curves of (a) SnO_2 and (b) $BiVO_4$. (c) Schematic illustration of the band alignment of SnO_2 and $BiVO_4$. (d) The ultraviolet photoelectron spectroscopy (UPS) for determining the valence band edge positions of SnO_2 and $BiVO_4$.

Table S1. Summary of recent key advances in $BiVO_4$-based photoanodes for PEC water splitting under AM 1.5G illumination.

Photoanode materials	Electrolyte	Photocurrent density (1.23 V vs. RHE)	Efficiency (IPCE value at 400 nm)	Stability	Ref
Mo:$BiVO_4$ /SnO_2/Si	0.5 M PBS (pH 7)	2.91	35%	~75% (30h)	1
$BiVO_4$/WO_3 /SnO_2	0.5 M Na_2SO_4 + 0.1 M NaPi (pH 7)	1.50	30%	Not given	2
Sb:SnO_2/ $BiVO_4$ NRAs	0.5 M PBS (pH 7)	1.70	Not given	~95% (1800s)	3
SnO_2/$BiVO_4$	0.5 M Na_2SO_4 + 0.1 M KPi (pH 7)	0.95	Not given	Not given	4
$BiVO_4$/SnO_2	0.2 M sodium borate (pH 9)	0.60	13.47%	~95% (300s)	5
$BiVO_4$/SnO_2 /WO_3	0.5 M PBS (pH 7)	2.38	40%	88.6% (900s)	6
SnO_2/$BiVO_4$	0.5 M Na_2SO_4 + 0.1 M NaPi (pH 7)	1.60	30%	~60% (1000s)	7
$BiVO_4$/SnO_2	0.3 M Na_2SO_4 + KPi (pH 7.5)	0.60	15%	Not given	8
C-QDs/ $BiVO_4$/SnO_2	0.5 M Na_2SO_4 (pH 6.6)	2.20	10%	~75% (3600s)	9
Fe/NiOOH-Mo:$BiVO_4$/WO_3	0.5 M Na_2SO_4 + 0.1 M Na_2SO_3 (pH 7)	5.79 ($J_{sulfite}$)	80% (sulfite)	97% (7200s)	10
Oxygen Vacancies -$BiVO_4$/CoPi	0.5 M KPi (pH 7)	3.42	Not given	~90% (10h)	11
WO_3/$BiVO_4$	0.5 M KPi (pH 7.2)	1.35	35%	Not given	12
Ni_4O_4/$BiVO_4$	0.2 M PBS (pH 7)	3.9	75%	~60% (1800s)	13
W-Doped $BiVO_4$/Co–Pi	0.1 M PBS (pH 7)	4.0	Not given	~95% (3600s)	14
Mo-Doped $BiVO_4$/Fe(Ni)OOH	0.5 M PBS (pH 7)	6.0	90%	~100% (6h)	15
SnO_2@$BiVO_4$ /Co-Pi	0.1 M PBS (pH 7)	2.63	47.4%	90.2% (3600s)	This work

* $J_{sulfite}$ means photocurrent for sulfite oxidation.

Table S2. Summary of electrochemical and PEC oxidation of urea in recent three years.

Electrode materials	Electrolyte	Onset oxidation potential	Year	Ref
Ni catalyst	0.1 M urea + 1.0 M KOH	0.35 V vs. Ag/AgCl	2016	16
Ni nanowire arrays	1.0 M urea + 6.0 M KOH	-0.2 V vs. Ag/AgCl	2016	17
Nickel Manganese Oxide	0.33 M urea + 1.0 M KOH	0.29 V vs. Ag/AgCl	2016	18
$Ni(OH)_2$ nanosheets	0.33 M urea + 1.0 M KOH	0.34 V vs. Ag/AgCl	2016	19
2D ultrathin MnO_2	0.5 M urea + 1.0 M KOH	0.32 V vs. Ag/AgCl	2016	20
Nickel phosphates	0.1 M urea + 1.0 M KOH	0.33 V vs. Ag/AgCl	2017	21
Se-$Ni(OH)_2$@NiSe	0.33 M urea + 1.0 M KOH	0.30 V vs. SCE	2017	22
Ni-Mo/graphene nanocatalysts	0.33 M urea + 1.0 M KOH	0.36 V vs. Ag/AgCl	2017	23
2D Ni-MOF	0.33 M urea + 1.0 M KOH	1.36 V vs. RHE	2017	24
MnO_2/$MnCo_2O_4$/Ni core–shell heterostructure	0.5 M urea + 1.0 M KOH	1.33 V vs. RHE	2017	25
β $Ni(OH)_2$	0.33 M urea + 1.0 M KOH	1.36 V vs. RHE	2018	26
Ni-WC/C catalyst	0.33 M urea + 1.0 M KOH	0.40 V vs. Hg/HgO	2018	27
Ni_2P@Ni foam	0.6 M urea + 5.0 M KOH	0.24 V vs. Ag/AgCl	2018	28
$NiCo_2O_4$	0.33 M urea + 1.0 M KOH	0.38 V vs. Hg/HgO	2018	29
$NiMoO_4$ nanosheets	0.5 M urea + 1.0 M KOH	0.34 V vs. Ag/AgCl	2018	30
α-$Ni(OH)_2$ nanosheets	0.33 M urea + 1.0 M KOH	0.35 V vs. Ag/AgCl	2018	31
Ni-TiO_2	0.33 M urea + 1.0 M NaOH	1.37 V vs. RHE (dark) 0.10 V vs. RHE (light)	2012	32
$Ni(OH)_2$/Ti-Fe_2O_3	0.1 M urea + 1.0 M KOH	Not given (dark) 0.50 V vs. RHE (light)	2015	33
SnO_2@$BiVO_4$/Co-Pi	0.33 M urea + 0.1 M PBS	1.60 V vs. RHE (dark) 0.20 V vs. RHE (light)	This work	

References:

(1) L. Zhang, X. Ye, M. Boloor, A. Poletayev, N. A. Melosh and W. C. Chueh, *Energy Environ. Sci.*, 2016, **9**, 2044 – 2052.

(2) S. M. López, C. Fàbrega, D. M. Satoca, M. D. H. Alonso, G. P. Pérez, A. Morata, J. R. Morante and T. Andreu, *ACS Appl. Mater. Interfaces* 2016, **8**, 4076 − 4085.

(3) L. Zhou, C. Zhao, B. Giri, P. Allen, X. Xu, H. Joshi, Y. Fan, L. V. Titova and P. M. Rao, *Nano Lett.* 2016, **16**, 3463 − 3474.

(4) S. Byun, B. Kim, S. Jeon and B. Shin, *J. Mater. Chem. A*, 2017, **5**, 6905 – 6913.

(5) M. Xie, Z. Zhang, W. Han, X. Cheng, X. Li and E. Xie, *J. Mater. Chem. A*, 2017, **5**, 10338 – 10346.

(6) J. H. Baek, B. J Kim, G. S. Han, S. W. Hwang, D. R. Kim, I. S. Cho and H. S. Jung, *ACS Appl. Mater. Interfaces* 2017, **9**, 1479 − 1487.

(7) S. S. M. Bhat, J. M. Suh, S. Choi, S. Hong, Sol A. Lee, C. Kim, C. W. Moon, M. G. Lee and H. W. Jang, *J. Mater. Chem. A*, 2018, **6**, 14633 – 14643.

(8) S. Chen, J. Yang and J. Wu, *ACS Appl. Energy Mater.* 2018, **1**, 2143 − 2149.

(9) Z. Zhang, X. Jiang, J. Mei, Y. Li, W. Han, M. Xie, F. Wang and E. Xie, *Chem. Eng.J.* 2018, **331**, 48 – 53.

(10) K. Kim, S. K. Nam, J. H. Park and J. H. Moon, *J. Mater. Chem. A* 2019, DOI: 10.1039/c8ta09886g.

(11) S. Byun, G. Jung, Y. Shi, M. Lanza and B. Shin, *Adv. Funct. Mater.* 2019, 1806662. DOI: 10.1002/adfm.201806662.

(12) Y. Liu, B. R. Wygant, K. Kawashima, O. Mabayoje, T. E. Hong, S. Lee, J. Lin, J. Kim, K. Yubuta, W. Li, J. Li and C. B. Mullins, *Appl. Catal. B- Environ.* 2019, **245**, 227 – 239.

(13) B. Gao, T. Wang, X. Fan, H. Gong, P. Li, Y Feng, X Huang, J He and J. Ye, *J. Mater. Chem. A*, 2019, **7**, 278–288.

(14) L. Han, F. F. Abdi, R. van de Krol, R. Liu, Z. Huang, H.-J. Lewerenz, B. Dam, M. Zeman and A. H. M. Smets, *ChemSusChem*, 2014, **7**, 2832 – 2838.

(15) S. Xiao, C. Hu, H. Lin, X. Meng, Y. Bai, T. Zhang, Y. Yang, Y. Qu, K. Yan, J. Xu, Y. Qiu and S. Yang, *J. Mater. Chem. A*, 2017, **5**, 19091 – 19097.

(16) F. Guo, K. Ye, M. Du, X. Huang, K. Cheng, G. Wang and D. Cao, *Electrochim. Acta.* 2016, **210**,

474 − 482.

(17) F. Guo, K. Ye, M. Du, K. Cheng, Y. Cao, G. Wang and D. Cao, *Electrochim. Acta.* 2016, **190**, 150 − 158.

(18) S. Periyasamy, P. Subramanian, E. Levi, D. Aurbach, A Gedanken and A. Schechter, *ACS Appl. Mater. Interfaces* 2016, **8**, 12176 −12185.

(19) X. Zhu, X. Dou, J. Dai, X. An, Y. Guo, L. Zhang, S. Tao, J. Zhao, W. Chu, X. Zeng, C. Wu, and Y Xie, *Angew. Chem.* 2016, **128**, 12653 –12657.

(20) S. Chen, J. Duan, A. Vasileff and S. Qiao, *Angew. Chem. Int. Ed.* 2016, **55**, 3804 –3808.

(21) X. Song, L. Gao, Y. Li, W. Chen, L. Mao and J. Yang, *Electrochim. Acta.* 2017, **251**, 284 − 292.

(22) C. Tang, Z. Zhao, J. Chen, B. Li, L. Chen and C. Li, *Electrochim. Acta.* 2017, **248**, 243 − 249.

(23) W. Shi, R. Ding, X. Li, Q. Xu and E. Liu, *Electrochim. Acta.* 2017, **242**, 247 − 259.

(24) D. Zhu, C. Guo, J. Liu, L. Wang, Y. Du and S. Qiao, *Chem. Commun.*, 2017, **53**, 10906 – 10909.

(25) C. Xiao, S. Li, X. Zhang and D. R. MacFarlane, *J. Mater. Chem. A*, 2017, **5**, 7825–7832.

(26) R. K. Singh and A. Schechter, *Electrochim. Acta.* 2018, **278**, 405 − 411.

(27) L. Wang, S. Zhu, N. Marinkovic, S. Kattel, M. Shao, B. Yang and J. G. Chen, *Appl. Catal. B-Environ.* 2018, **232**, 365 – 370.

(28) G. Wang, K. Ye, J. Shao, Y. Zhang, K. Zhu, K. Cheng, J. Yan, G. Wang and D. Cao, *Int. J. Hydrogen Energy,* 2018, **43**, 9316 − 9325.

(29) A. Schranck, R. Marks, E. Yates and K. Doudrick, *Environ. Sci. Technol.* 2018, **52**, 8638 − 8648.

(30) Y. Tong, P. Chen, M. Zhang, T. Zhou, L. Zhang, W. Chu, C. Wu, and Y. Xie, *ACS Catal.* 2018, **8**, 1 − 7.

(31) C. Lin, Z. Gao, F. Zhang, J Yang, B. Liu and J. Jin, *J. Mater. Chem. A*, 2018, **6**, 13867 – 13873.

(32) G. Wang, Y. Ling, X. Lu, H. Wang, F. Qian, Y. Tong and Yat Li, *Energy Environ. Sci.*, 2012, **5**, 8215 − 8219.

(33) D. Xu, Z. Fu, D. Wang, Y. Lin, Y. Sun, D. Meng and T. Xie, *Phys. Chem. Chem. Phys.*, 2015, **17**, 23924 − 23930.