Electronic Supplementary Information

Highly self-diffused Sn doping in α-Fe_2O_3 nanorod photoanodes initiated from β-FeOOH nanorod/FTO by hydrogen treatment for solar water oxidation

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Table S1. Structural parameters calculated from Fe K-edge EXAFS fits for α-Fe_2O_3 photoanodes.

Sample	R_1 (Å)[a]	R_2 (Å)[b]	σ^2 (Å^2)[c]
A800	1.947	2.118	0.0039
H340A800	1.953	2.124	0.0037
H360A800	1.953	2.124	0.0036
H380A800	1.939	2.109	0.0035
H400A800	1.941	2.111	0.0037

[a,b]Fe-O bond distance (uncertainty < 0.005), [c]Debye-Waller factor (indicator of the structural disorder) (uncertainty < 0.009)

Table S2. Donor density (N_D) calculated from Mott-Schottky plots for the as-prepared hematite photoanodes.

Sample	N_D (cm^{-3})
A800	1.39×10^{20}
H340A800	5.30×10^{20}
H360A800	4.96×10^{20}
H380A800	3.78×10^{20}
H400A800	3.26×10^{20}

Table S3. PL lifetime parameters of the corresponding PL decays for hematite nanorod photoanodes A800 and H800.

Sample	A_1 (%)	τ_1 (ns)	A_2 (%)	τ_2 (ns)
A800	56	0.12	44	0.31
H800	94	0.17	6	0.60

Fig. S1 Photograph of the as-prepared samples. The transformation procedures are interpreted using the following path.

$$\beta\text{-FeOOH} \xrightarrow[H_2]{\text{Reduction}} Fe_3O_4\,(\,Fe\,) \xrightarrow[\text{Air}]{\text{Oxidation}} \alpha\text{-}Fe_2O_3$$

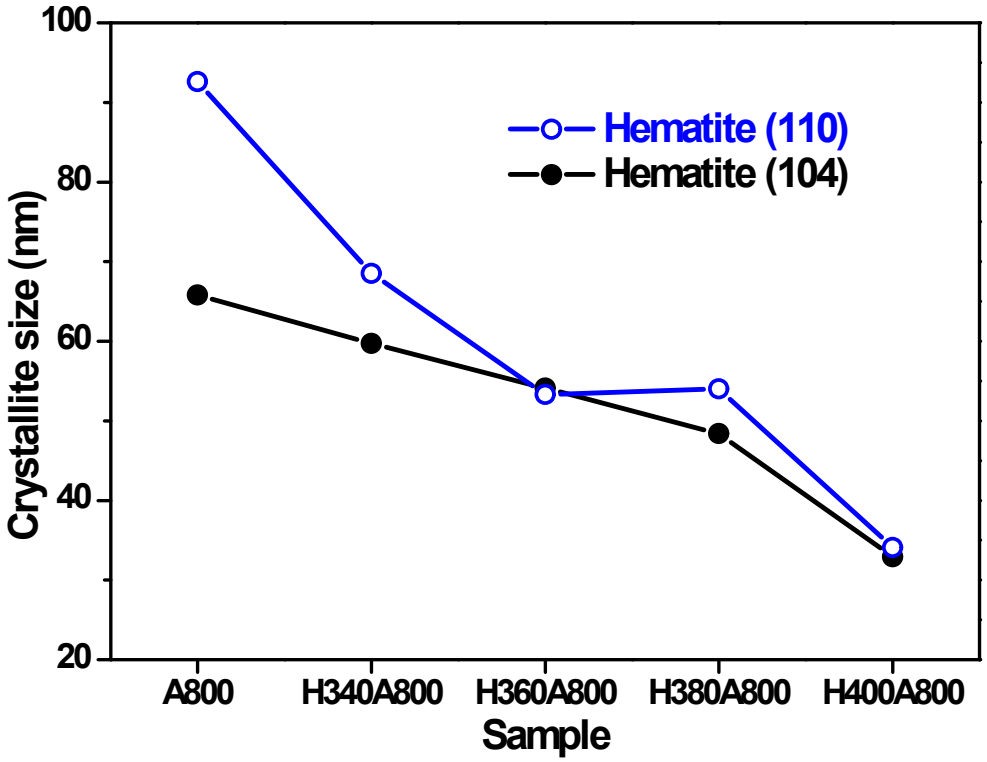

Fig. S2 Crystallite size of (104) and (110) peaks for the as-synthesized hematite photoanodes.

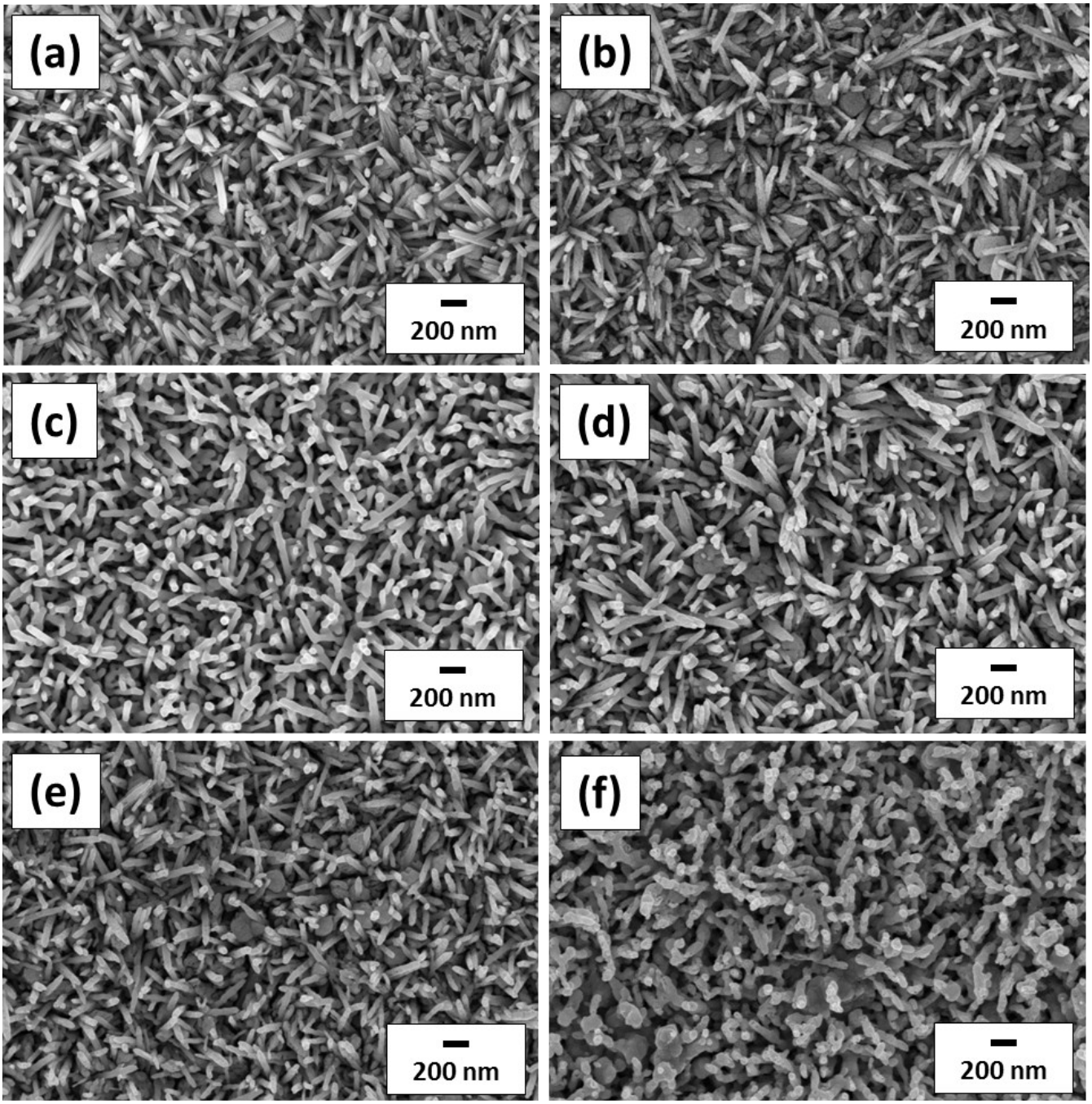

Fig. S3 Top view FESEM images of (a) β-FeOOH, (b) H360, (c) H340A800, (d) H360A800, (e) H380A800 and (f) H400A800.

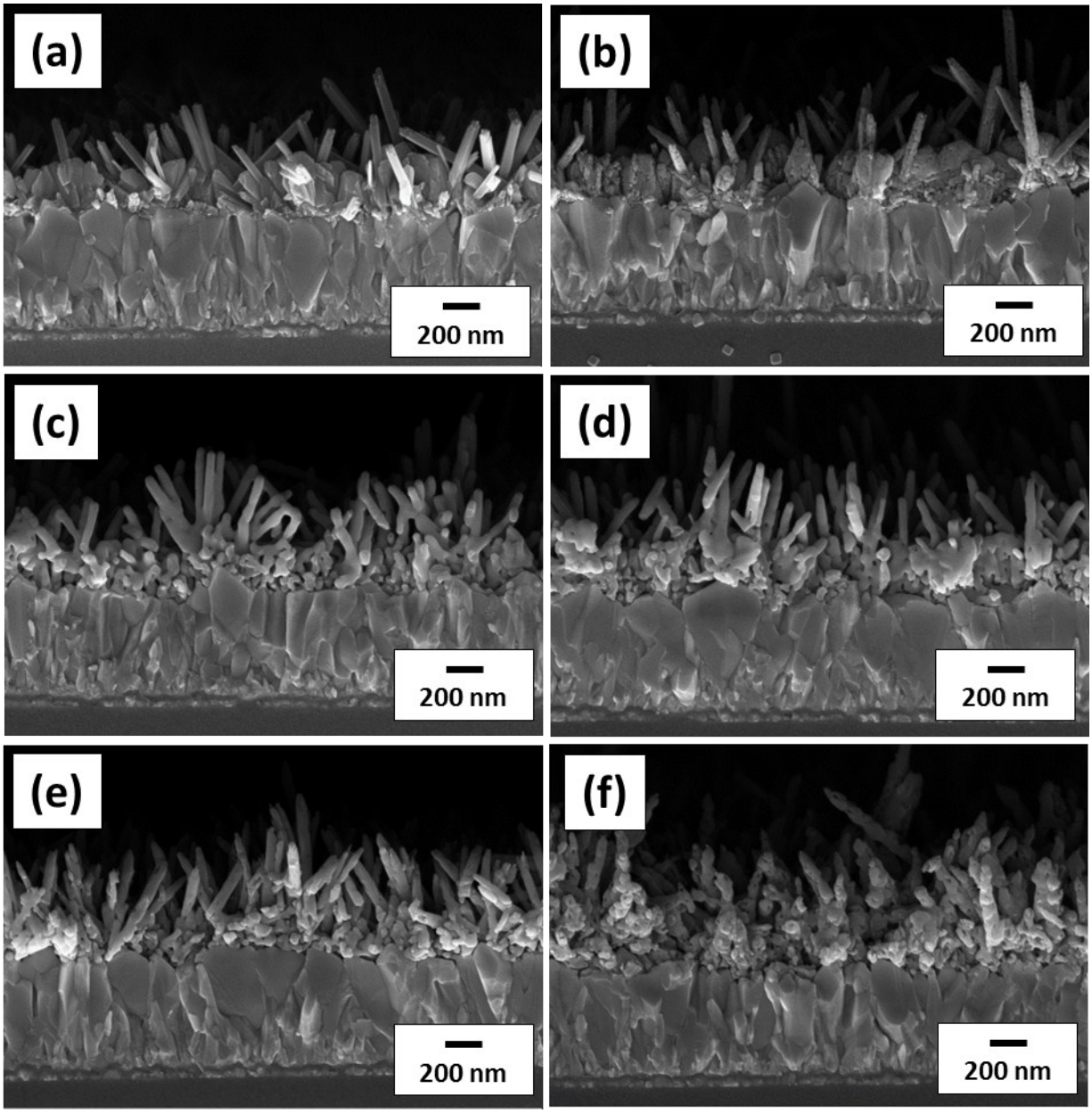

Fig. S4 Cross sectional FESEM images of (a) β-FeOOH, (b) H360, (c) H340A800, (d) H360A800, (e) H380A800 and (f) H400A800.

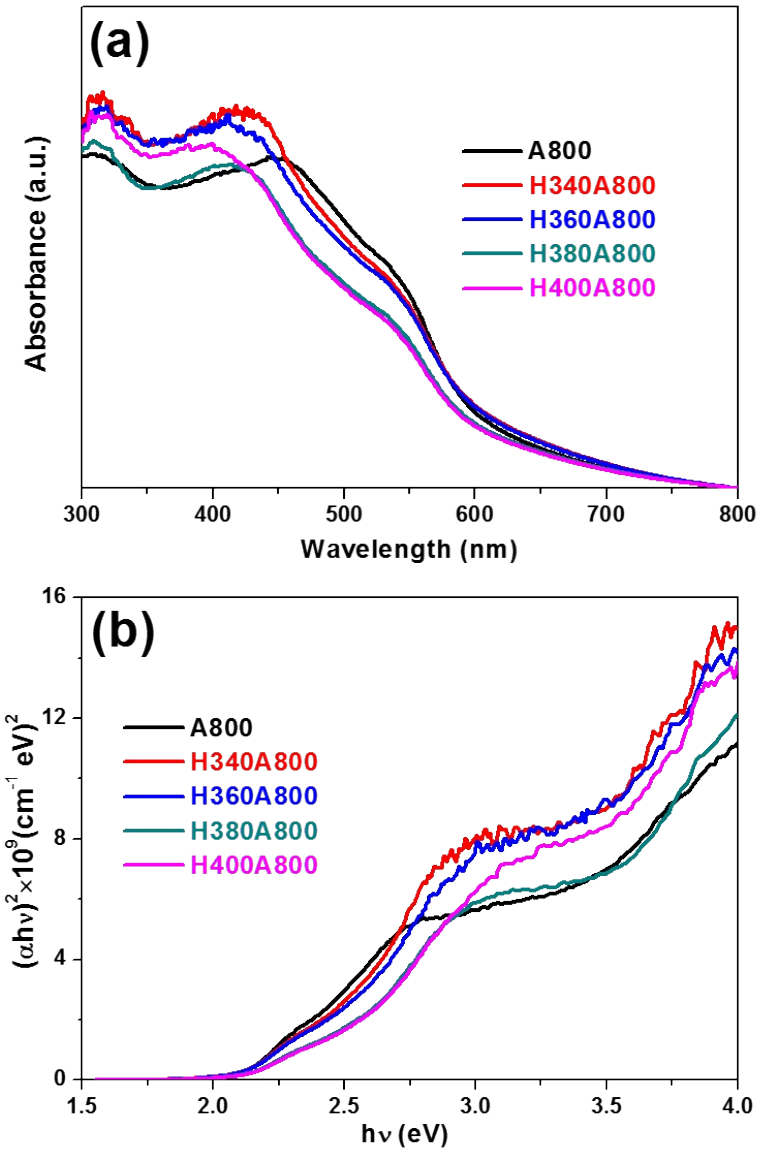

Fig. S5 (a) Absorbance spectra of the as-synthesized hematite photoanodes, (b) Tauc plots for the determination of optical band gap for the as-synthesized hematite photoanodes.

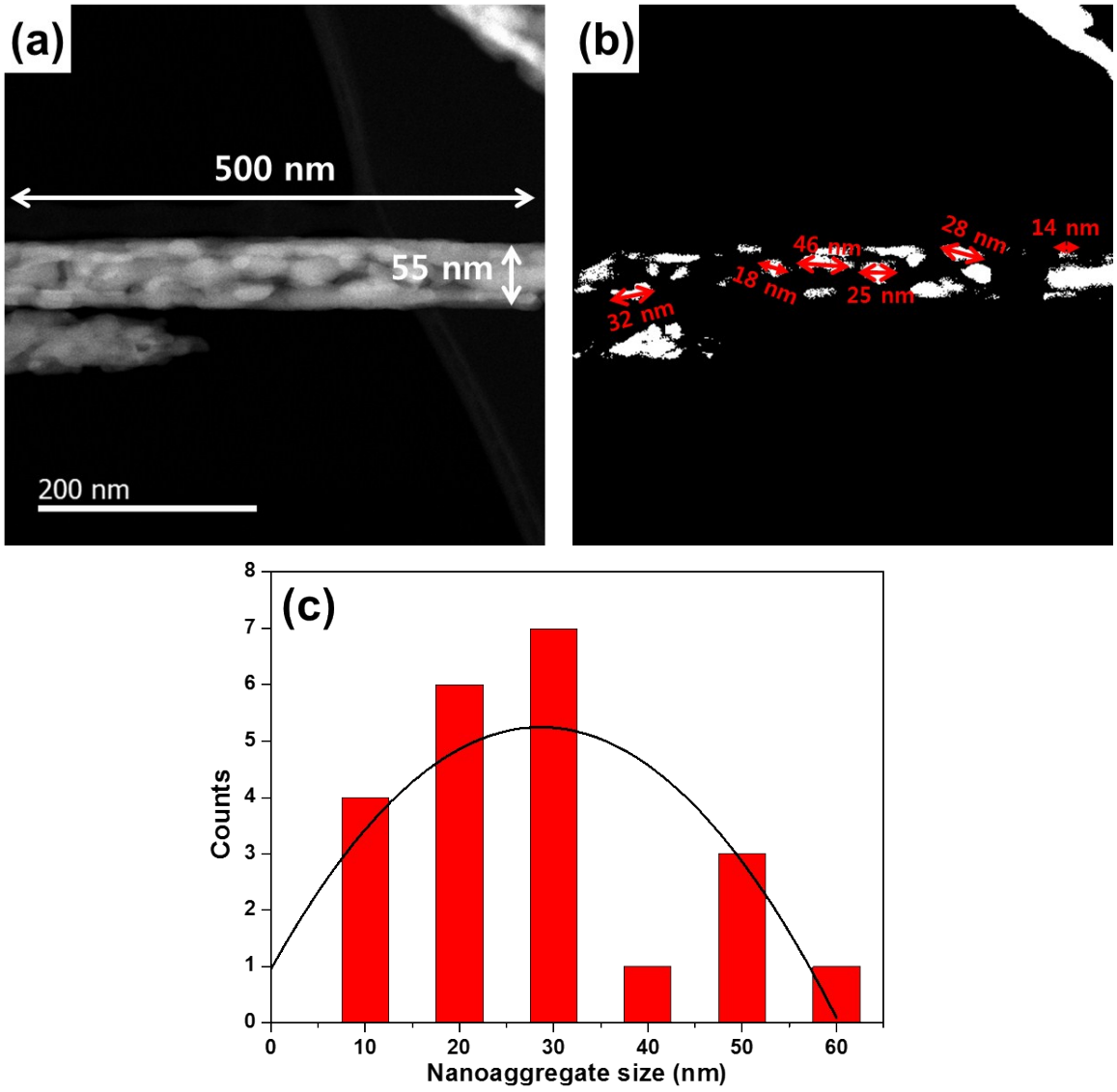

Fig. S6 (a) ADF-STEM images of the sample H360, (b) Binary phase analysis on the ADF image, and (c) Nanoaggregate size distribution histograms of the sample H360.

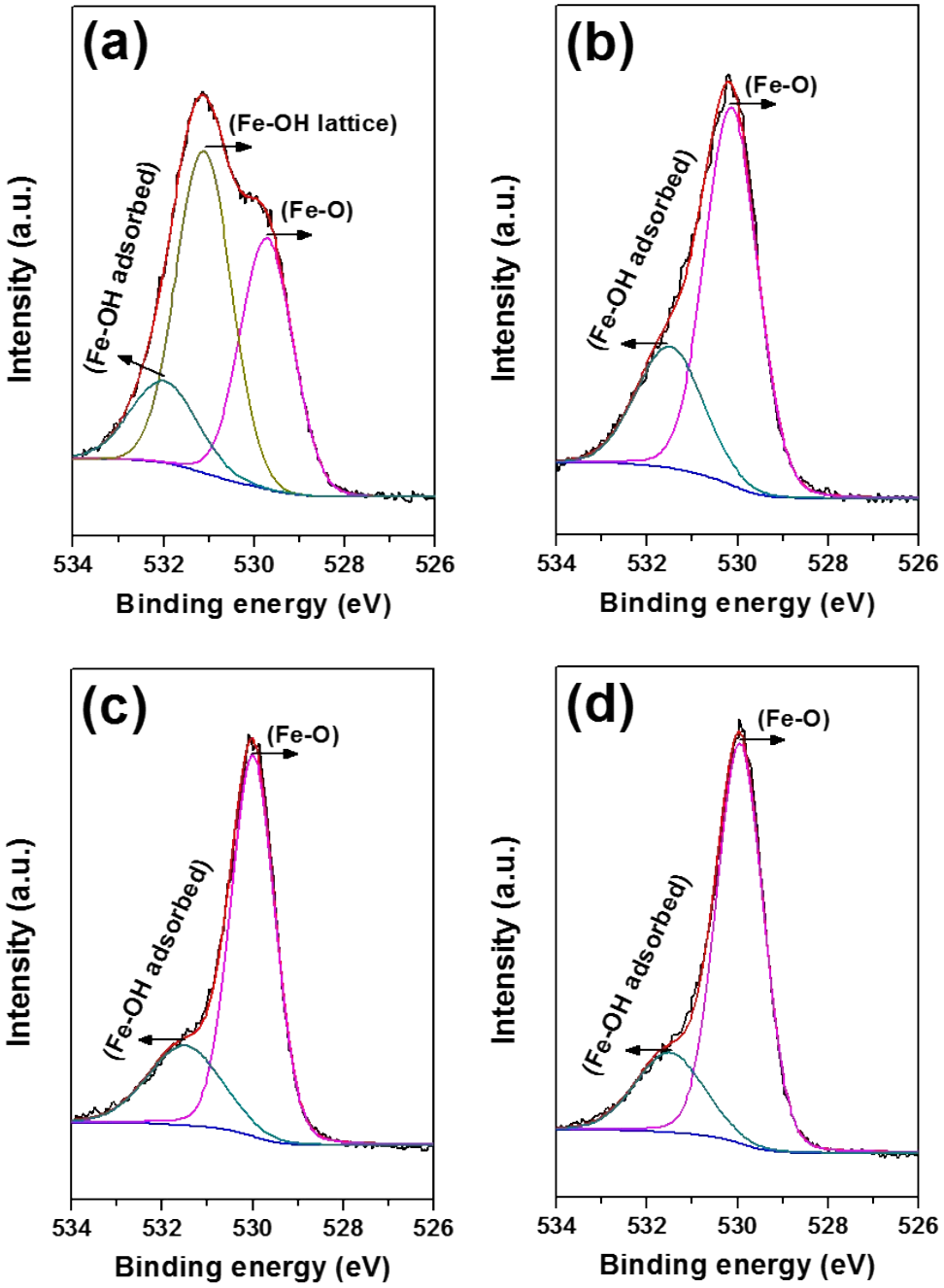

Fig. S7 Deconvolution of the O1s spectra for (a) β-FeOOH, (b) H360, (c) A800, and (d) H360A800.

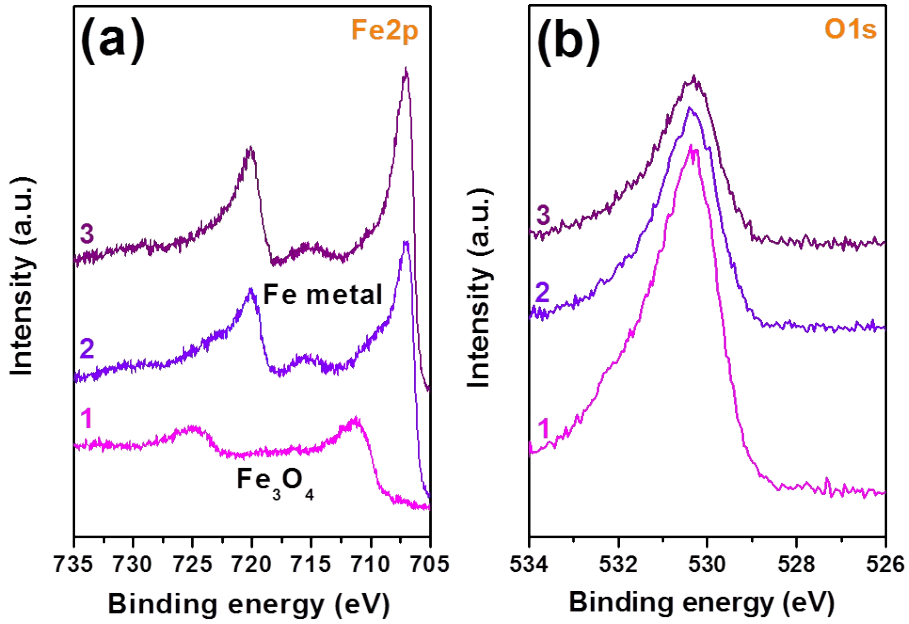

Fig. S8 XPS Fe2p spectra of H400 sputtered with various depths: (a) Fe2p, and (b) O1s. *Curve 1*, 0 nm; *Curve 2*, 15.3 nm; and *Curve 3*, 30.6 nm.

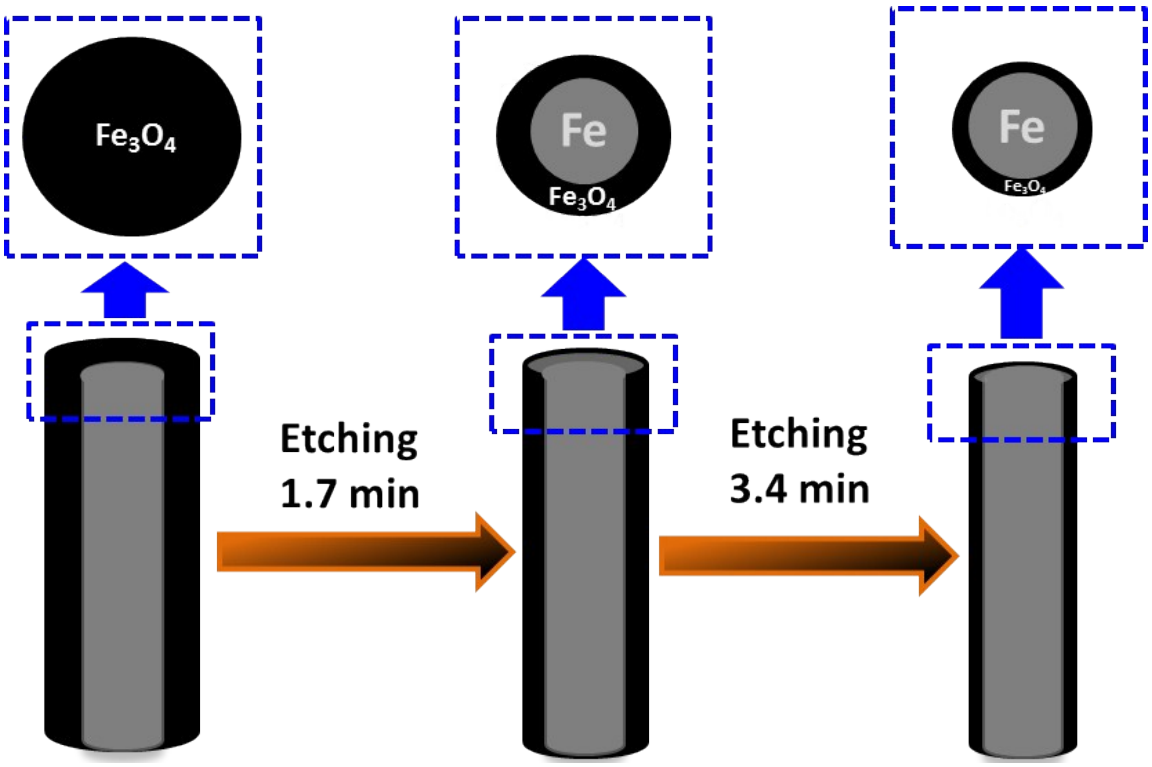

Fig. S9 Illustration of mechanism in XPS depth profiles of H400 sample.

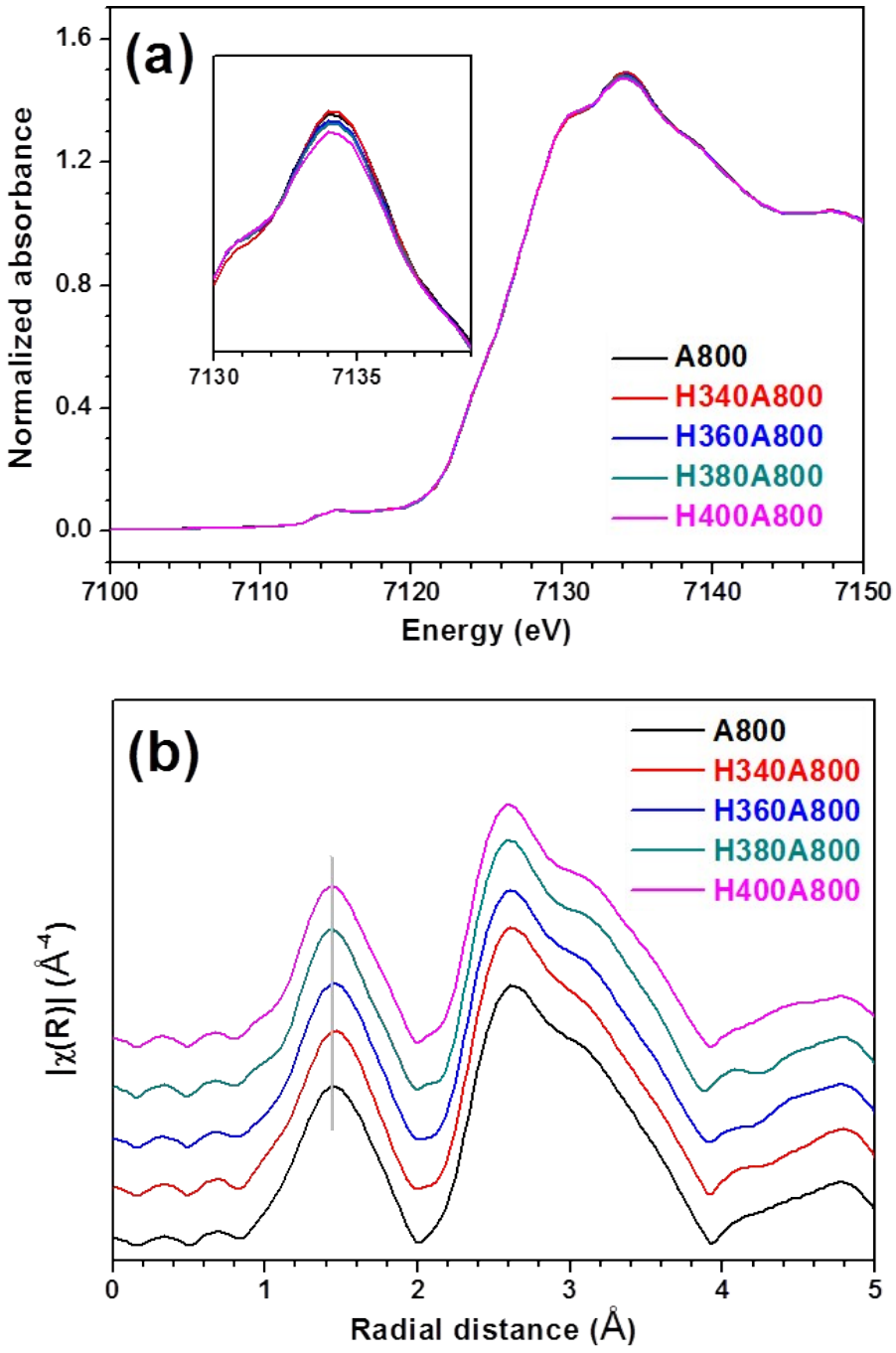

Fig. S10 XANES spectra (a) and Fourier transforms of k^3-weighted EXAFS functions (b) for Fe K-edges of the as-synthesized hematite photoanodes. Inset plot in (a) shows a magnified feature around 7134 eV.

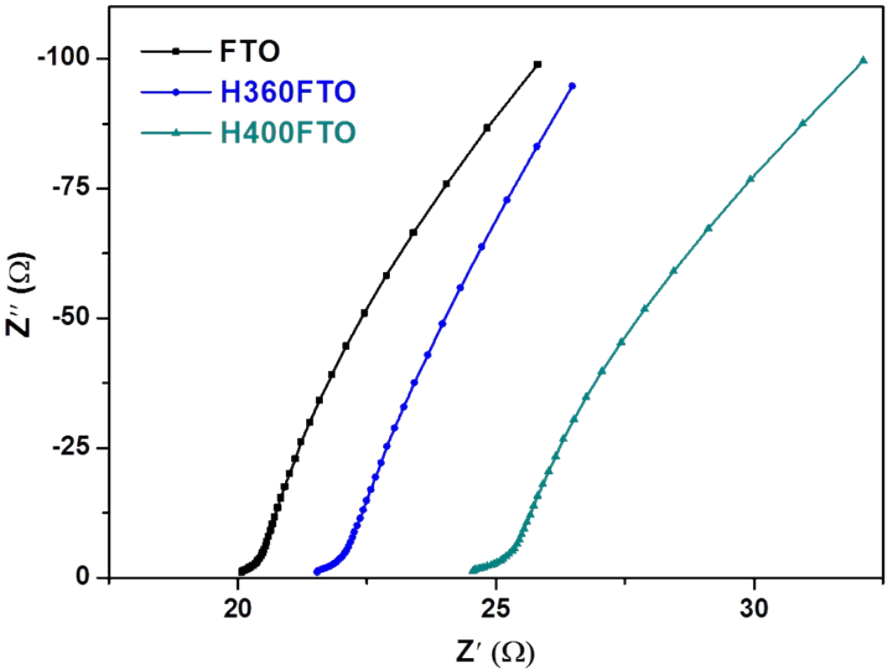

Fig. S11 Nyquist plots of bare and hydrogen annealed FTO substrates at 360 °C and 400 °C, using 1 M NaOH electrolyte under one sun illumination at 1.23 V *vs.* RHE.