## **Supporting Information for**

# Effect of Sn-self Diffusion via H2 Treatment on Low

## Temperature Activation of Hematite Photoanode

Haiqing Ma,<sup>§,a</sup> Jeong An Kwon,<sup>§,b</sup> Mahadeo A. Mahadik,<sup>a</sup> Sarang Kim <sup>a</sup> Hyun Hwi Lee,<sup>c</sup> Sun Hee Choi,<sup>c</sup> Weon-Sik Chae,<sup>d</sup> Dong-Hee Lim<sup>b,\*</sup> and Jum Suk Jang<sup>a,\*</sup>

<sup>a</sup> Division of Biotechnology, College of Environmental and Bioresource Sciences, Chonbuk National University, Iksan 54596, Republic of Korea.

<sup>b</sup> Department of Environmental Engineering, Chungbuk National University, Cheongju, 28644, Republic of Korea.

<sup>c</sup> Pohang Accelerator Laboratory (PAL), Pohang University of Science and Technology (POSTECH), Pohang 37673, Republic of Korea.

<sup>d</sup> Korea Basic Science Institute, Daegu Center, Daegu 41566, Republic of Korea.

<sup>§</sup>Authors with equal contribution.

### \* Corresponding authors

Tel.: +82 63 850 0846; fax: +82 63 850 0834.

\*E-mail: jangjs75@jbnu.ac.kr (J. S. J.). \*E-mail: limkr@cbnu.ac.kr (D. H. L.).

	A type s	ample	H type sample		
	<i>D,</i> ε, Crystallite Size Micro-strain		<i>D,</i> Crystallite Size	<i>є,</i> Micro-strain	
650°C	248 nm	17.3X10 <sup>-4</sup>	184 nm	21.6X10 <sup>-4</sup>	
700°C	263 nm	12.7X10 <sup>-4</sup>	178 nm	19.0X10 <sup>-4</sup>	
750°C	230 nm	8.3X10 <sup>-4</sup>	173 nm	18.4X10 <sup>-4</sup>	
800°C	239 nm	5.4X10 <sup>-4</sup>	196 nm	16.9X10 <sup>-4</sup>	
variation	< 5%	68%↓	< 7%	22%↓	

**Table S1.** Hematite crystallite size (D) and mean micro-strain  $(\varepsilon)$  determined from Williamson-Hall plots.

Sample	Fe (At %)	O (At %)	Sn (At %)
A650	33.1	66.8	0.09
A700	32.9	66.9	0.16
A800	31.4	68.0	0.51
H650	30.7	66.7	2.66
H700	31.0	66.1	2.90
H800	28.7	66.7	4.52
β-FeOOH	30.0	69.9	0
Fe <sub>3</sub> O <sub>4</sub>	28.6	67.3	4.01

Table S2. Atomic percentages of elements in the as-prepared samples were obtained by XPS.

Sample	$E_{g}(eV)$
A650	2.14
A700	2.16
A750	2.10
A800	2.09
H650	2.17
H700	2.18
H750	2.11
H800	2.11

**Table S3.** Band gap energy  $(E_g)$  obtained from direct transaction of Tauc analysis for the asprepared samples.

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Sample	J (mA/cm <sup>2</sup> ) at 1.23 V vs. RHE	$J (mA/cm^2)$ at 1.4 V vs. RHE		
A650	0.04	0.04		
A700	0.23	0.28		
A750	0.74	0.96		
A800	0.89	1.15		
H650	1.17	1.48		
H700	1.35	1.79		
H750	1.29	1.87		
H800	1.30	1.89		
Sn650	0.05	0.05		
Sn700	0.73	0.86		
Sn750	1.23	1.69		
Sn800	1.01	1.49		

**Table S4.** The photocurrents of A-type samples, H-type samples and ex-situ Sn-doped hematite samples at 1.23 V *vs.* RHE and 1.4 V *vs.* RHE were from *J-V* curves.

Sample	$N_{\rm D}({\rm cm}^{-3})$
A650	3.26 x 10 <sup>19</sup>
A700	4.64 x 10 <sup>19</sup>
A750	$1.26 \ge 10^{20}$
A800	$1.52 \ge 10^{20}$
H650	$2.20 \ge 10^{20}$
H700	2.94 x 10 <sup>20</sup>
H750	8.82 x 10 <sup>20</sup>
H800	8.82 x 10 <sup>20</sup>

**Table S5.** Donor density  $(N_{\rm D})$  calculated from Mott-Schottky plots for the as-prepared samples.

Synthetic technique	Heat treatment condition	J <sub>ph</sub> (mA/cm <sup>2</sup> ) at 1.23 V vs. RHE	$J_{ph}$ (mA/cm <sup>2</sup> ) at 1.4 V vs. RHE	
Electrodeposited nanowire networks with post-Ti doping <sup>[8]</sup>	at 650°C for 1 h	0.48	0.82	
Chemical bath deposited nanorods	at 550°C for 30 min	0.61	1 45	
with TiO <sub>2</sub> underlayer <sup>[9]</sup>	& 600°C for 30 min	0.01	1.10	
Hydrothermally deposited	at 350°C for 1 h (N <sub>2</sub> )		0.10	
nanowires <sup>[34]</sup>	& 350°C for 30 min	0.03		
	(air)			
	at 450°C for 2 h (air)		0.13	
Spin-coated ultrathin films <sup>[54]</sup>	& 450°C for 2 h (5%	0.06		
	H <sub>2</sub> in Ar)			
	at 400°C for 4 h			
Hydrothermally deposited thin	(alkene reduction)	0.45	0.88	
films <sup>[55]</sup>	& 500°C for 0.5 h	0.43	0.88	
	(air)			
Spin coated thin films <sup>[56]</sup>	at 650°C for 1 h	0.38	0.44	
Chemical bath deposited nanorods	at 600°C for 2 h	0.95	1.0	
on SnO <sub>2</sub> backbone <sup>[60]</sup>	& 650°C for 24 h	0.83	1.0	
Hydrothermally nanorods ( In this work )deposited	at 360°C for 1 h (H <sub>2</sub> ) and 650°C for 10 min (air)	1.17	1.48	

**Table S6.** Comparative photocurrents ( $J_{ph}$ ) of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photoanodes prepared by different synthetic methods without high-temperature activation.

Sample	$A_{1}\left(\%\right)$	$\tau_1$ (ns)	$A_{2}\left(\%\right)$	$\tau_{2}\left(ns\right)$	<\mathcal{\tau} < (ns)
A650	98.6	0.23	1.4	3.35	0.78
A700	97.8	0.24	2.2	3.87	1.22
H650	96.4	0.22	3.6	4.25	1.88
H700	96.1	0.23	3.9	4.60	2.15

**Table S7.** PL lifetime parameters of hematite nanorod photoanodes prepared at differentconditions (A650, A700, H650 and H700), respectively.



Fig. S1 XRD profiles of  $\beta$ -FeOOH and Fe<sub>3</sub>O<sub>4</sub>. Diffraction peaks for SnO<sub>2</sub> (JCPDS 77-0452), akaganeite (JCPDS 75-1594), and magnetite (JCPDS 19-0629) are labeled with F, A, and M, respectively.



Fig. S2 XPS Sn3d spectra of  $\beta$ -FeOOH and Fe<sub>3</sub>O<sub>4</sub>.



**Fig. S3** Top view and cross-sectional FESEM images of (A) A-type samples (a) A650, (b) A700, (c) A750, (d) A800 and (B) H-type samples (a) H650, (b) H700, (c) H750, (d) H800.



Fig. S4 Top view and cross-sectional FESEM images of (a)  $\beta$ -FeOOH, and (b) Fe<sub>3</sub>O<sub>4</sub> photoanodes



**Fig. S5** The plots of absorbance versus wavelength for (a) A650, A700, A750, A800 and (b) H650, H700, H750, H800. The inset fig. 5(a, b) represents Tauc plots for the determination of optical band gap for each sample.



**Fig. S6** (a) Photocurrent density-voltage curves of A650, Sn650, and H650. (b) Photocurrent density-voltage curves of A700, Sn700, and H700.



**Fig. S7** (a) Photocurrent density-voltage (*J-V*) curves, and (b) transient photocurrent responses of A700 and H700 photoanodes measured at 1.4 V *vs.* RHE during on/off condition.



**Fig. S8** Photoelectrochemical stability curves of A700 and H700 recorded under one sun illumination at 1.4 V *vs.* RHE for 1 h.



Fig. S9 Complex plane plots of the IMPS responses for A700 and H700 at 1.2 V vs. RHE.

### **DFT Section**

#### 1. Lattice parameters of akaganeite depending on Cl<sup>-</sup> occupancy

The lattice parameters of akaganeite are varied depending on the number of Cl<sup>-</sup> ion occupancy.<sup>[S1]</sup> The akaganeite bulk structures with one and two Cl<sup>-</sup> ions (Fe<sub>8</sub>O<sub>16</sub>H<sub>8</sub>ClH and Fe<sub>8</sub>O<sub>16</sub>H<sub>8</sub>Cl<sub>2</sub>H<sub>2</sub> charge-balanced by cosorbed protons (H<sup>+</sup>), respectively) were optimized and the relative stability ( $^{E}_{stab}$ ) of the two structures upon Cl<sup>-</sup> insertion were compared by Equation (S1).  $^{E}_{stab}$  was -7.74 eV, indicating that another Cl<sup>-</sup> ion insertion into bulk Fe<sub>8</sub>O<sub>16</sub>H<sub>8</sub>ClH was thermodynamically stable.

$$E_{stab} = E_{Fe_8 O_{16} H_8 Cl_2 H_2} - \left( E_{Fe_8 O_{16} H_8 Cl_1 H_1} + \frac{E_{Cl_2}}{2} + \frac{E_{H_2}}{2} \right)$$
(S1)

where,  ${}^{E_{Fe_8}o_{16}H_8Cl_2H_2}$ ,  ${}^{E_{Fe_8}o_{16}H_8Cl_1H_1}$ ,  ${}^{E_{Cl_2}}$ , and  ${}^{E_{H_2}}$  are the total DFT energies of bulk Fe<sub>8</sub>O<sub>16</sub>H<sub>8</sub>Cl<sub>2</sub>H<sub>2</sub>, bulk Fe<sub>8</sub>O<sub>16</sub>H<sub>8</sub>Cl<sub>1</sub>H<sub>1</sub>, Cl<sub>2</sub>, and H<sub>2</sub>, respectively.

Although both bulk Fe<sub>8</sub>O<sub>16</sub>H<sub>8</sub>Cl<sub>2</sub>H<sub>2</sub> and bulk Fe<sub>8</sub>O<sub>16</sub>H<sub>8</sub>Cl<sub>1</sub>H<sub>1</sub> can be used for the DFT modeling of the current study, we employed the Fe<sub>8</sub>O<sub>16</sub>H<sub>8</sub>Cl<sub>2</sub>H<sub>2</sub> structure because of the thermodynamic stability upon two Cl<sup>-</sup> ion insertion and more accurate reproducibility of the lattice parameters (Fig. S10). The DFT-calculated lattice parameters of bulk Fe<sub>8</sub>O<sub>16</sub>H<sub>8</sub>Cl<sub>1</sub>H<sub>1</sub> containing one Cl<sup>-</sup> and H<sup>+</sup> ions were predicted as a = 10.494 Å, b = 2.991 Å, c = 9.952 Å,  $\alpha = \gamma = 90^{\circ}$ , and  $\beta = 91.3^{\circ}$  with error percent ( $\varepsilon$ ) of  $\varepsilon_a = -1.00 \sim 0.13$  %,  $\varepsilon_b = -2.52 \sim -1.08$  %,  $\varepsilon_c = -5.64 \sim -5.20$  %, and  $\varepsilon_{\beta} = 1.30 \sim 2.21$  % for the experimental values, <sup>[S2-S4]</sup> and with  $\varepsilon_a = -1.01 \sim 0.13$  %,  $\varepsilon_b = -1.45 \sim -1.08$  %,  $\varepsilon_c = -5.64 \sim -5.30$  %,  $\varepsilon_{\beta} = 1.30$  % for the theoretical lattice stability is a stability of the theoretical lattice stability is a stability of the stability of the stability of the stability of the theoretical lattice stability of the stability of the theoretical stability of the theoretical stability of the stability of the theoretical lattice stability of the theoretical lattice stability of the theoretical stability of the theoretical stability of the theoretical lattice stability of the theoretical lattice stability of the theoretical lattice stability of the stability of the theoretical lattice stability of the stability of the stability of the stability of the theoretical lattice stability of the stability o

values<sup>[S4-S6]</sup> (where  $\varepsilon_a$ ,  $\varepsilon_b$ ,  $\varepsilon_c$ , and  $\varepsilon_\beta$  represent the error rates of lattice parameters of *a*, *b*, *c*, and  $\beta$ , respectively.



**Fig. S10** Top (A) and C)) and side (B) and D)) views of the optimized akageneite structures of  $Fe_8O_{16}H_8ClH$  (A) and B)) and  $Fe_8O_{16}H_8Cl_2H_2$  (C) and D)), respectively. Brown, red, light green and white spheres represent Fe, O, Cl and H, respectively.

#### 2. Bader charges of the constituting atoms in magnetite and akaganeite

Table S8 and table S9 show the Bader charges and excess Bader charges of the constituting atoms in magnetite and akaganeite, respectively. The excess Bader charge was calculated by subtracting the Bader charges of the bulk structure from those of the Sn-replaced structure. Positive and negative excess Bader charge values represent the gain and loss of the charge upon the Sn replacement, respectively.

The locations for replacing a Fe atom with a Sn atom were determined based on the Bader charge analysis. Based on the number of O atoms adjacent to a Fe atom, there are two types of Fe sites in magnetite and akaganeite: octahedral-sites and tetrahedral-sites. Fe atoms at octahedral and tetrahedral-sites are located in the center of the octahedron and the tetrahedron in which neighboring oxygen atoms are located at six and four vertices, respectively. Magnetite has 16 octahedral- and 8 tetrahedral-site Fe atoms and akageneite has 8 octahedral-site Fe atoms in each supercell. As shown in table S8, the Fe atoms of magnetite showed the Bader charge values of 6.449*e* at the octahedral-sites and 6.341*e* at the tetrahedral-sites. The two locations (i.e., one for the octahedral- and the other for the tetrahedral-sites) were thus selected for the Sn replacement in magnetite. On the other hand, in the case of akaganeite, five Fe locations were selected because the Bader charge values of Fe atoms were varied from 6.287 to 6.458*e* (Table S9).

**Table S8.** Bader charge and excess Bader Charge of magnetite. (A), (B), and (C) represent Bader charge of bulk magnetite, magnetite with the Fe vacancy, and Sn-replaced magnetite, respectively.

Atom	Site type	Without vacancy	With vacancy	Replaced with Sn	Excess Bader Charge <sup>a)</sup>	Rep. Pos. No. <sup>b)</sup>
		(Ā)	(B)	(C)		
Sn	Oct <sup>c)</sup>			1.971		
Fe01		6.449				<u>S1</u>
Fe02		6.449	6.390	6.355	-0.094	
Fe03		6.449	6.390	6.355	-0.094	
Fe04		6.449	6.390	6.355	-0.094	
Fe05	$Oct^{(c)}$	6.449	6.390	6.355	-0.094	
Fe06		6.449	6.390	6.355	-0.094	
Fe07		6.449	6.390	6.355	-0.094	
Fe08		6.449	6.647	6.654	0.205	
Fe09		6.449	6.322	6.745	0.296	
Fe10		6.449	6.322	6.745	0.296	

Fe11	·	6.449	6.322	6.745	0.296	
Fe12		6.449	6.322	6.745	0.296	
Fe13		6.449	6.647	6.654	0.205	
Fe14		6.449	6.322	6.745	0.296	
Fe15		6.449	6.322	6.745	0.296	
Fe16		6.449	6.647	6.654	0.205	
Fe17		6.341	6.336	6.318	-0.023	S2
Fe18		6.341	6.336	6.320	-0.021	
Fe19		6.341	6.324	6.320	-0.021	
Fe20	Tat d)	6.341	6.324	6.318	-0.023	
Fe21	Tet ×	6.341	6.324	6.318	-0.023	
Fe22		6.341	6.324	6.318	-0.023	
Fe23		6.341	6.324	6.318	-0.023	
Fe24		6.341	6.324	6.318	-0.023	

a) The difference between Column (C) and column (A) [(C) - (A)]

b) The numbers of Sn Replacement locations (Refer to the main article)

c) The octahedral site

d) The tetrahedral site

**Table S9.** Bader charge and excess Bader Charge of akaganeite, (A), (B), and (C) represent Bader charges of bulk akaganeite, akaganeite with the Fe vacancy, and Sn-replaced akaganeite, respectively.

	Atom	Site type	Without vacancy	With vacancy	Replaced with Sn	Excess Bader charge <sup>a)</sup>	Rep. Pos. No. <sup>b)</sup>
			(A)	(B)	(C)		
	Sn	Oct <sup>c)</sup>			1.788		
	Fe01		6.287				S6
	Fe02		6.304	6.294	6.519	0.215	S3
	Fe03		6.289	6.294	6.282	-0.008	S4
	Fe04	(Oatd)	6.304	6.341	6.390	0.086	S5
	Fe05	Octa	6.289	6.314	6.368	0.079	
	Fe06		6.458	6.289	6.347	-0.111	S7
	Fe07		6.287	6.300	6.599	0.312	
	Fe08		6.458	6.307	6.357	-0.101	
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a) The difference between Column (C) and column (A) [(C) - (A)]

b) The numbers of Sn Replacement locations (Refer to the main article)

c) The octahedral site

d) The tetrahedral site

#### 3. Density of State (DOS)

Fig. S10 and S11 shows the projected density of states (PDOS) of a replaced Sn atom, O atoms adjacent to the Sn atom, and Fe atoms neighboring the Sn atom in the Sn-replaced magnetite and akageneite. As shown in the Fig. S11 (A, B), the 3d orbitals of the Fe atom and the 4d orbitals of the Sn atom were well hybridized in both magnetite and akaganeite. The 2p orbitals of the O atoms were also well hybridized with the 5p orbitals (Fig. S11(C and D)) and the 4d orbitals (Fig. S11(E) and (F)) of the Sn atom in both magnetite and akageneite, demonstrating the stable Sn replacement in both minerals.



**Fig. S11** Projected density of states (PDOS) of the Sn-replaced magnetite (A), C), and E)) and Sn-replaced akaganeite (B), D), and F)). A) and B) represent the PDOS of the 3d orbitals of the Fe atom neighboring the Sn atom and the 4d orbitals of the Sn atom. The PDOS of the 2p

orbitals of the O atom directly bound to the Sn atom was compared with the 5p (C) and d)) and 4d (E) and F)) orbitals of the inserted Sn atom.

#### References

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