Electronic Supplementary Information for

Surface treatment of hematite photoanodes with zinc acetate for water oxidation

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Experimental Details

1. Preparation of hematite films. The blocking layer was prepared by spin coating method. Before spin coating, a small FTO area was protected by masking with thermal-tape to provide a contact to the potentiostat during photoelectrochemical measurements. A solution of 20 mM SnCl₂ (99%, Sigma) in ethanol was spin-coated on F:SnO₂ substrates (Nippon Sheet Glass Co Ltd, 15 Ω/\Box). The spin-coating rate was 1000 rpm for 45 sec. After that, the substrates were annealed at 350 ° C for 5 min. This process was repeated for a further two cycles and attained a thickness of SnO₂ of around 10 nm. Hematite photoanodes were fabricated by spray pyrolysis. 70 ml solution of 0.20 M iron acetyl acetonate (Fe(acac)₃, 97%, Sigma) in ethanol was sprayed at 540 °C. Aluminum foil was used to protect FTO area during spray for the same reason as mentioned above. The spray pyrolysis was carried out using 20 seconds on cycles and 20 second off cycles. Compressed air was used as the carrier gas. The resulting films were then further annealed in air at 550 °C for 2 hr. Surface treatments of photoanodes involved spin-coating of a

solution of 25 mM of zinc acetate (ZnAc, 99%, Sigma) in ethanol. The solution was spin-coated with a speed of 1500 rpm for 45s followed by annealing at 400 °C for 20 min.

2. Characterizations. Morphology of samples was characterized by FESEM (JEOL, JSM-7600F, 5kV). Thin film X-ray diffraction (XRD) studies were carried out on a Shimadzu LabX-XRD-6000 using Cu K_{α} radiation. Ultraviolet-visible (UV-Vis) absorption spectra of the films were obtained using a Shimadzu UV-1800 spectrophotometer. Photoelectrochemical measurements were performed using CHI 660D work station (CH Instruments, Inc.) in a three-electrode electrochemical system with 1 M NaOH electrolyte. Platinum mesh and Ag/AgCl were employed as counter and reference electrodes, respectively. Working surface area was 0.2 cm². The light source was simulated sunlight from a 150 W xenon solar simulator (96000, Newport Corp.) through a solar filter with a measured intensity equivalent to standard AM1.5 sunlight (100 mW/cm^2) at the sample face. The hematite electrode was scanned at 10 mV s⁻¹ between -400 mV and 1000 mV vs Ag/AgCl. The Electrochemical Impedance Spectroscopy (EIS) measurements were carried out using an automated potentiostat (Solartron-analytical, 1470E) coupled with a frequency response analyzer (Solartron-analytical, 1255B) in a three-electrode electrochemical system. Counter electrode and electrolyte were same as that of PEC measurements, but reference electrode was saturated calomel electrode (SCE). The EIS data were measured with a sinusoidal voltage perturbation of 10 mV amplitude at 10 kHz in dark. The analysis of gaseous product under irradiation was performed using a gas chromatograph (GC) (Agilent 7890A). The gas was manually injected inside GC. The potential of the working electrode was controlled at 0.2 V vs Ag/AgCl in a three-electrode system. The active area is 1 cm². Other conditions are same as that of PEC measurements. XPS measurements were carried by VG Escalab 220i XL and the binding energies were calibrated with respect to the residual C (1s) peak at 285.0 eV.

Electronic Supplementary figures and captions.



Fig. S1 (a) Schematic diagram of photoelectrochemical solar water oxidation. (b) SEM image of SnOx blocking layer. (c) Cross-sectional SEM images of hematite film sintered at 550 °C for 2 hr.



Fig. S2 XPS spectra of hematite films before and after ZnAc treatment.



Fig. S3 Chopped photocurrent-potential curves after 3 cycles of ZnAc treatment.



Fig. S4 Band alignment of hematite/electrolyte after ZnAc treatment under reverse bias and light conditions. Note: It can be seen that after surface treatment, electron donation from ZnO to the Fe_2O_3 interface would take place and shift the band edge to more negative value. This conclusion is consistent with that of Fan et al.¹

negative potential (-)



Fig. S5 Band alignment of hematite/electrolyte under forward bias and dark conditions. Note: Ideality factor is calculated from the slope of the forward bias region of a ln (I) vs V plot. Since hematite is n-type semiconductor, the forward bias region of the I-V curve is at negative potential. In this region, the recombination of charge carriers at the interface can be studied.



Fig. S6 (a) UV-Vis absorption and (b) Tauc-Plots of films of hematite before and after ZnAc treatment.



Fig. S7 Photocurrent stability profile of hematite after 3 cycles of ZnAc treatment.

References

1. Z. Fan, X. Wen, S. Yang and J. G. Lu, Appl. Phys. Lett., 2005, 87, 013113.