Interface Passivation to Overcome Shunting in Semiconductor-Catalyst Junctions

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Experimental:

Hematite thin films were prepared on Fluorine-doped tin oxide (FTO) coated aluminoborosilicate glass substrate (Solaronix, 10 Ω/sq) via electrodeposition (ED) and atomic layer deposition (ALD) methods using the procedure described previously.[1,2] Before hematite deposition, FTO substrates were cleaned by sequential sonication in soap, water, and isopropyl alcohol for about 15 min, followed by drying in an N_2 stream. The electrodeposition of hematite thin film was performed by submerging the FTO substrate in a solution of 0.1 M $FeCl_2.4H_2O$ (pH~4.3) at 60 °C by applying the constant potential of 1.2 V vs. Ag/AgCl for 30 min under gentle stirring. Then, amorphous FeOOH film was converted to crystalline Fe_2O_3 by annealing at 800 °C for 10 min. The thickness of the hematite film prepared with this method measured to be 25 nm using atomic force microscopy (AFM).

Hematite film was also deposited on 2 nm Ga_2O_3 underlayer by ALD method. Ga_2O_3 underlayer was deposited on FTO substrate by ALD using a modified version of the previously reported procedure.[3] The Ga_2O_3 was deposited using tris-(dimethylamido) gallium (III) ($Ga_2(NMe_2)_6$) (Strem Chemical Inc.) as the metal precursor and H_2O as an oxidant. During the deposition of Ga_2O_3, Ga cylinder was heated to 150 °C and pulsed for 0.2 s under exposure mode for 8 s, followed by a 12 s purge. In order to oxidize gallium precursor a 0.015 s pulse of H_2O was then introduced under the same exposure time. Using spectroscopic ellipsometry (Horiba Jobin

Yvon, Smart-SE), the growth rate of ~1.1 A˚ Ga_2O_3 per cycle was measured on silicon wafers. Then ~30 nm hematite was deposited on Ga_2O_3 underlayer. The precursors for deposition of ALD-hematite was ferrocene, and wet ozone was used as the oxidation source. During the deposition, the ferrocene cylinder was heated to 70 °C and pulsed for 20 s, followed by purging. Then, an oxidation cycle consists of 10 sub-cycles of a 0.015 s H_2O pulse followed by a 2 s ozone pulse where each sub-cycle was separated by a 5 s purge. In the end, ALD-Fe_2O_3 film was annealed at 500 °C for 2 h and followed by annealing in a preheated furnace at 800 °C for 4 min.

Electrodeposition of poly (phenylene oxide) (PPO): To block exposed FTO on ED-hematite films, poly (phenylene oxide) (PPO) blocking layer, was selectively polymerized onto the exposed FTO. The electropolymerization of PPO was performed according to the previous report.[4] Briefly, the ED-hematite electrodes were submerged in a solution containing 60 mM phenol, 90 mM 2-allylphenol, and100 mM $LiClO_4$ in 10/10/1 water/ethanol/2-butoxyethanol. The solution was adjusted to pH 9 by the addition of 10 mM tetrabutylammonium hydroxide in methanol. The potential of the electrodes was then scanned in the dark with the scan rate of 100 mV s^{-1} from 0.1 to 1.5 V versus Ag/AgCl for 75 cycles. In order to remove unreacted monomers and oligomers, the electrode was soaked in 10 mM tetrabutylammonium hydroxide in methanol for 10 min. In the end, the electrode was rinsed with ethanol, and cured in the air at 150 °C for 30 min. We measured the thickness of the PPO layer to be 12 nm using ellipsometry (Horiba Jobin Yvon, Smart-SE) on a silicon wafer coated with gold subjected to the same polymerization treatment as described above.

Catalyst deposition: $Ni_{0.75}Fe_{0.25}O_xH_y$ catalyst was deposited on 1 cm^2 of freshly prepared ED-hematite photoanode through the spin coating of the metal precursor solution.[5] Before catalyst deposition, hematite films were rinsed with deionized water and dried with N_2. Iron (III) 2-ethyl

hexanoate (50% w/w in mineral spirits, Strem Chemicals), and nickel (II) 2-ethyl hexanoate (78% w/w in 2-ethyl hexanoic acid, Strem Chemicals) were used as a precursor. An appropriate amount of metal precursor was dissolved in hexane to obtain a total concentration of 15% w/w metal complex, and further diluted with hexane to obtain a total metal concentration of 50 mM. Approximately 200 µL of the precursor solution was placed on the substrate, and spinning was performed at 3000 rpm for 60 s. The as-prepared catalyst/ED-hematite photoelectrode was treated with UV light for 2 h to decompose organic residues (254 nm, 4 W) followed by annealing in a preheated furnace at 100 °C in air for 1 h. The thickness of $Ni_{0.75}Fe_{0.25}O_xH_y$ is is ~ 220 nm, determined using AFM, cross-sectional scanning electron microscopy (SEM) and spectroscopic ellipsometry (SE).

Measured thickness with AFM	Measured thickness with SE	Measured thickness with cross-sectional SEM
220 nm	210 nm	220 nm

Table S1. The measured and calculated thickness of the Ni75 on hematite using AFM and SEM, and on silicon wafer using SE.

(Photo)electrochemical measurements: All electrochemical and photoelectrochemical measurements were taken in a custom made photoelectrochemical cell setup with an Eco Chemie Autolab potentiostat (Nova electrochemical software) in back illumination configuration (photon passing through the glass before reaching to the electrode surface). A homemade saturated Ag/AgCl and high surface area Pt mesh were used as reference and counter electrode, respectively. All (photo) electrochemical measurements were performed at room temperature and in 1.0 M

KOH. Aqueous solutions were prepared with ultra-pure water (resistivity 18 MΩ.cm) from a Milli-Q water purifier.

A 450 W Xe arc lamp (Horiba Jobin Yvon) was used as a white light source with an AM 1.5 solar filter to obtain a simulated solar spectrum with 100 mW cm^{-2} (1 sun) intensity. All electrochemical potentials vs. Ag/AgCl were converted to the reversible hydrogen electrode (RHE) by using equation 1:

$$E_{RHE} = E_{\mathrm{Ag/AgCl}} + 0.197\ \mathrm{V} + (0.059\ \mathrm{V}) \times pH \qquad \text{eq.1}$$

$Ni_{0.75}Fe_{0.25}O_xH_y$ film was conditioned by a series of cyclic voltammograms between 0.5 and 1.6 V vs. RHE under illumination until Ni reduction peak remains constant. The *J-E* data shown for the catalyst-modified electrodes are from the final measurement.

Material characterization: Scanning electron microscope (SEM) images were taken using JEOL 7500F (field emission emitter). The cross-sectional sample for scanning transmission electron micrograph (STEM) was prepared using Thermal Fisher Helios 650 Nanolab SEM/FIB. Gold and platinum were deposited at the surface of the sample to protect it during the sample preparation. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive x-ray (EDX) analysis were taken on a Thermo Fisher Scientific Talos F200X operated at 200 kV. The X-ray photoelectron spectroscopy (XPS) data were collected using PerkinElmer Phi 5600 ESCA system equipped with a monochromatic Mg Kα source to illuminate the sample at a takeoff angle of 45°.

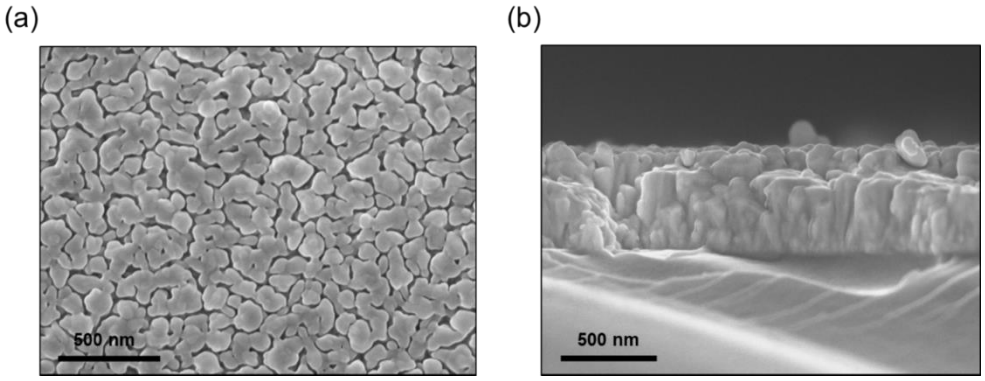

Figure S1. Scanning electron microscopy images of ED-hematite on FTO substrate. (a) top view (b) cross-sectional view

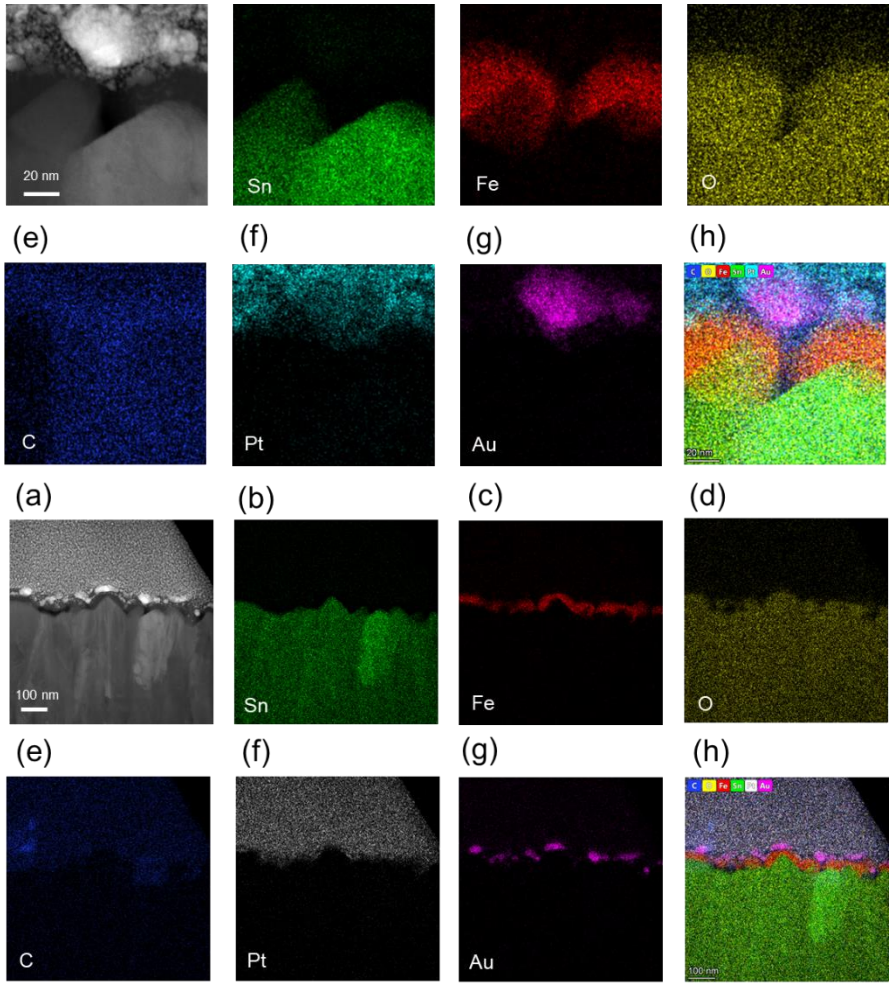

Figure S2. HAADF-STEM and EDX elemental mapping of the PPO-modified ED-hematite. (a) HAADAF-STEM image and (b-h) EDX mapping of tin (b), iron (c), oxygen (d), carbon (e), platinum (f), gold (g) and their overlay (h).

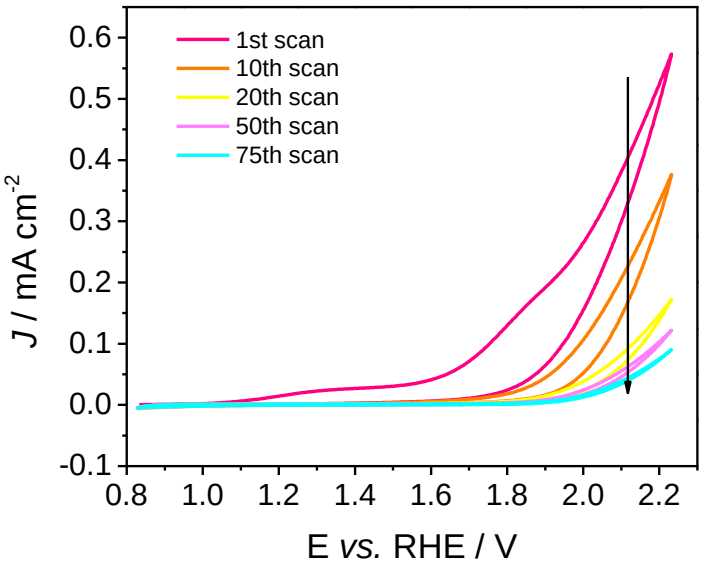

Figure S3. Current density measurements during electrodeposition of PPO into the ED-hematite pinholes. The progressive decrease in the current density indicates the growth of the insulating PPO film. Scan rates are 100 mV s^{-1}.

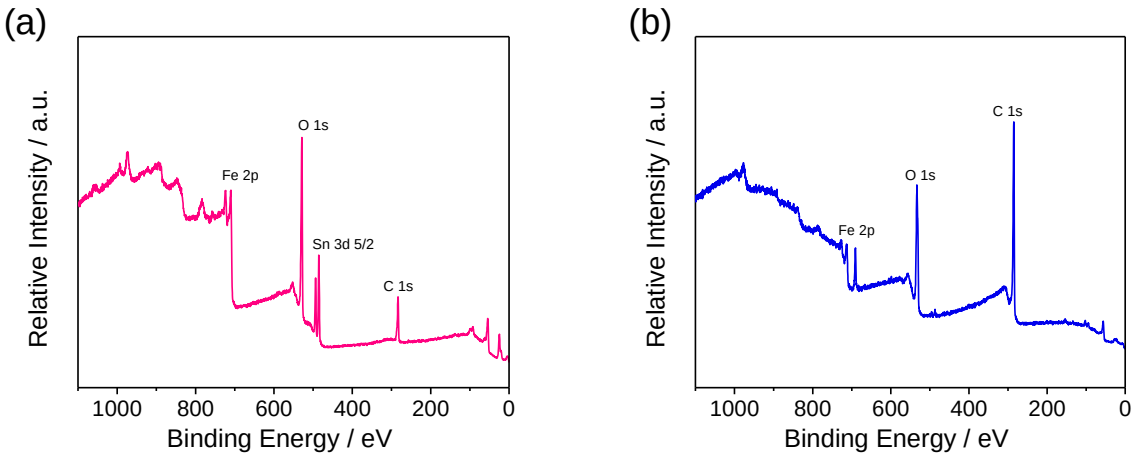

Figure S4. XPS measurement of (a) bare ED-hematite and (b) PPO modified ED-hematite.

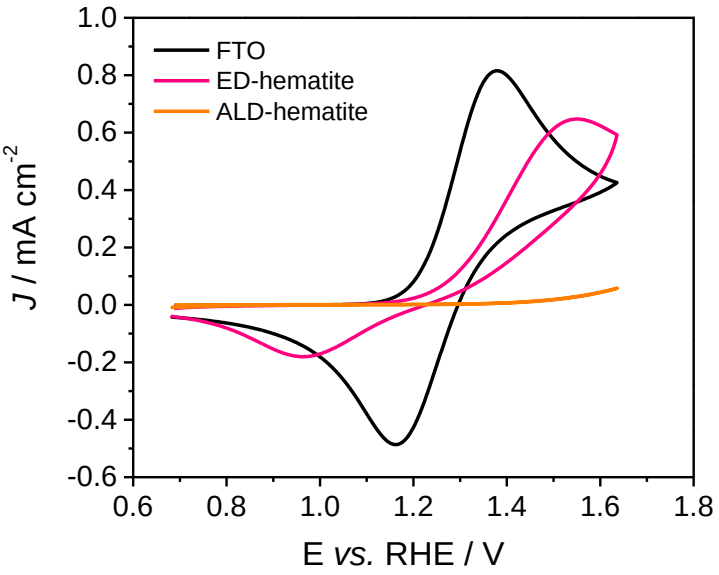

Figure S5. Pinhole-free hematite thin film prepared via ALD. Dark CV response of the bare FTO (black), ED-hematite (pink) and ALD-hematite (orange) in 1.0 M KOH containing 10 mM $k_4[Fe(CN)_6]$ solution. The scan rates are 10 mVs^{-1}. The negligible current density recorded for the ALD-hematite compared to the FTO and ED-hematite indicates a pinhole-free hematite thin film achieved.

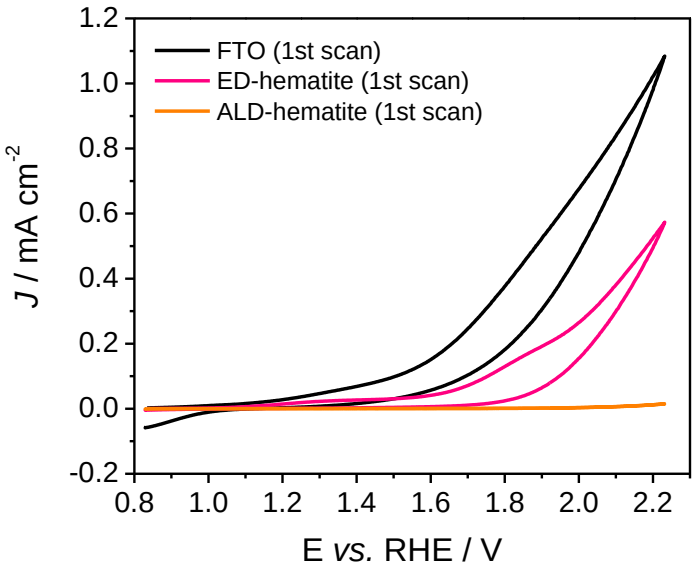

Figure S6. Evidence of selective PPO deposition on FTO. The measured current density during the first scan of PPO electrodeposition on different surfaces, including bare FTO (black), ED-hematite (pink) and ALD-hematite (orange). A negligible current was recorded for pinhole-free ALD-hematite suggests that hematite surface is electrocatalytically inactive for PPO deposition. Scan rates are 100 mVs^{-1}.

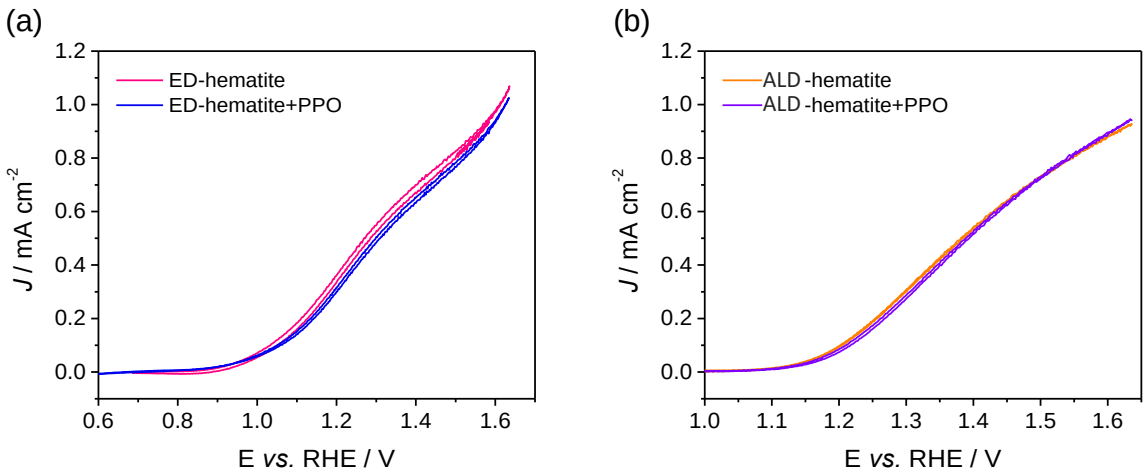

Figure S7. PPO deposition does not compromise the hematite performance for PEC OER. Comparing the *J-E* responses for the a) ED-hematite before (pink) and after deposition of PPO (blue) and b) ALD-hematite before (orange) and after deposition of PPO (violet). Measurements were executed at a scan rate of 10 mV s^{-1} under 1 sun illumination in 1.0 M KOH.

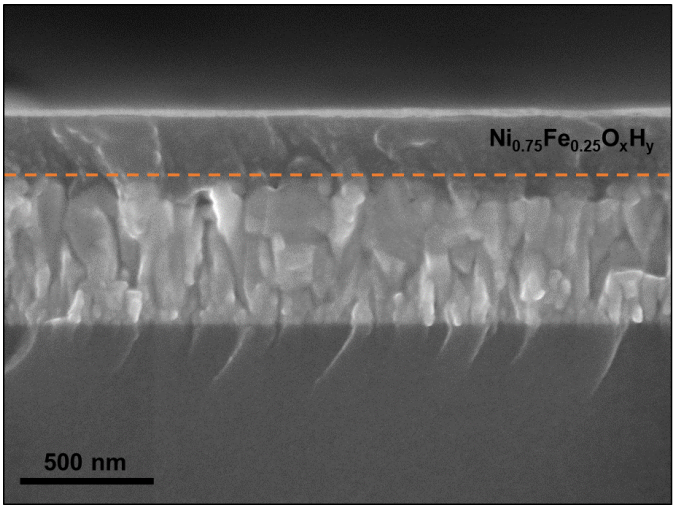

Figure S8. Cross-sectional scanning electron microscopy image of ED-hematite modified with $Ni_{0.75}Fe_{0.25}O_xH_y$.

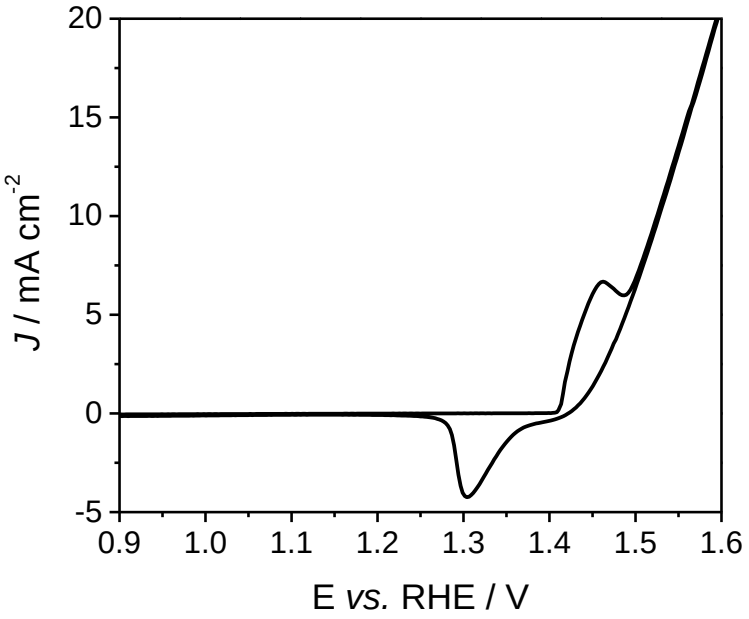

Figure S9. *J-E* response of the $Ni_{0.75}Fe_{0.25}O_xH_y$ electrocatalyst deposited on the FTO substrate.

References:

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