## Supporting information

Substrate dependent solar water oxidation performance of ultrathin  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> electrodes

Omid Zandi, Joseph A. Beardslee, Thomas Hamann\*

Department of Chemistry, Michigan State University, East Lansing, MI 48824-1322, USA

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA.

\*Email: hamann@chemistry.msu.edu



**Figure 1S**. *J-V* curves of  $\sim 18$  nm hematite electrodes with (solid dark blue) and without (dashed red) Ga<sub>2</sub>O<sub>3</sub> underlayer, under water oxidation condition in dark.



**Figure 2S**. *J-V* curves of ~18 nm hematite electrodes with 1 (dash-dotted orange), 2 (solid dark blue) and 4 nm (dashed green)  $Ga_2O_3$  underlayer, under water oxidation condition and 1 sun illumination.



**Figure 3S**. *J-V* curves of ~18 nm hematite electrodes with a 2 nm (18 ALD cycles)  $Ga_2O_3$  underlayer (dark blue) and the same thickness of hematite without underlayer but doped with the same ALD cycles of  $Ga_2O_3$  (green). *J-V*s obtained under water oxidation condition in pH 7 and 1 sun illumination.



Figure 4S. Transmittance of FTO (dashed red) and FTO coated with 2 nm  $Ga_2O_3$  (solid dark blue).



Figure 5S. Absorbance spectra of  $\sim 18$  nm hematite with (solid dark blue) and without (dashed red) a Ga<sub>2</sub>O<sub>3</sub> underlayer.



Figure 6S. XPS depth of hematite films with (dashed lines) and without (solid lines)  $Ga_2O_3$  underlayer deposited on  $SnO_2$  coated Si wafer.



**Figure 7S**. a) Absorptance spectra of 18 nm hematite films with (pink) and without (red) Nb<sub>2</sub>O<sub>5</sub> underlayer before (dashed lines) and after (solid lines) annealing in 500 °C.



**Figure 8S**. IPCE of 60 nm hematite electrodes with (dark blue squares) and without (red circles)  $Ga_2O_3$  underlayer under the condition of back (solid shapes) and front side (open shapes) illumination at 1.78 V vs RHE.



**Figure 9S**. Raman spectrum of a 60 nm hematite (red) film deposited on FTO overlaid with that of the FTO substrate (grey).



Figure 10S. SEM images of 18 nm hematite on FTO with 2 nm  $Nb_2O_5$  underlayer. Scale bar is 100 nm.



Figure 11S. SEM images of 18 nm hematite on FTO with (a and b) and without (c and d) a  $Ga_2O_3$  underlayer. The scale bar is 20 nm in each case.



Figure 12S. Experimental and Gaussian fit of two Raman phoneme modes for 18 nm hematite films deposited on different underlayers. A table of fit FWHM values is also shown.