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## **Supporting Information**

### **Strong O 2p-Fe 3d Hybridization Observed in Solution-Grown Hematite**

#### **Films by Soft X-ray Spectroscopies**

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Table S1: The thicknesses of the hematite films investigated in this work. The hematite samples were milled by a focused beam microscope system (FIB, JOEL 4500 multibeam system).

<b>Sample Number</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
<b>Sample code</b>	ALD 500	ALD 800	sdH	rgH I	rgH II	rgH III
<b>Thickness (nm)</b>	10-20	10-20	130	250	460	530

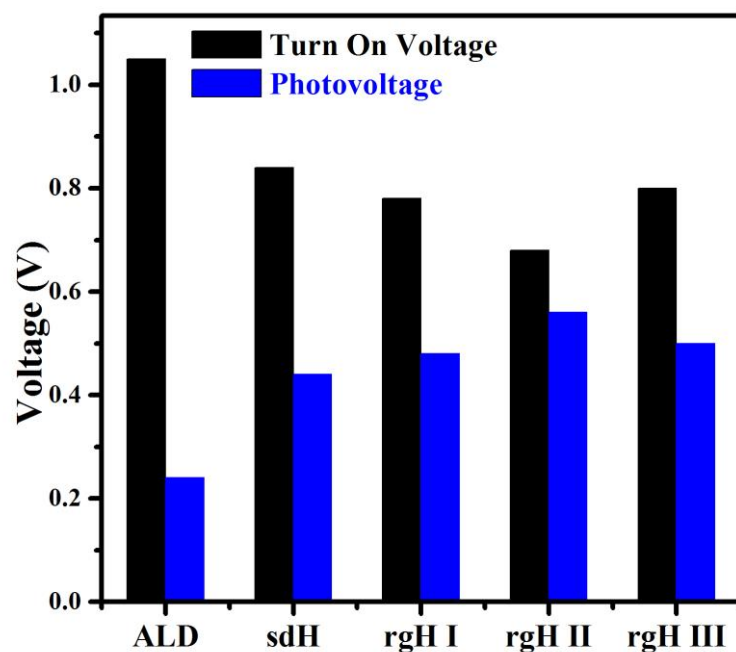


Figure S1: The PEC performance characterization of hematite films synthesized by different methods. The turn-on voltage and photovoltage values of the hematite photon anode were plotted in black and blue. The results indicated that the rgH II sample showed the best PEC performance with the highest photovoltage and lowest turn-on voltage among the investigated samples.

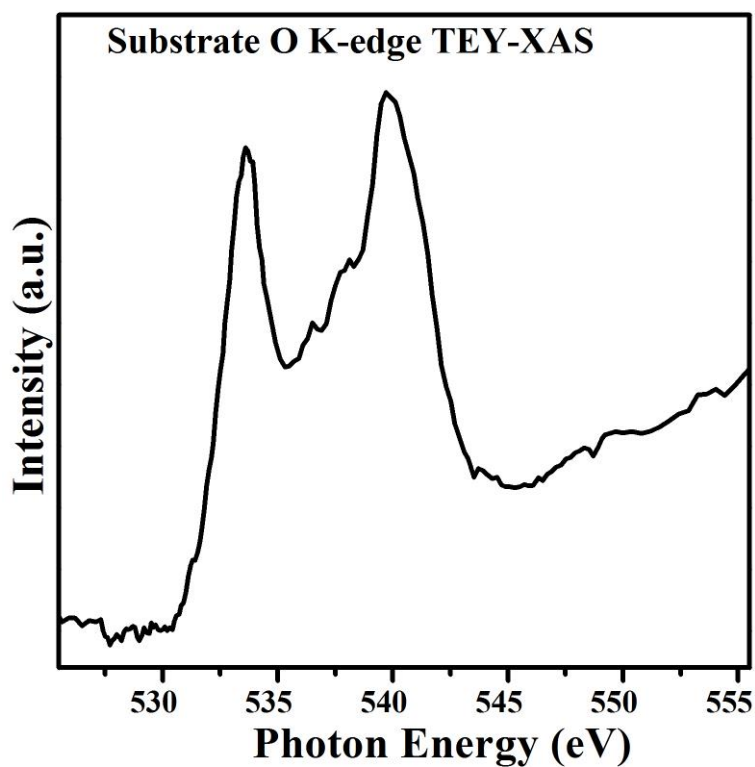


Figure S2: The O K-edge XAS of the substrate of the hematite samples.

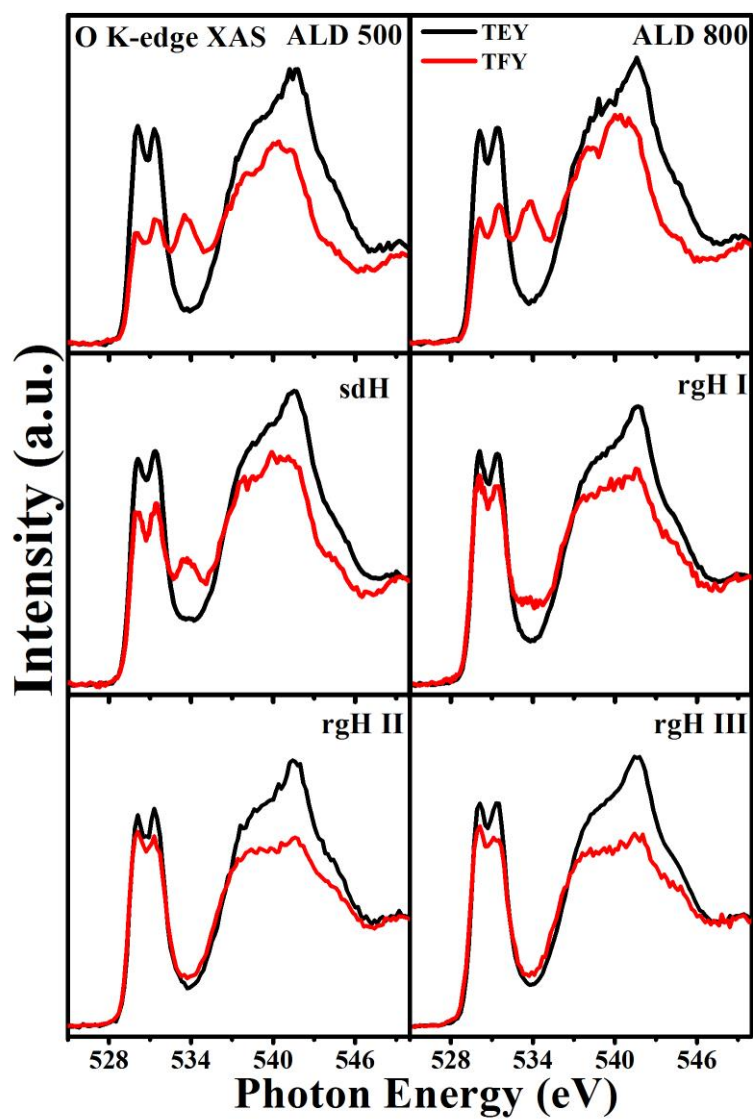


Figure S3: The O K-edge TEY and TFY XAS signals of hematite films synthesized by different methods. The TEY and TFY signal were plotted to get easy comparison.

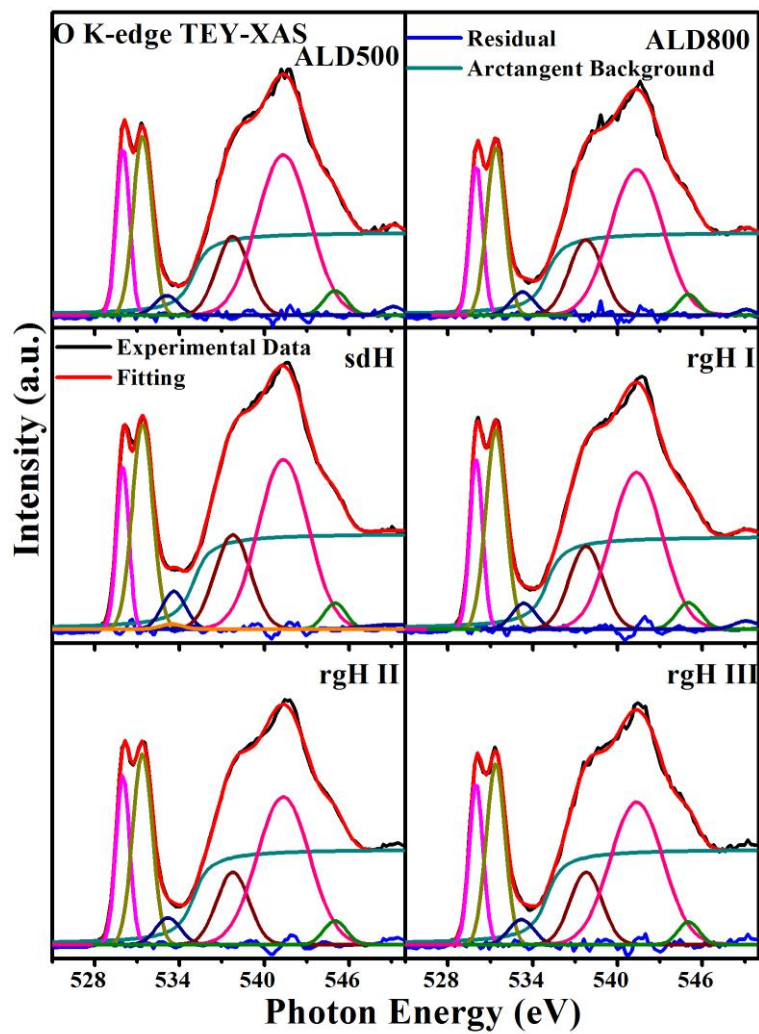


Figure S4: The O K-edge TEY-XAS signals of hematite films synthesized by different methods. After subtracting an arctangent background, several Gaussian functions were employed to fit the XAS spectrum. For easy comparison, the Y axis range was fixed for the six spectra.

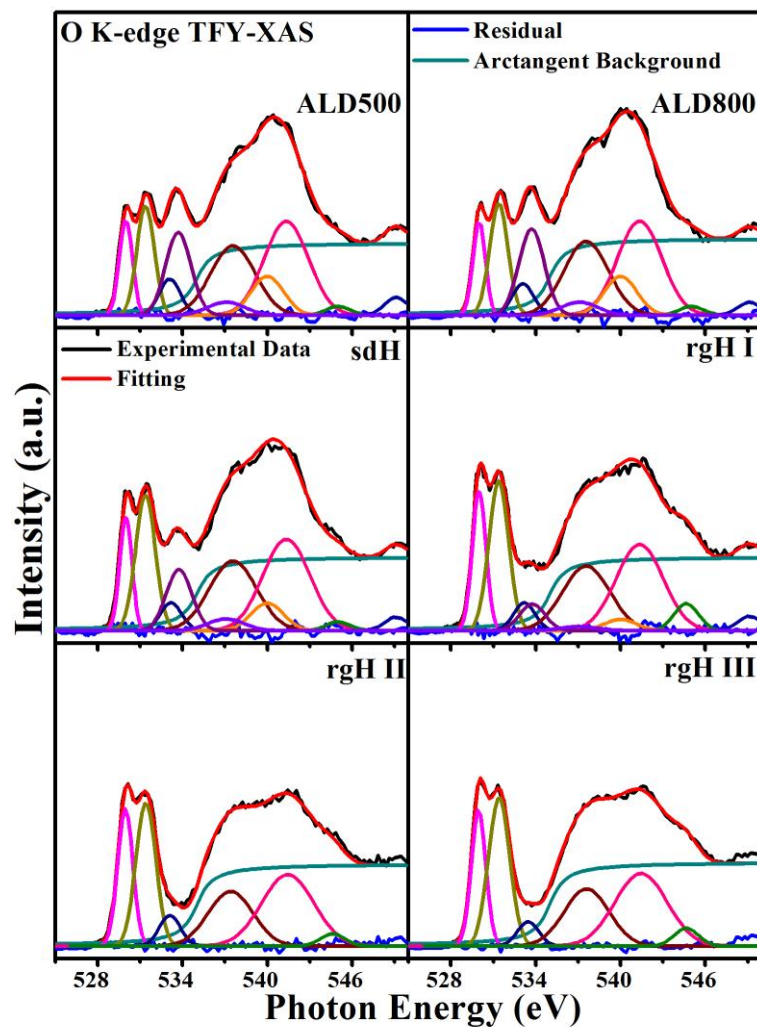


Figure S5: The O K-edge TFY-XAS signals of hematite films synthesized by different methods. After subtracting an arctangent background, several Gaussian functions, corresponding to signals from both the hematite films and FTO substrate, were employed to fit the XAS spectrum. Three peaks were employed to fit the substrate signals, the intensity ratio among these features are fixed during the fitting process. For easy comparison, the Y axis range was fixed for the six spectra.

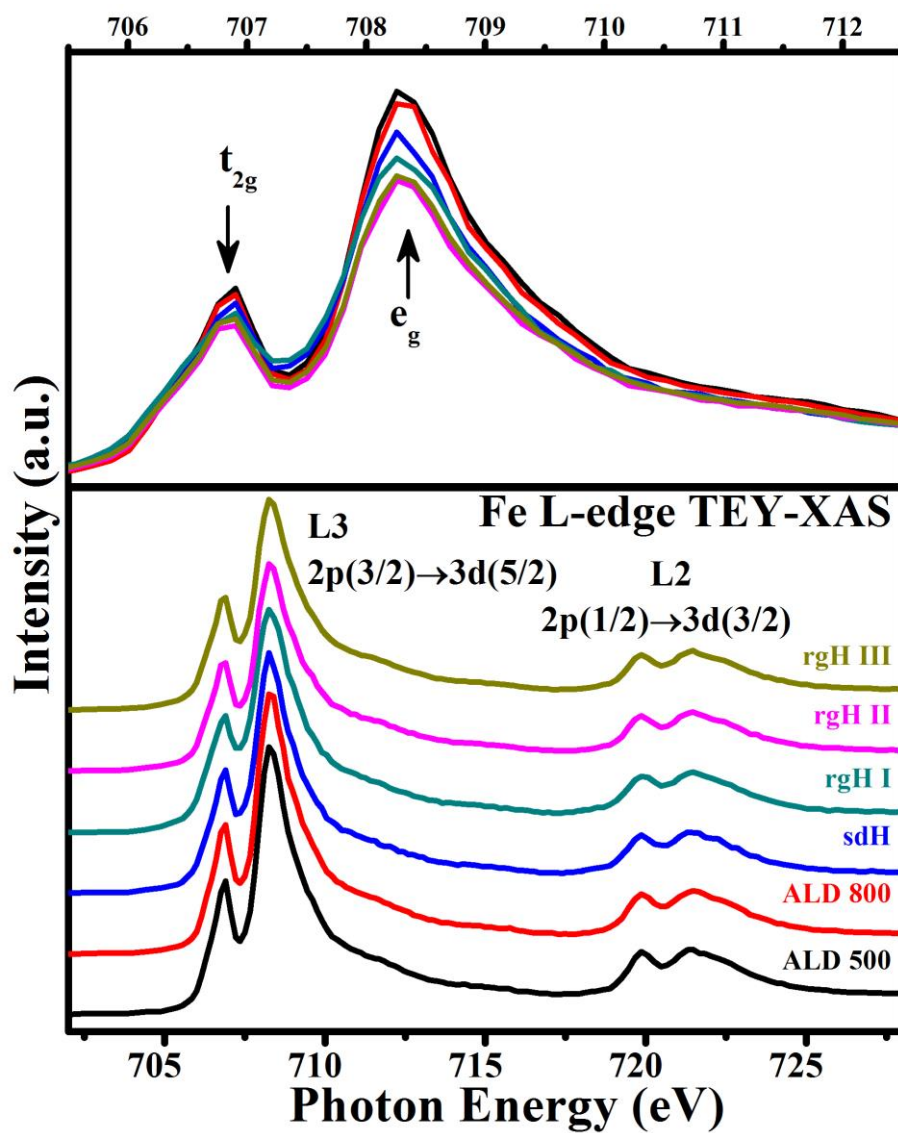


Figure S6: The Fe L-edge TEY XAS signals of hematite films synthesized by different methods, the L3-edge XAS spectra are shown in the inset of the Figure 3.

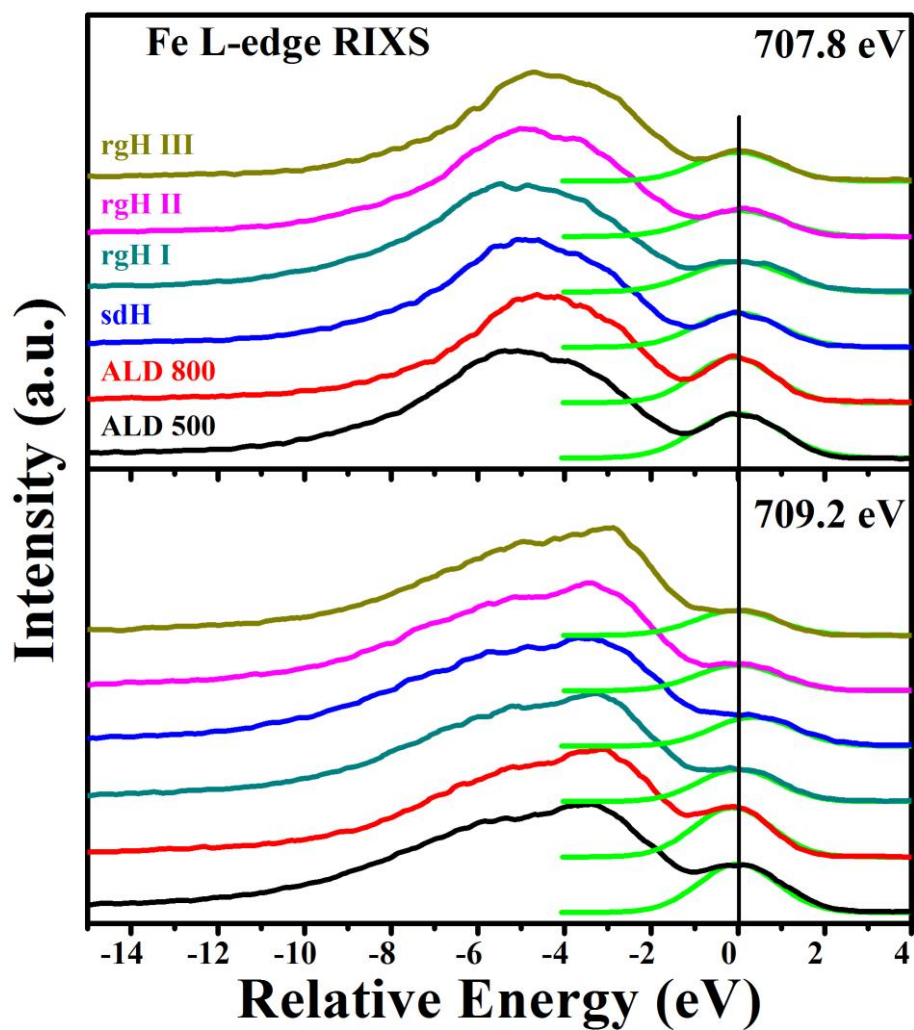


Figure S7: The Fe L-edge RIXS signals of hematite films synthesized by different methods. The elastic peak was fitted with a Gaussian function and plotted in green lines. The zero-energy position was indicated by a solid line.



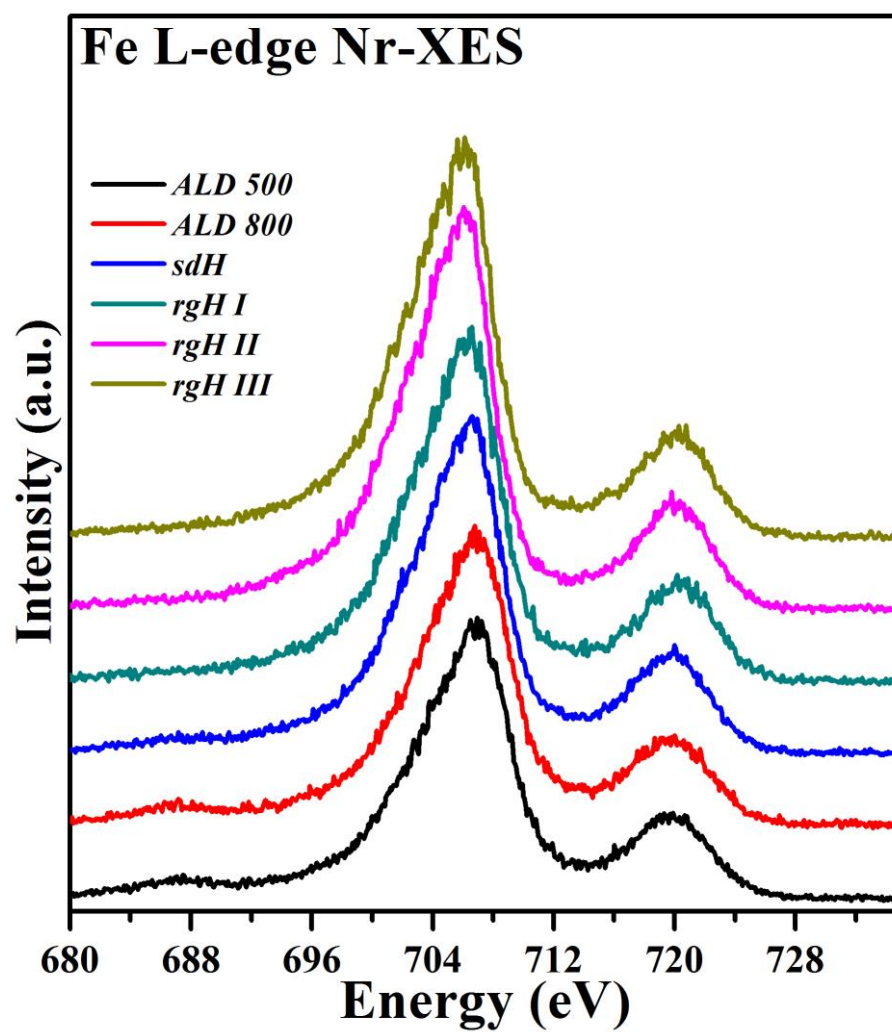


Figure S8: The Fe L-edge Nr-XES signals of hematite films synthesized by different methods.