Supplementary Information

Facile Preparation of Fe_2O_3 Thin Film with Photoelectrochemical Properties

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SI 1. Preparation & Characterization of Fe_2O_3 films

Preparation of Fe_2O_3 films. Iron Chloride hexahydrate (98%, Aldrich), sodium hydroxide (93%, Duksan, Korea), and mucasol (Merz) were used as received without further purification. F-doped tin oxide (FTO) coated glass was obtained from Pilkington (Toledo, OH). Several pieces of FTO glasses (10 mm × 10 mm) were cleaned with ultrasound sonication in 3% mucasol solution and subsequently rinsed with copious distilled deionized water (DDW). The synthesis gel for hematite film grown on FTO glass was simply prepared as following: $FeCl_3 \cdot 6H_2O$ (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 $FeCl_3 \cdot 6H_2O$. The synthesis gels were then transferred to Teflon lined autoclaves with capacity 25 mL and subsequently cleaned FTO glassed were immersed into the gel solutions. The synthesis gels were heated at various temperatures (130, 150, and 170 °C, respectively) for 1-7 h under the static condition in the oven. The produced hematite films were washed with copious ethanol and DDW, respectively. Finally, these pristine films were calcined at 500 °C for 4 h under the air.

Preparation of Pt doped Fe_2O_3 films. For the preparation of Pt-doped Fe_2O_3 thin film, the same experimental procedure was used, however, the precursor chloroplatinic acid hexahydrate (1 mol% for Fe concentration) was added to above-mentioned solution.

SI 2. Measurement and Characterization of Fe_2O_3 devices

SI 2-1. Photocurrent Measurements

The photoelectrochemical characteristics of Fe_2O_3 thin film electrodes (diameter = 0.7 cm, dimension = 0.38 cm^2) as photoanodes were measured using CHI 1000 potentiostat in a three-electrode cell with 1 M KOH (pH 13.6) as electrolyte using Ag/AgCl in saturated KCl as a reference electrode and Pt wire as a counter electrode. The photoanodes were scanned between 300 and 700 mV *vs* Ag/AgCl at a rate of 50 mVs^{-1}. The photocurrent *vs* potential (*I-V*) curves were obtained in 1 M KOH (pH 13.6) in the dark or under illumination. The chronoamperometry curves were measured at 0.23 V *vs* Ag/AgCl. The potentials are reported *vs* Ag/AgCl (measured) or RHE (obtained using the relationship $E_{RHE} = E_{Ag/AgCl} + 0.0591 \times pH + 0.1976$ V). 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.

SI 2-2. EIS (electrochemical impedance spectroscopy) Measurement.

Electrochemical impedance spectroscopy was carried out in the dark to investigate electrical properties of the Fe_2O_3 film in 1 M KOH 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 3000 Hz. Recorded impedance spectra were fitted to calculate the values for flat-band potential (V_{fb}) and charge carrier concentration (N_D) using Mott-Schottky plots. The details about this electrochemical measurement are discussed elsewhere [1].

SI 2-3. Instrumentation

SEM images of hematite film were obtained from a FE-SEM (Hitachi S-4300) at an acceleration voltage of 20 keV with an energy dispersive X-ray spectrometer (EDX) operated at accelerating 20 keV. TEM images, SAED pattern, and Chemical composition were obtained from a JEOL transmission electron microscope (JEM 2100F) installed with an EDX operated at accelerating 200 keV. In a brief procedure, sample of nanoparticles scratched off the Fe_2O_3 film were redispersed in ethanol by ultrasonic agitation. A small volume of the suspension was dropped on the carbon-enhanced copper grids and dried in air. UV-vis spectra of the Fe_2O_3 film were taken with a Shimadzu UV-310PC. F-doped tin oxide was used as a blank. Grazing Incident X-ray diffraction (GIXRD) patterns for Fe_2O_3 films were acquired with a Rigaku Ultima IV X-ray differactometer using the fixed monochromater (U4) of Cu K_α radiation source (λ = 0.1540 nm) at an incident angle of 1.2^o. Surface states of the sample were analyzed using XPS (model: SIGMA PROBE, ThermoVG, U.K). The XPS spectra were acquired using monochromatic Al Kα photon source operating at 15 kV and 15 mA. The binding energy of the O (1s) peak was calibrated with respect to the C (1s) peak at 284.6 eV. The software provided by the manufacturer was used for all XPS analyses. [2].

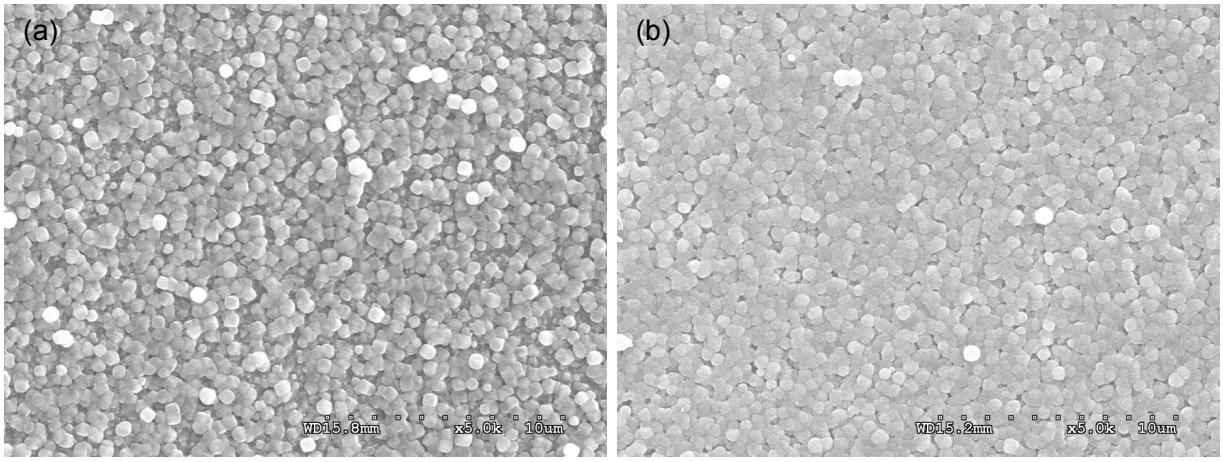
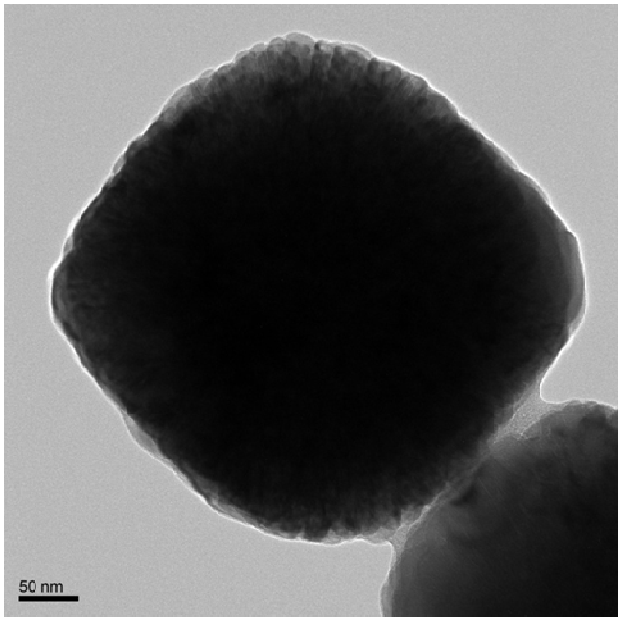
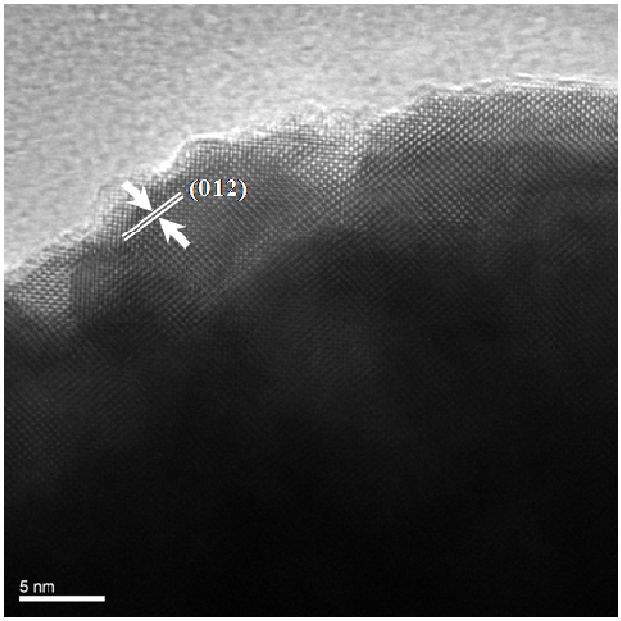
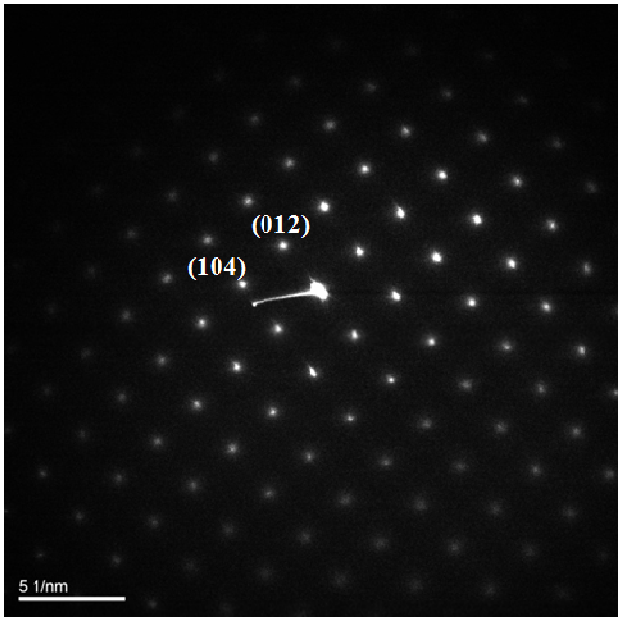
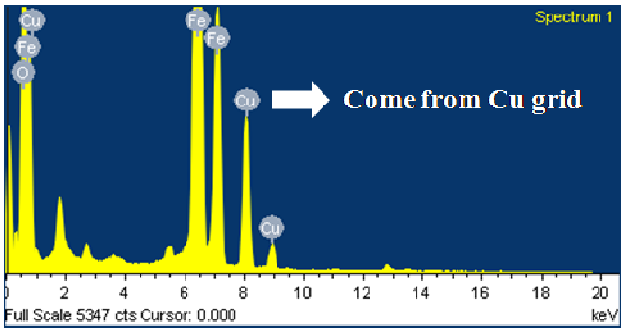


Fig. S1. SEM images of Fe_2O_3 films prepared at various temperature (a: 130 ^oC, b: 170 ^oC).









Element	Weight%	Atomic%
O K	17.55	42.88
Fe K	75.25	52.69
Cu K	7.20	4.43
Totals	100.00	

Fig. S2. TEM image, magnified HRTEM, SAED pattern, and EDS spectrum of the sample scratched off the Fe_2O_3 film.

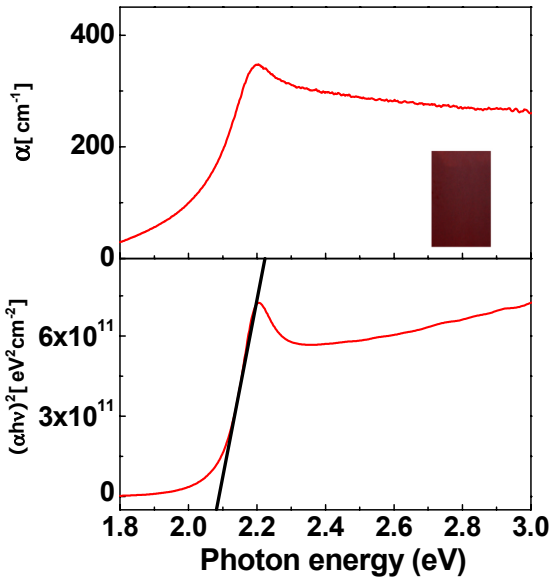


Fig. S3. Absorption spectra and extrapolating the linear part of $(\alpha h\nu)^2$ vs $h\nu$ plots of Fe_2O_3 film prepared at 170 ^oC for 5 h.

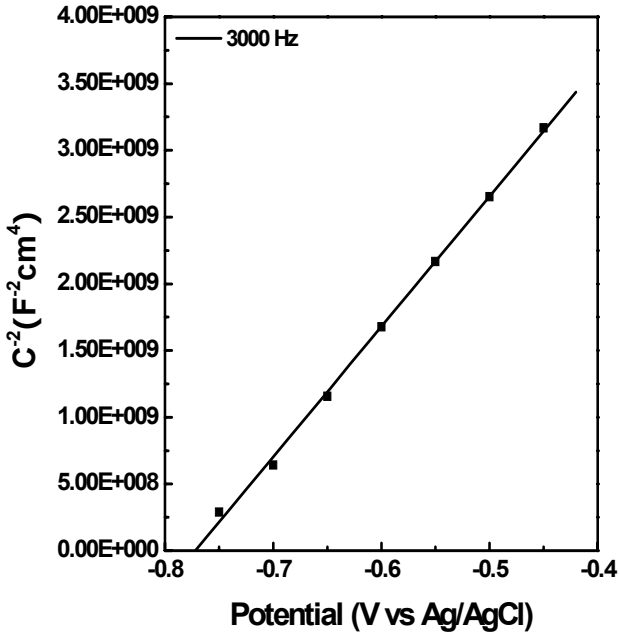
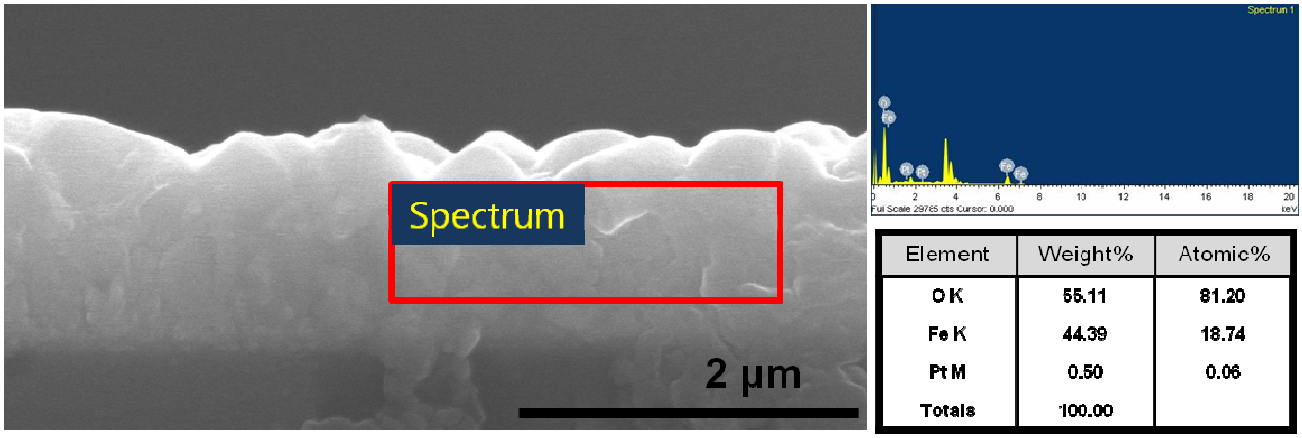


Fig. S4. Mott-Schttoky ($1/C^2$ vs. potential, where C is the capacitance) plot for Fe_2O_3 films measured at an AC frequency of 3000 Hz under dark condition using an electrolyte solution of 0.1 M KOH (pH 13.6) and and AC amplitude 10 mV; The dielectric constant of Fe_2O_3 was used as 12. The reference electrode was Ag/AgCl.



Element	Weight%	Atomic%
O K	55.11	81.20
Fe K	44.39	18.74
Pt M	0.50	0.06
Totals	100.00	

Fig. S5. SEM-associated EDX area analysis of the cross-section of Pt doped Fe_2O_3 film shown in micrograph, suggesting significant chemical composition in sample.

Reference

[1] S. R. Morrison, *Electrochemistry at Semiconductor and Oxidized Metal Electrodes*; Plenum Press: New York, 1980.
[2] H. S. Jung, J. K. Lee, S. W. Lee, K. S. Hong, H. H. Shin, *J. Phys. Chem. C* 2008, **112**, 8476.