# **Supporting Information**

## Effect of Sn Valence State in situ-growth of FeOOH Precursor on

## Performance of α-Fe<sub>2</sub>O<sub>3</sub> Photoanode

Weiwei Xia<sup>a\*</sup>, Zichun Chai<sup>Ta</sup>, Rui Zhang<sup>a</sup>, Junhui He<sup>a</sup>, Xianghua Zeng<sup>a,b\*</sup>

<sup>a</sup> College of Physics Science and Technology & Institute of Optoelectronic Technology, Yangzhou University, Yangzhou 225002, P.R. China

<sup>b</sup> College of Electrical, Energy and Power Engineering, Yangzhou University, Yangzhou 225127, P. R.

China

### **Supporting Information**

Results and discussion

Figure S1. Tauc's plots of the synthesized Fe<sub>2</sub>O<sub>3</sub>, Sn<sup>2+</sup>-Fe<sub>2</sub>O<sub>3</sub> and Sn<sup>4+</sup>-Fe<sub>2</sub>O<sub>3</sub> films.

		Table 51. Relative percentage of 51 for $1^{\circ}c_{2}o_{3}$ , 51 $-1^{\circ}c_{2}o_{3}$ and 51 $-1^{\circ}c_{2}o_{3}$ finits.				
_		Fe	0	Sn		
	Samples	At%	At%	At%		
_	Fe <sub>2</sub> O <sub>3</sub>	24.07	75.93	*		
	Sn <sup>2+</sup> -Fe <sub>2</sub> O <sub>3</sub>	20.82	68.74	10.44		
	Sn <sup>4+</sup> -Fe <sub>2</sub> O <sub>3</sub>	21.45	77.90	0.65		

Table S1. Relative percentage of Sn for Fe<sub>2</sub>O<sub>3</sub>, Sn<sup>2+</sup>-Fe<sub>2</sub>O<sub>3</sub> and Sn<sup>4+</sup>-Fe<sub>2</sub>O<sub>3</sub> films.

Table S2. Relative percentage of  $O_L$  and  $O_V$  components for  $Fe_2O_3$ ,  $Sn^{2+}$ - $Fe_2O_3$  and  $Sn^{4+}$ - $Fe_2O_3$  films.

	0	L	0	$\mathbf{v}$
Samples	BE	At%	BE	At%
Fe <sub>2</sub> O <sub>3</sub>	529.63	51.50	531.44	48.50
Sn <sup>2+</sup> -Fe <sub>2</sub> O <sub>3</sub>	529.93	60.98	531.51	39.02

\* Corresponding authors. Email: <u>www.ia@yzu.edu.cn;</u> <u>xhzeng@yzu.edu.cn</u>

Sn <sup>4+</sup> -Fe <sub>2</sub> O <sub>3</sub>	529.47	43.35	531.38	56.65	
					_

Material/	Electrolyte IPCE (%)	Photocurrent	Annealing	
Reference		IFCE (70)	density(mA/cm <sup>2</sup> )	temperature/Time
Sn-Fe <sub>2</sub> O <sub>3</sub>	1M NaOH	$23.7 (1.4 V_{RHE})$	$1.63 (1.4 V_{RHE})$	800°C/10min
nanostructures <sup>[1]</sup>				
E-I-Sn-Fe <sub>2</sub> O <sub>3</sub>	1M KOH	$27~(0.23V_{Ag/AgCl})$	$1.36 \ (0.23 V_{Ag/AgCl})$	800°C/20min (HF
NWs <sup>[2]</sup>				Etching SiO <sub>2</sub>
				encapsulation)
Sn-Fe <sub>2</sub> O <sub>3</sub>	1M NaOH	19.8 (1.23V <sub>RHE</sub> )	$1.86 (1.23 V_{RHE})$	800°C/20min
nanocorals <sup>[3]</sup>				
Sn-Fe <sub>2</sub> O <sub>3</sub> <sup>[4]</sup>	1M NaOH	$17 (1.23 V_{RHE})$	$0.86 (1.23 V_{RHE})$	800°C/20min
Sn-Fe <sub>2</sub> O <sub>3</sub>	1M NaOH		$1.35 (1.23 V_{RHE})$	800°C/10min
nanorod <sup>[5]</sup>				
Sn-Fe <sub>2</sub> O <sub>3</sub>	1M NaOH		$1.00 (1.23 V_{RHE})$	800°C/10min
nanorod <sup>[6]</sup>				
Sn-Fe <sub>2</sub> O <sub>3</sub>	1M KOH	$22 (1.23 V_{RHE})$	$0.93 (1.23 V_{RHE})$	800°C/3min
nanorod <sup>[7]</sup>				
Sn-Fe <sub>2</sub> O <sub>3</sub>	1M NaOH		$0.65 (1.23 V_{RHE})$	750°C/30min
nanotubes <sup>[8</sup> ]				
Sn-Fe <sub>2</sub> O <sub>3</sub> <sup>[9]</sup>	1M NaOH		$0.96 (1.23 V_{RHE})$	750°C/15min
Sn(8%)-Fe <sub>2</sub> O <sub>3</sub> <sup>[10]</sup>	1M KOH	9.9 (1.6V <sub>RHE</sub> )	$0.298 (1.6V_{RHE})$	600°C/240min

Table S3. Comparison of PEC performance and morphology for different hematite reported previously.



Figure S2. Cyclic voltammetry (CV) for  $Fe_2O_3$ ,  $Sn^{2+}$ - $Fe_2O_3$  and  $Sn^{4+}$ - $Fe_2O_3$  photoanodes at various scan rates.

Figure S3. EIS Nyquist for Fe<sub>2</sub>O<sub>3</sub>, Sn<sup>2+</sup>-Fe<sub>2</sub>O<sub>3</sub> and Sn<sup>4+</sup>-Fe<sub>2</sub>O<sub>3</sub> photoanodes.

#### Reference

[1] A. Annamalai, P.S. Shinde, T.H. Jeon, H.H. Lee, H.G. Kim, W. Choi, J.S. Jang, Fabrication of superior  $\alpha$ -Fe2O3 nanorod photoanodes through ex-situ Sn-doping for solar water splitting, Solar Energy Materials and Solar Cells, 144 (2016) 247-255.

[2] M. Li, Y. Yang, Y. Ling, W. Qiu, F. Wang, T. Liu, Y. Song, X. Liu, P. Fang, Y. Tong, Y. Li, Morphology and Doping Engineering of Sn-Doped Hematite Nanowire Photoanodes, Nano Letters, 17 (2017) 2490-2495.

[3] Y. Ling, G. Wang, D.A. Wheeler, J.Z. Zhang, Y. Li, Sn-Doped Hematite Nanostructures for Photoelectrochemical Water Splitting, Nano Letters, 11 (2011) 2119-2125.

[4] A.G. Tamirat, W.-N. Su, A.A. Dubale, H.-M. Chen, B.-J. Hwang, Photoelectrochemical water splitting at low applied potential using a NiOOH coated codoped (Sn, Zr)  $\alpha$ -Fe2O3 photoanode, J. Mater. Chem. A, 3 (2015) 5949-5961.

[5] H. Ma, M.A. Mahadik, J.W. Park, M. Kumar, H.S. Chung, W.S. Chae, G.W. Kong, H.H. Lee, S.H. Choi, J.S. Jang, Highly self-diffused Sn doping in  $\alpha$ -Fe2O3 nanorod photoanodes initiated from  $\beta$ -FeOOH nanorod/FTO by hydrogen treatment for solar water oxidation, Nanoscale, 10 (2018) 22560-22571.

[6] A. Annamalai, H.H. Lee, S.H. Choi, S.Y. Lee, E. Gracia-Espino, A. Subramanian, J. Park, K.-j. Kong, J.S. Jang, Sn/Be Sequentially co-doped Hematite Photoanodes for Enhanced Photoelectrochemical Water Oxidation: Effect of Be2+ as co-dopant, Scientific Reports, 6 (2016).

[7] J. Wang, C. Du, Q. Peng, J. Yang, Y. Wen, B. Shan, R. Chen, Enhanced photoelectrochemical water splitting performance of hematite nanorods by Co and Sn co-doping, Int. J. Hydrog. Energy, 42 (2017) 29140-29149.

[8] S.-F. Duan, Y.-Y. Geng, X.-B. Pan, X.-Q. Yao, Y.-X. Zhao, X. Li, C.-L. Tao, D.-D. Qin, Tubular morphology preservation and doping engineering of Sn/P-codoped hematite for photoelectrochemical water oxidation, Dalton Transactions, 48 (2019) 928-935.

[9] J. Cai, H. Chen, C. Liu, S. Yin, H. Li, L. Xu, H. Liu, Q. Xie, Engineered Sn- and Mg-doped hematite photoanodes for efficient photoelectrochemical water oxidation, Dalton Transactions, 49 (2020) 11282-11289.

[10] T.H. Jeon, H.-i. Cho, H. Park, H.-i. Kim, W. Choi, Synergistic effect of Sn doping and hydrogenation on hematite electrodes for photoelectrochemical water oxidation, Materials Chemistry Frontiers, 5 (2021) 6592-6602.