Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Manual Assembly of Nanocrystals for Enhanced Photoelectrochemical Efficiency of Hematite Film

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Materials and Experiments

Materials. Iron chloride hexahydrate (98%, Aldrich), sodium hydroxide (93%, Duksan, Korea), polyethyleneimine (PEI, Aldrich, M_w = 2500) and mucasol (Merk) were used as received without further purification. F-doped tin oxide (F:SnO_2 glass, FTO) coated glass was obtained from Pilkington (Toledo, OH). Several pieces of FTO glasses (20 mm × 20 mm) were cleaned with ultrasound sonication in 3% mucasol solution and subsequently rinsed with copious distilled deionized water (DDW).

Synthesis of hematite crystals. A typical synthesis of hematite crystals was done as following: $FeCl_3$• $6H_2O$ (2 mmol, 0.54 g) was dissolved into aqueous NaOH solution (0.4 M, 20 ml) at room temperature with continuous stirring for 10 min. Gel solution turned turbid after adding $FeCl_3$• $6H_2O$. The synthesized gel was then transferred to Teflon lined autoclaves with capacity of 25 ml. The synthesis gels were heated at 150 ^oC for 1 - 5 h under the static condition in the oven. The produced hematite crystals were washed with copious ethanol and DDW, respectively.

(012) plane orientated hematite continuous film. 0.7 wt% PEI was coated on rinsed FTO glass by spin-coating at 2000 rpm for 30 s. It was placed on a clean weighing paper. Subsequently, hematite crystals were placed on PEI coated FTO glass and gently rubbed by a finger. The (012) plane orientated hematite crystals were annealed at 500 ^oC for 3 h under the air not only to improve adhesion between hematite crystals and FTO glass but also to remove PEI from produced film. The annealed film was immersed into gel solution and then heated at 150 ^oC for 1 - 5 h under the static condition in the oven. (012) plane orientated hematite continuous film prepared by secondary growth was repeatedly annealed at 500 ^oC for 3 h.

Random orientated hematite film. $FeCl_3$• $6H_2O$ (2 mmol, 0.54 g) was dissolved into aqueous NaOH solution (0.4 M, 20 ml) at room temperature with continuous stirring for 10 min. Gel solution turned turbid after adding $FeCl_3$• $6H_2O$. The synthesis gel transferred to Teflon lined autoclaves with capacity of 25 ml with rinsed FTO substrate. The synthesized gels were heated at 150 ^oC for 4 h under the static condition in the oven. The synthesized hematite film annealed at 500 ^oC for 3 h. These above procedure repeated twice to get proper thickness of hematite thin film.

Photocurrent measurements. The photoelectrochemical characteristics of (012) plane oriented hematite continuous film electrode (diameter = 0.7 cm, dimension = 0.38 cm^2) as photoanode was carried out in the three-electrode electrochemical cell using Pt wire as a counter electrode and an Ag/AgCl electrode as a reference electrode. An aqueous solution of

1.0 M NaOH with a pH 13.6 was used as the electrolyte, deaerated by purging N_2 gas into electrolyte. The photocurrent vs potential (J-V) curves were obtained under the dark and light illumination between -0.3 and 0.7 V vs Ag/AgCl at a rate of 50 mV/s. The transient photocurrent was measured at 0.4 V vs Ag/AgCl. The samples were illuminated with simulated sunlight from a 300 W xenon lamp (Asahi Spectra HAL-320, ozone free) using HAL AM 1.5G filter with a measured intensity of 1 sun (100 $mWcm^{-2}$, spectrally corrected) at the sample face. Electrochemical impedance spectroscopy (EIS) measurement of random and (012) plane orientated hematite film was carried out in the dark and light illumination to investigate electrical properties of the hematite film in 1.0 M NaOH solution using IM6 (Zahner). The electrochemical cell was in the three-electrode configuration as mentioned above. Impedance measurement was performed under computer-controlled potentiostat using a small-signal perturbation of 10 mV, while the frequency was 3 kHz.

Instrumentations. Film surface morphologies were imaged with SEM by a Hitachi S-4300 FE-SEM. TEM image and SAED pattern were obtained from a JEOL transmission electron microscope (JEM 2100F) at accelerating 200 keV. The cross-sectional specimen for HRTEM observation was prepared by focus ion beam cutter and mounted to a copper TEM grid with Pt layer. UV-vis spectra of the hematite film were taken with a Shimadzu UV-310PC. FTO glass was used as a blank. The X-ray powder diffraction patterns for the identification of the hematite crystals and films were obtained using Rigaku D/MAX-2500/pc diffractometer with CuK_α radiation source (λ = 0.154 nm). Pole figure analysis was conducted on a PANalytical X'Pert ProMPD equipped with open eulerian cradle sample stage. A polycapillary X-ray collimator was used in the incident optics to reduce the effect of defocusing.

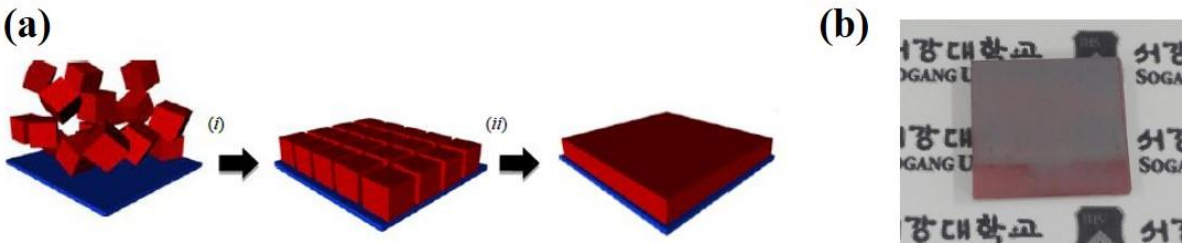
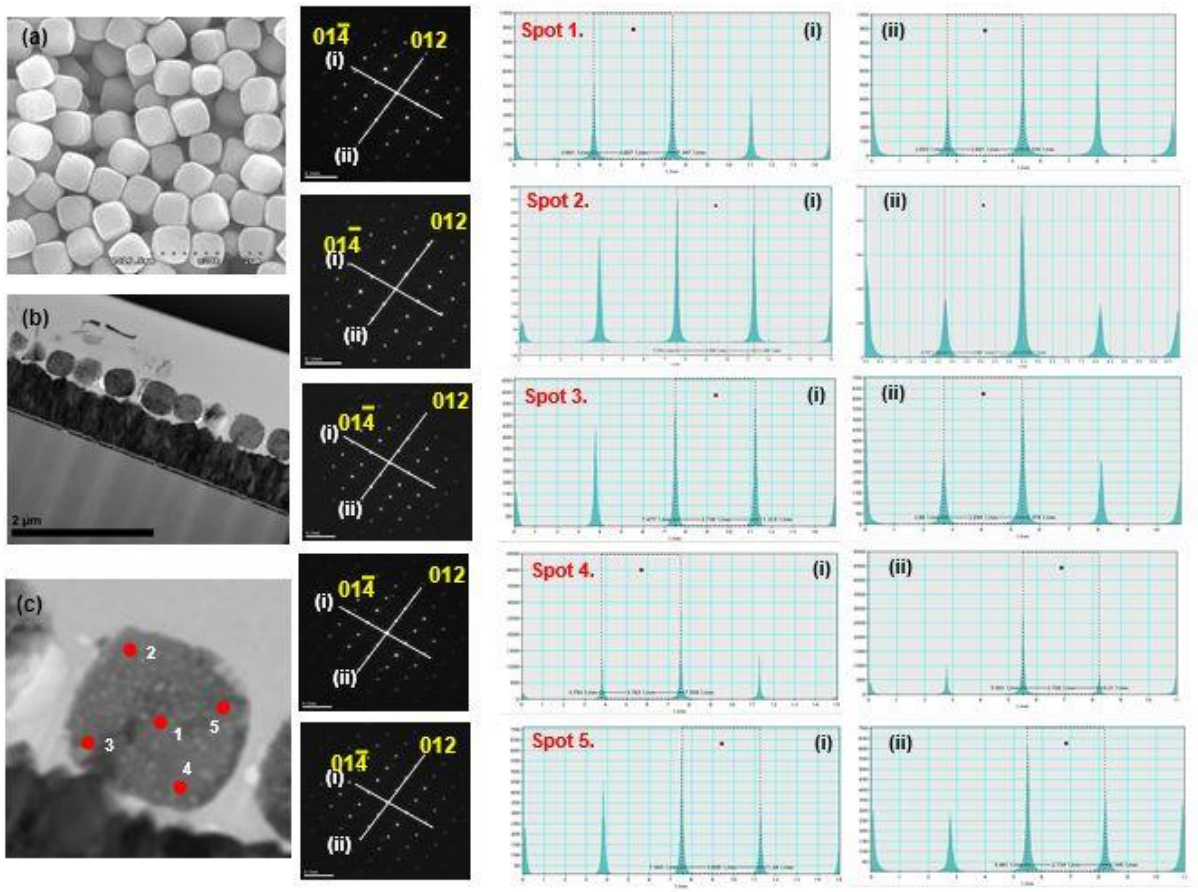


Figure S1. (a) Schematic drawing for the preparation process of (012) facet orientated semiconductor film on substrates. (i) manual rubbing of hematite crystals and (ii) secondary growth, (b) optical image of (012) oriented hematite film after 4 h secondary growth and annealing process.



FigureS2. (a) SEM image, (b) TEM images of (012) plane oriented hematite crystals prepared by FIB cutter. (c) Selected area electron diffraction (SAED) patterns were taken from five spots in TEM image. Each reciprocal lattice constant in SAED pattern was calculated by line profile in (i) and (ii)

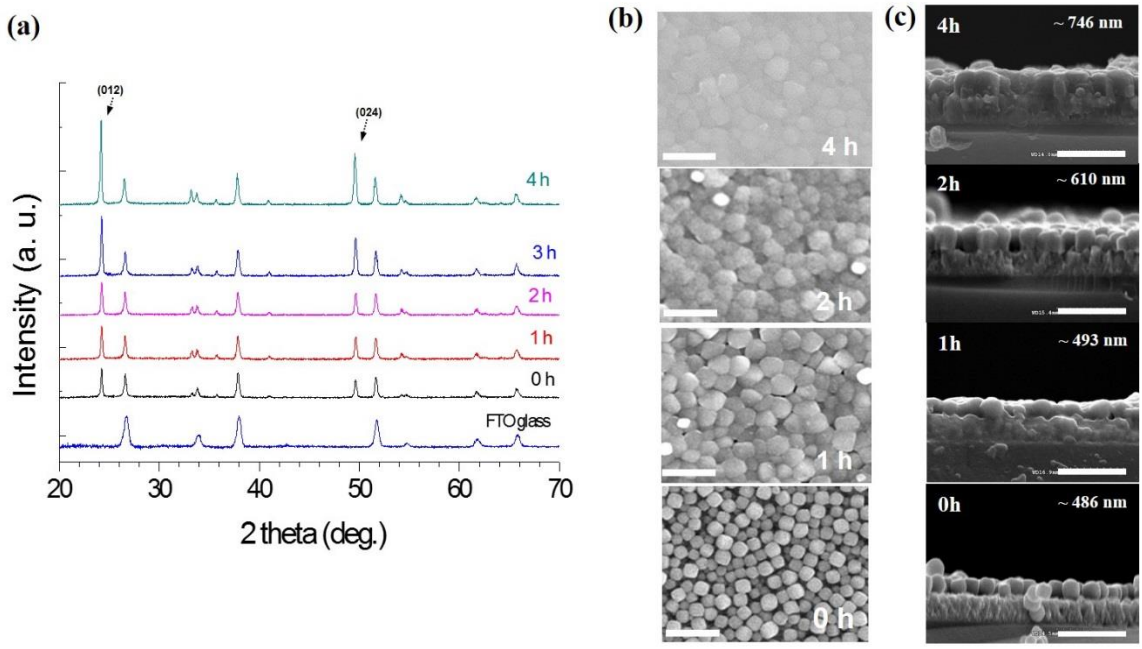


Figure S3. (a) Powder X-ray diffraction plots of (012) plane oriented hematite crystal film with different secondary growth time. (b) SEM top- view images and (c) cross-sectional Images with different secondary growth time. (all scale bar is 1μm)

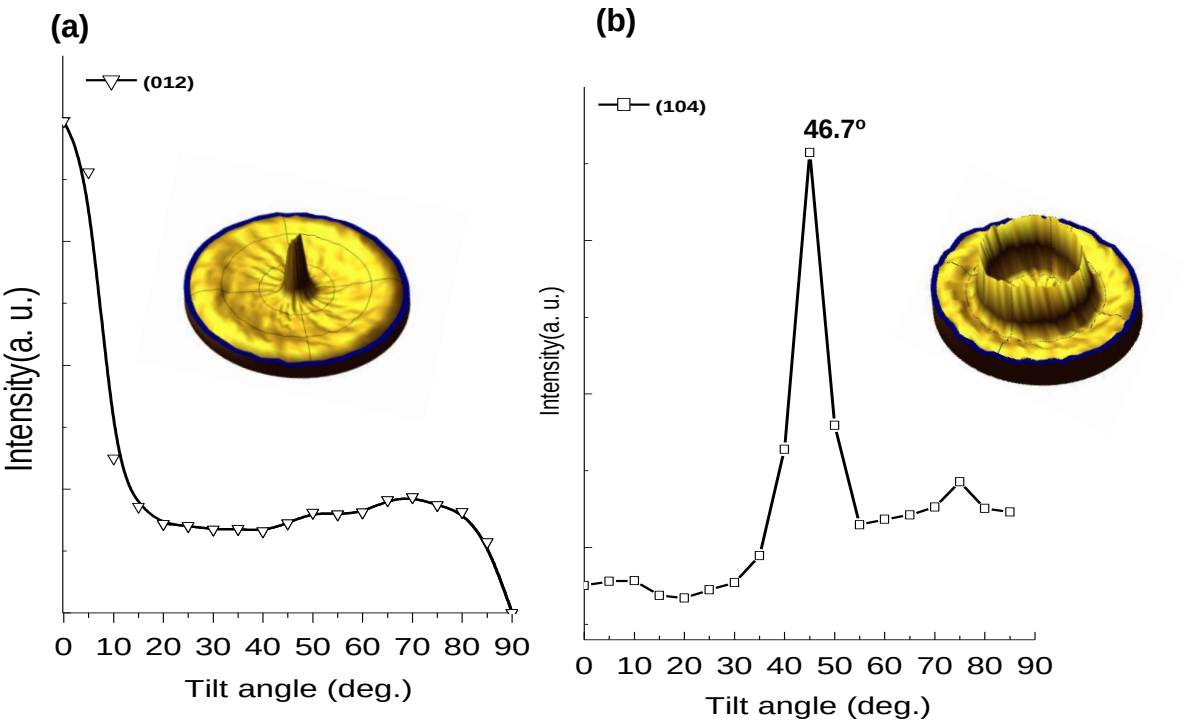
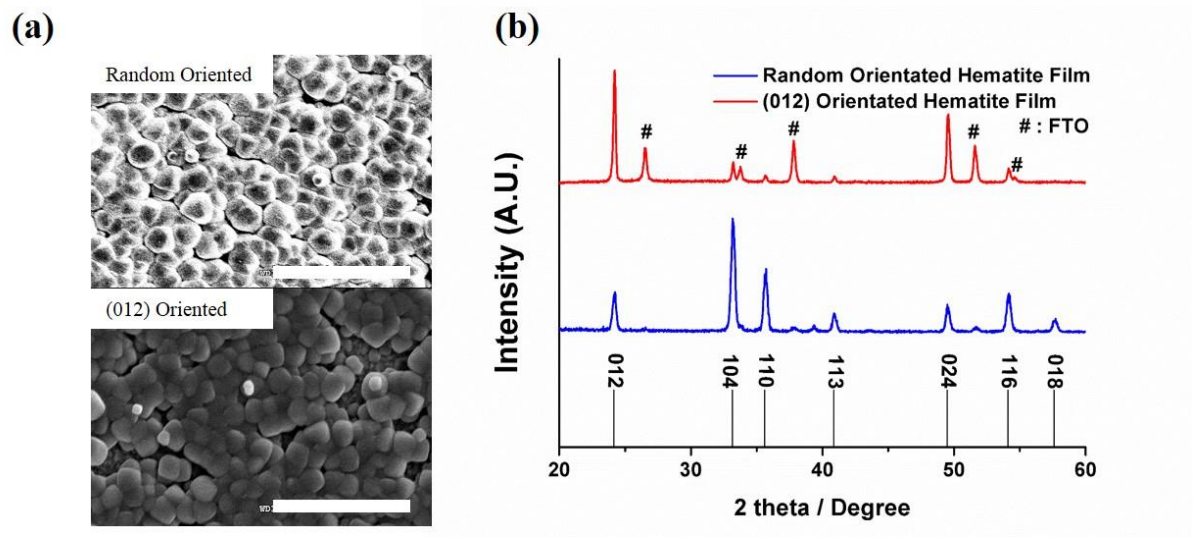
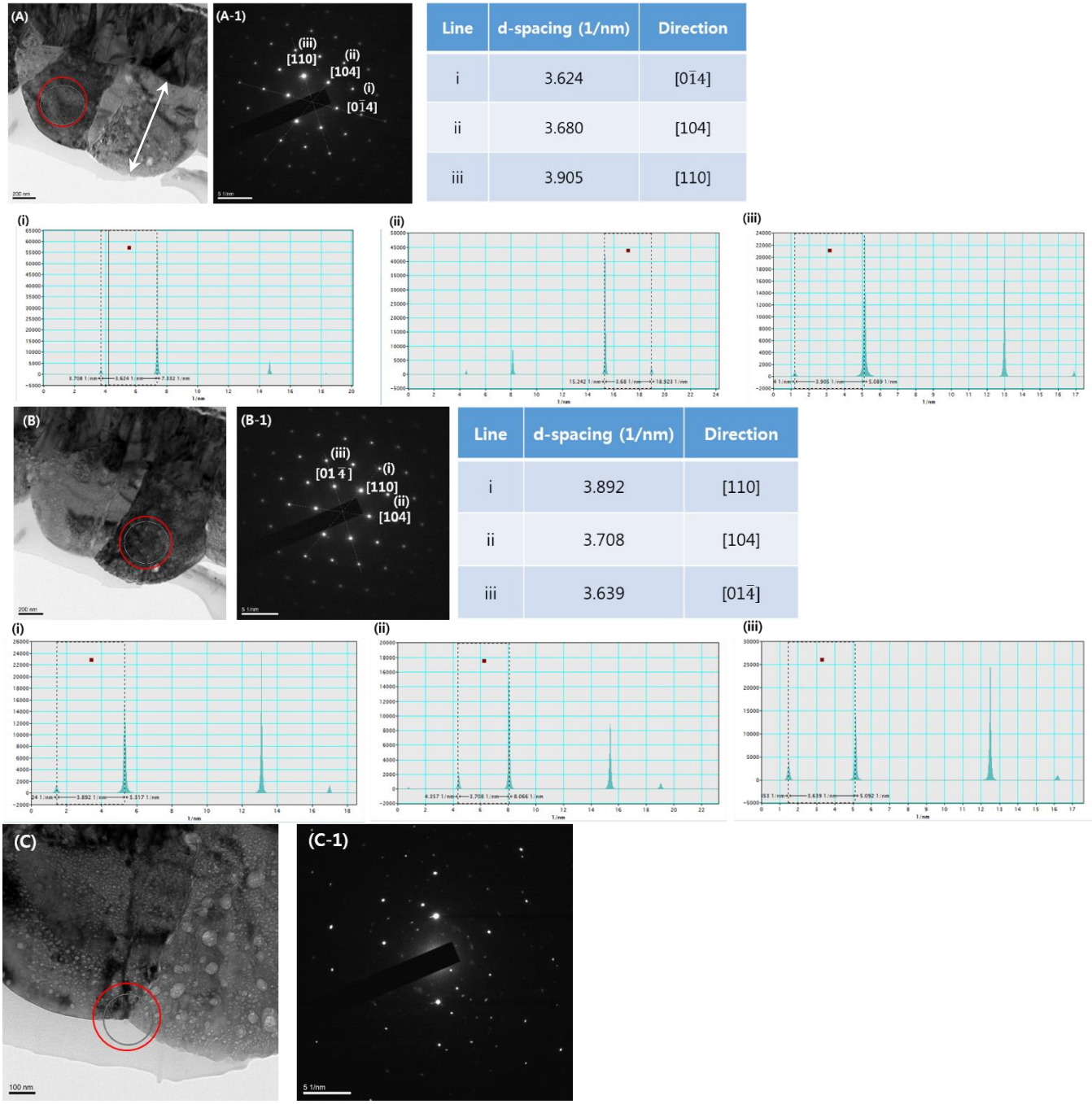


Figure S4. XRD pole figure analyses of the (a) (012) and (b) (104) reflections for (012) plane oriented hematite continuous film.



FigureS5. (a) SEM images and (b) XRD patterns for (012) orientated hematite film after secondary growth on FTO substrate (blue) and random orientated hematite film after secondary growth on FTO substrate (red). (all scale bars are 5 μm).



Line	d-spacing (1/nm)	Direction
i	3.624	[0$\bar{1}$4]
ii	3.680	[104]
iii	3.905	[110]

Line	d-spacing (1/nm)	Direction
i	3.892	[110]
ii	3.708	[104]
iii	3.639	[01$\bar{4}$]

Figure S6. TEM images and SAED patterns of random orientated hematite films. (A) Left side grain TEM image and its SAED pattern (A-1), (b) right side grain TEM image and SAED pattern (B-1), (C) TEM image at interface between hematite crystals and SAED pattern (C-1). Plane orientation has calculated by line profiling (i, ii and iii).

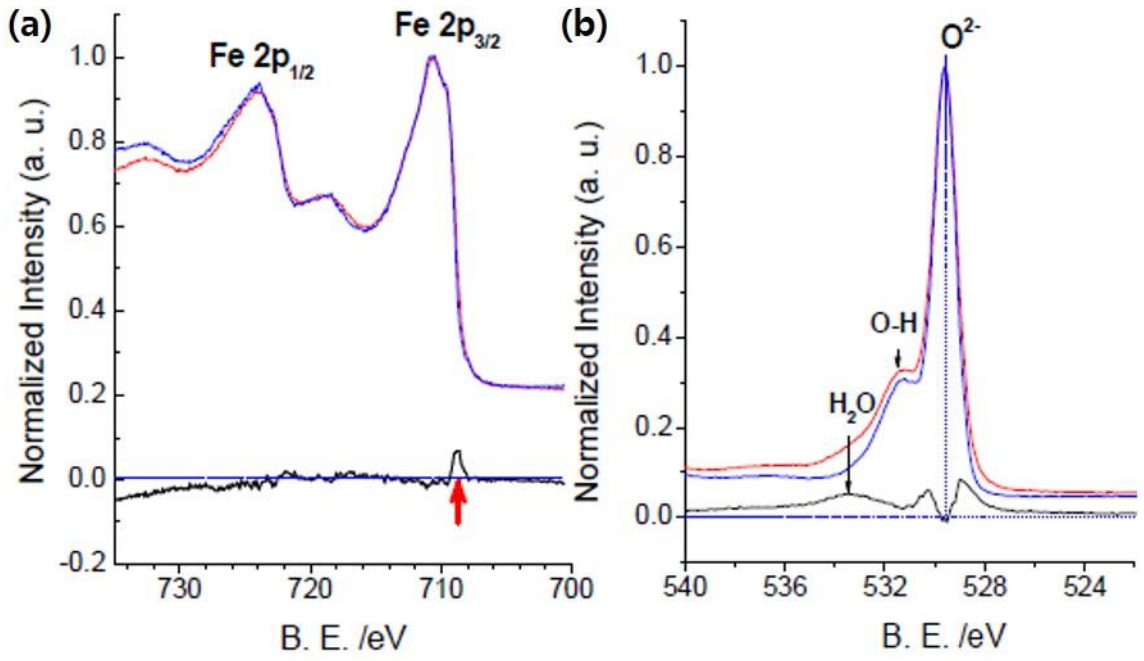


Figure S7. X-ray Photoelectron Spectroscopy (XPS) spectra in hematite crystals (red line) and (012) plane oriented hematite film grown for 4 h at 150 ℃ (blue line). Overlay of high resolution (A) Fe_{2p} and (B) O_{1s} as well as their intensity difference (black line)..

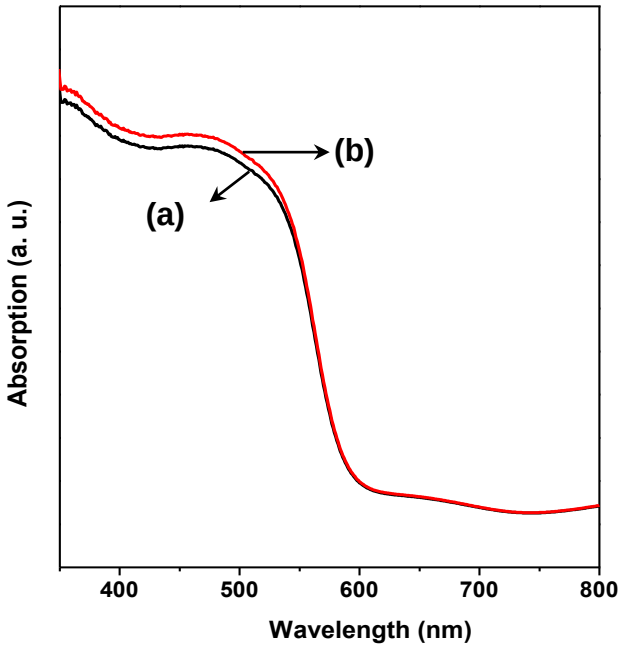


Figure S8. UV-vis spectra of (a) random oriented hematite film and (b) (012) orientated hematite films. (black line; random orientation, red line; (012) plane orientation)

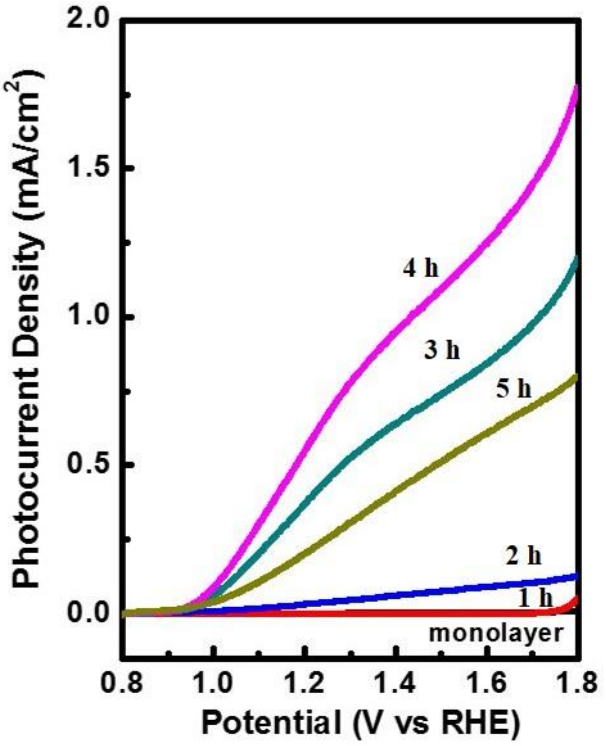


Figure S9. Photoelectrochemical performances of (012) plane orientated hematite films between 0.8 and 1.8 V vs. RHE at different secondary growth time in 1.0 M NaOH (pH 13.6).

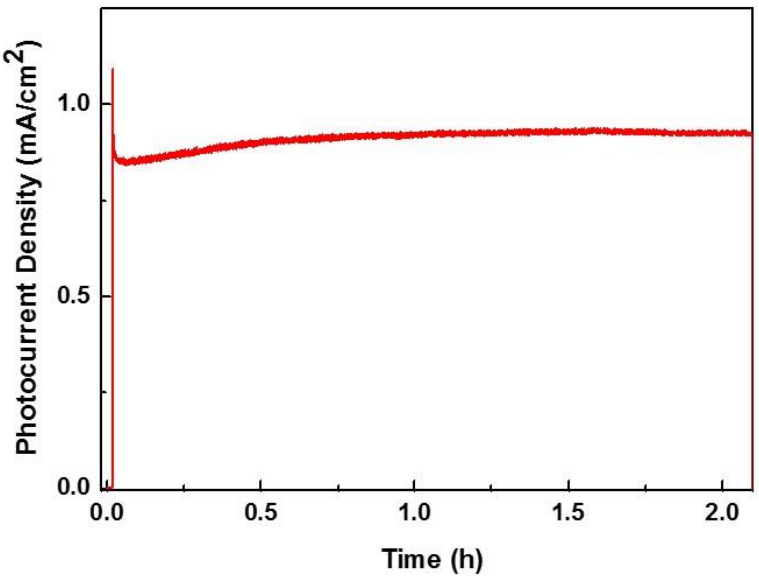


Figure S10. Photocurrent density curve during 2 hours for (012) plane oriented hematite film prepared by secondary growth at 150 ^{o}C for 4 h on the FTO glass. (1.23 V vs. RHE has applied as external potential, 1.0 M NaOH used as an electrolyte).

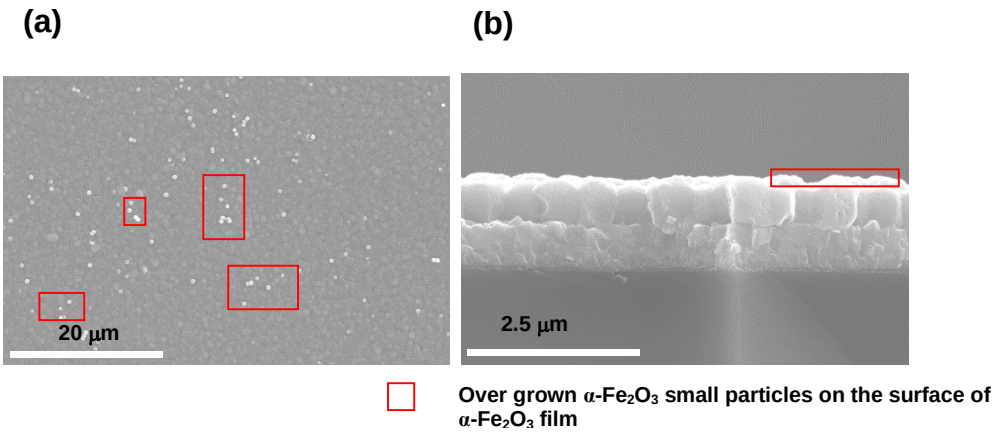


Figure S11. (a) Top and (b) cross-sectional SEM images of (012) plane oriented hematite continuous film made by secondary growth at 150 °C for 5 h on the FTO glass.

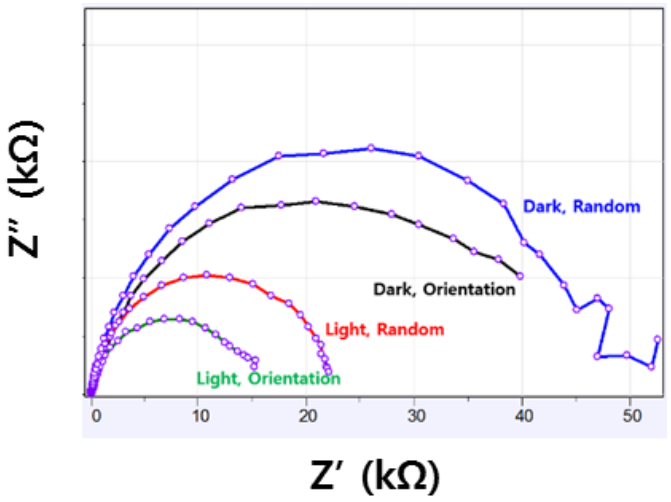


Figure S12. Nyquist plots of random orientated hematite film and (012) orientated hematite film for 4 h at 150 °C under dark and light illumination condition.