Supplementary Information

Effect of Low Oxygen Annealing on Photoelectrochemical Water Splitting Properties of α-Fe_2O_3

Yoichi Makimizu,[ab] JeongEun Yoo,[a] Mahshid Poornajar,[a] Nhat Truong Nguyen,[a]† Hyo-Jin Ahn,[ac]‡ Imgon Hwang,[a] Stepan Kment[c] and Patrik Schmuki*[acd]

[a] *Department of Materials Science and Engineering, University of Erlangen-Nuremberg, Martensstrasse 7, D-91058 Erlangen, Germany*

[b] *Steel Research Laboratory, JFE Steel Corporation, 1, Kokan-cho, Fukuyama, Hiroshima 721-8510, Japan*

[c] *RCPTM, Faculty of Science, Palacky University, 17. listopadu 12, 771 46, Olomouc, Czechia*

[d] *Chemistry Department, Faculty of Sciences, King Abdulaziz University, 80203 Jeddah, Saudi Arabia Kingdom*

† Current address: *Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6, Canada*

‡ Current address: *German Engineering Research and Development Center LSTME Busan, Affiliate Institute to FA Universität 7 Erlangen, 1276, Jisa-Dong, Gangseo-Gu, Busan 46742, Republic of Korea*

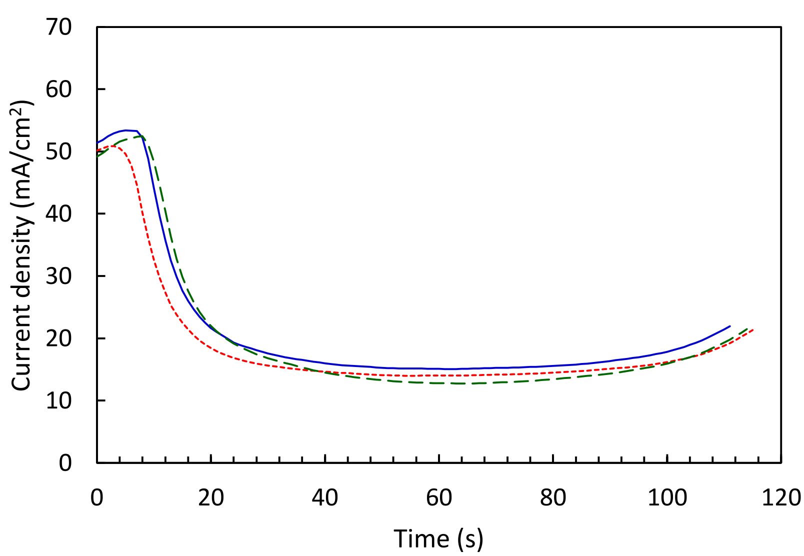


Figure S1. Some examples of anodization anodic current-time curves for Fe layers on FTO glass.

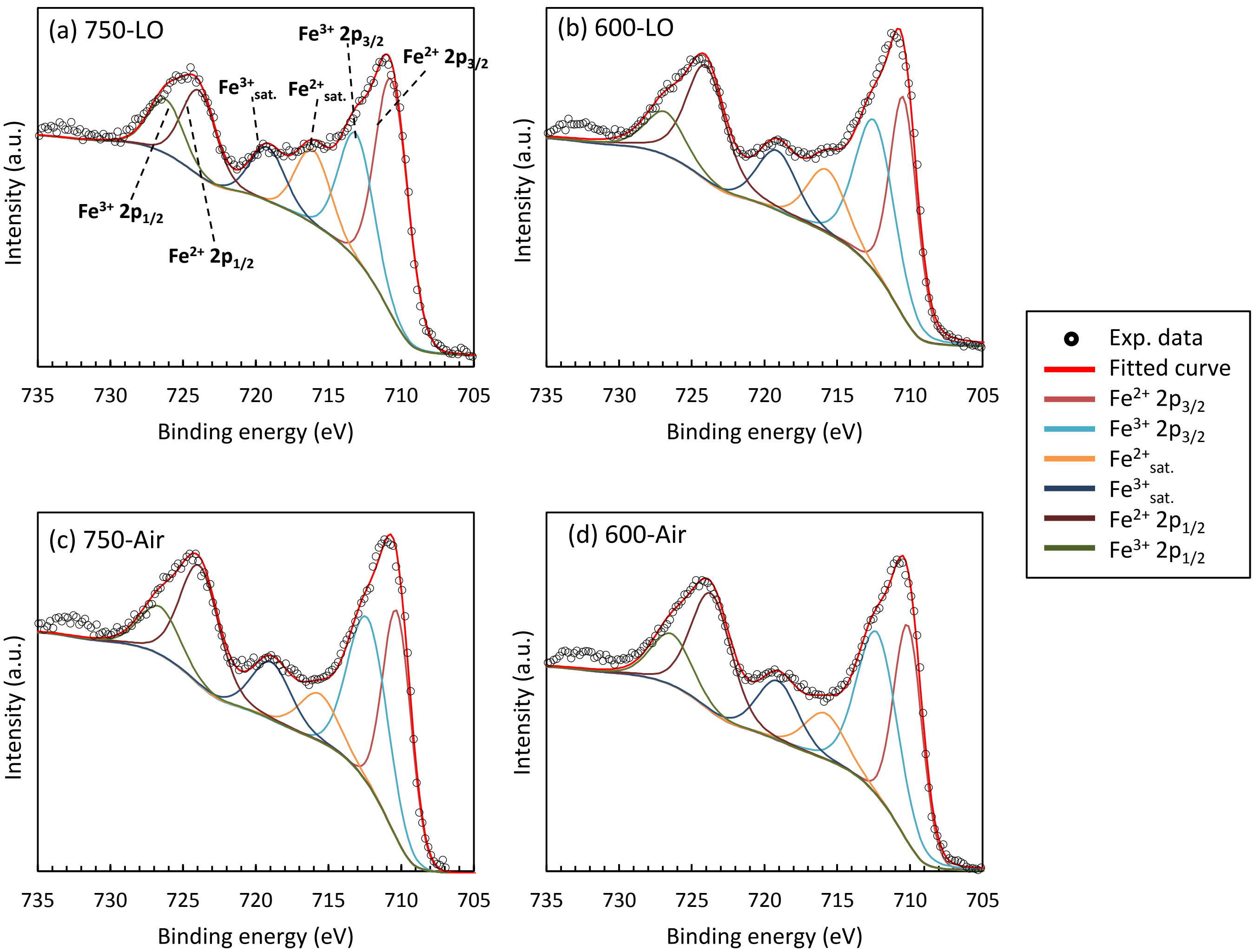


Figure S2. X-ray photoelectron spectra of Fe 2p shown in Fig. 3(d) and curves fitted to Fe^{2+} and Fe^{3+} for α-Fe_2O_3 annealed under various conditions.

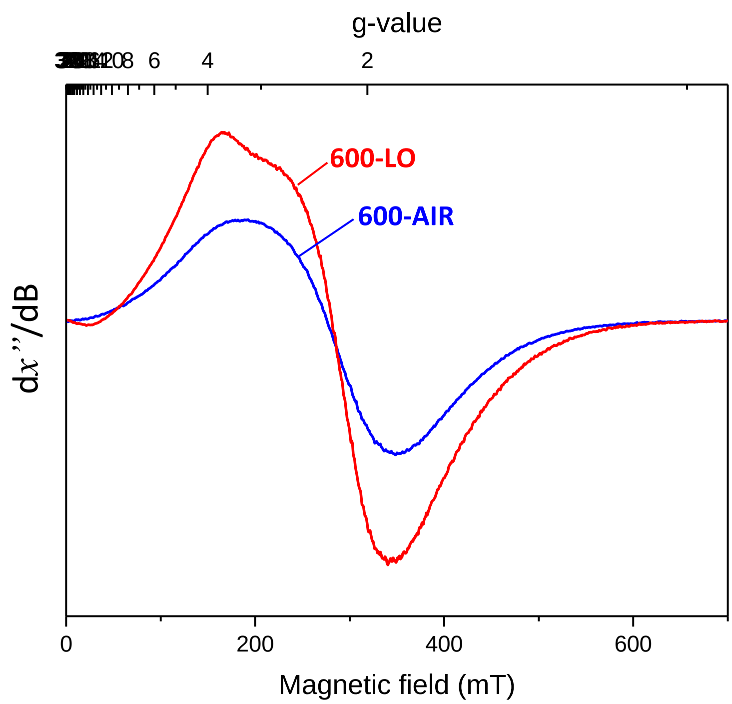


Figure S3. EPR spectra of α-Fe_2O_3 after annealing at 600 ℃ in 0.03% O_2-Ar and air ambient.

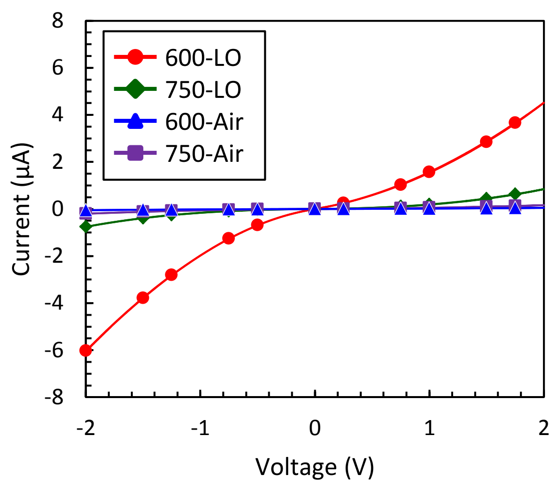
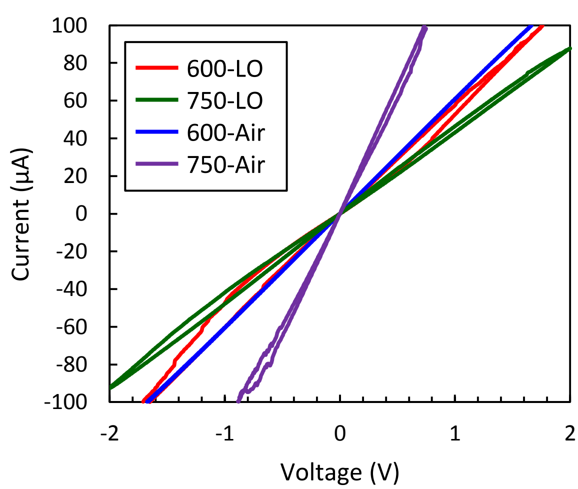


Figure S4. *I-V* curves collected by conductivity measurements for α-Fe_2O_3 annealed under various conditions.



	750-LO	600-LO	750-Air	600-Air
Resistance (Ω)	21.33	17.26	7.64	16.44

Figure S5. *I-V* curves and resistance value collected by conductivity measurements for FTO substrate annealed under various conditions.

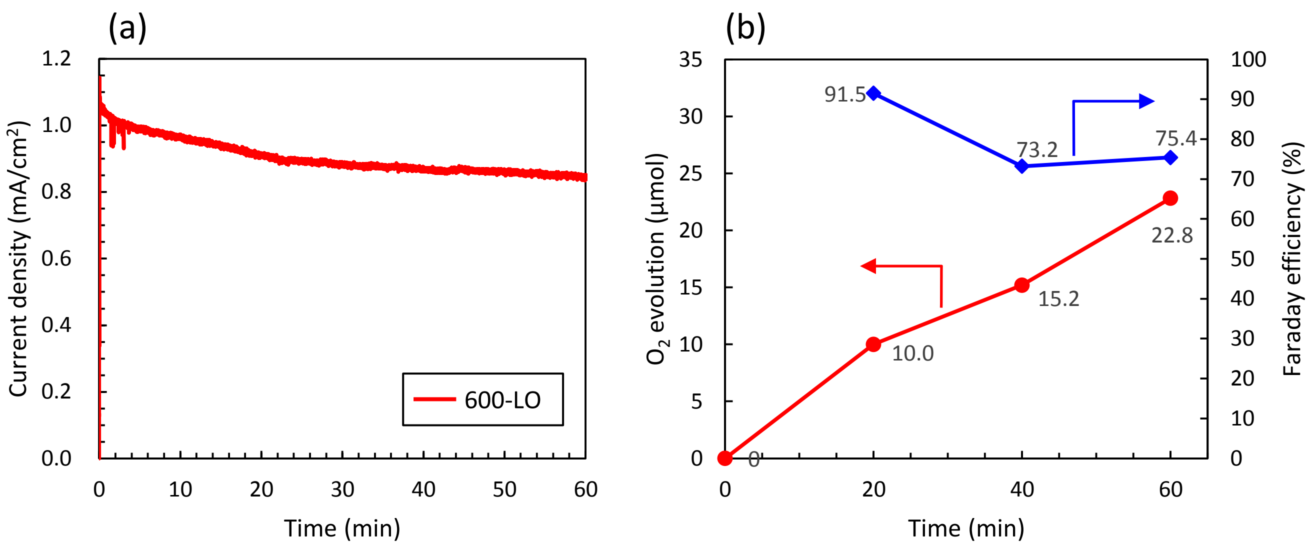


Figure S6. (a) Photocurrent-time (*J*-*t*) curves and (b) amount of oxygen generation measured under illumination (AM 1.5 G, 100 mW/cm^2) at 1.5 V vs. RHE in 1.0 M KOH electrolyte for α-Fe_2O_3 layers after annealing at 600 °C in 0.03% O_2-Ar ambient.

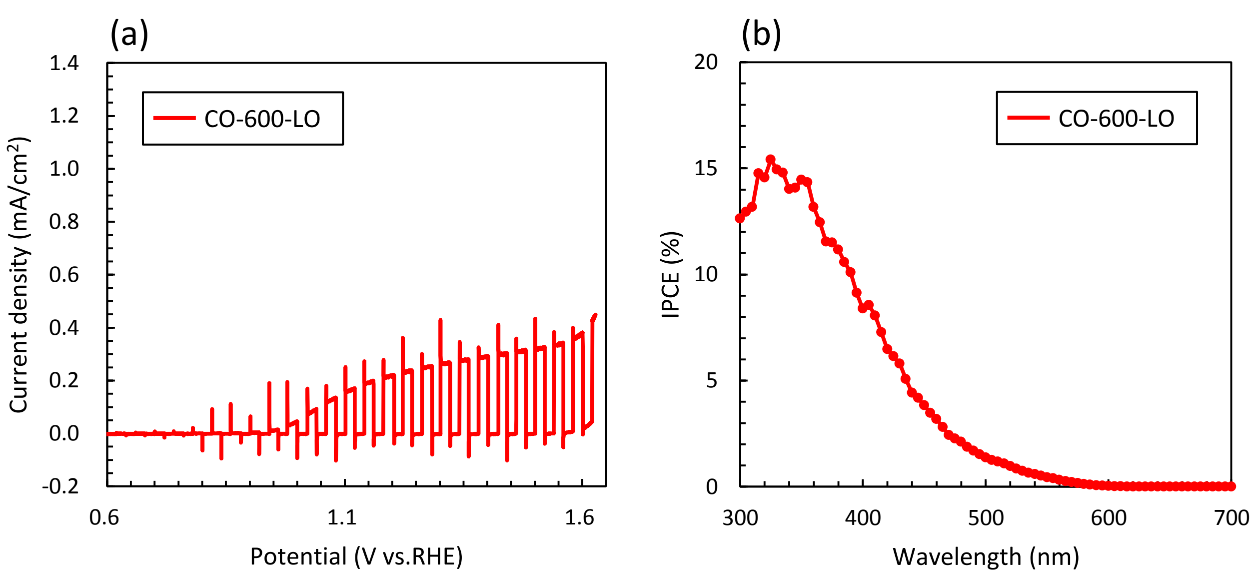


Figure S7. (a) Photocurrent-potential (*J*-*V*) curves with chopped light illumination (AM 1.5G, 100 mW/cm^2) and (b) IPCE spectra measured at 1.5 V vs. RHE for compact α-Fe_2O_3 layers annealed at 600 °C in 0.03% O_2-Ar ambient. All samples were measured in 1.0 M KOH electrolyte.

Table S1. EIS fitting results for α-Fe_2O_3 annealed under various conditions.

	600-LO	750-Air	750-LO	600-Air
R_S (Ω)	301	13	151	13
R_1 (Ω)	611	1980	2351	15800
R_2 (Ω)	3526	3834	8861	19187
C_1 (F)	5.05 x 10^{-4}	3.33 x 10^{-5}	2.47 x 10^{-5}	5.94 x 10^{-6}
C_2 (F)	2.44 x 10^{-5}	8.70 x 10^{-6}	4.10 x 10^{-5}	2.39 x 10^{-5}

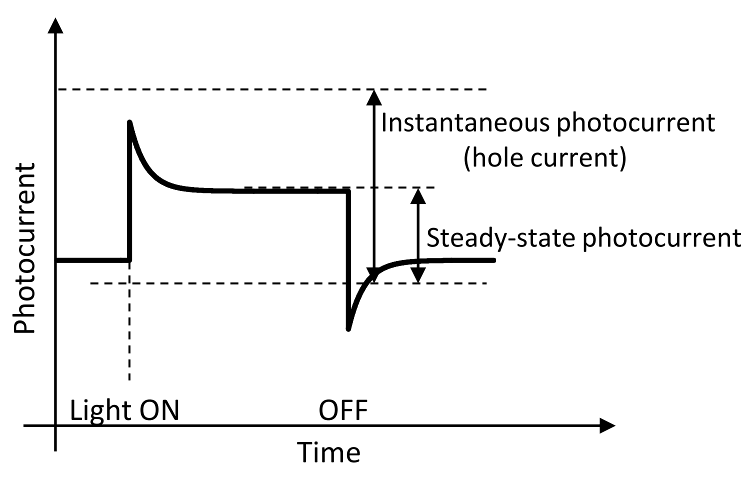


Figure S8. Typical transient photocurrent response of α-Fe_2O_3 electrode.

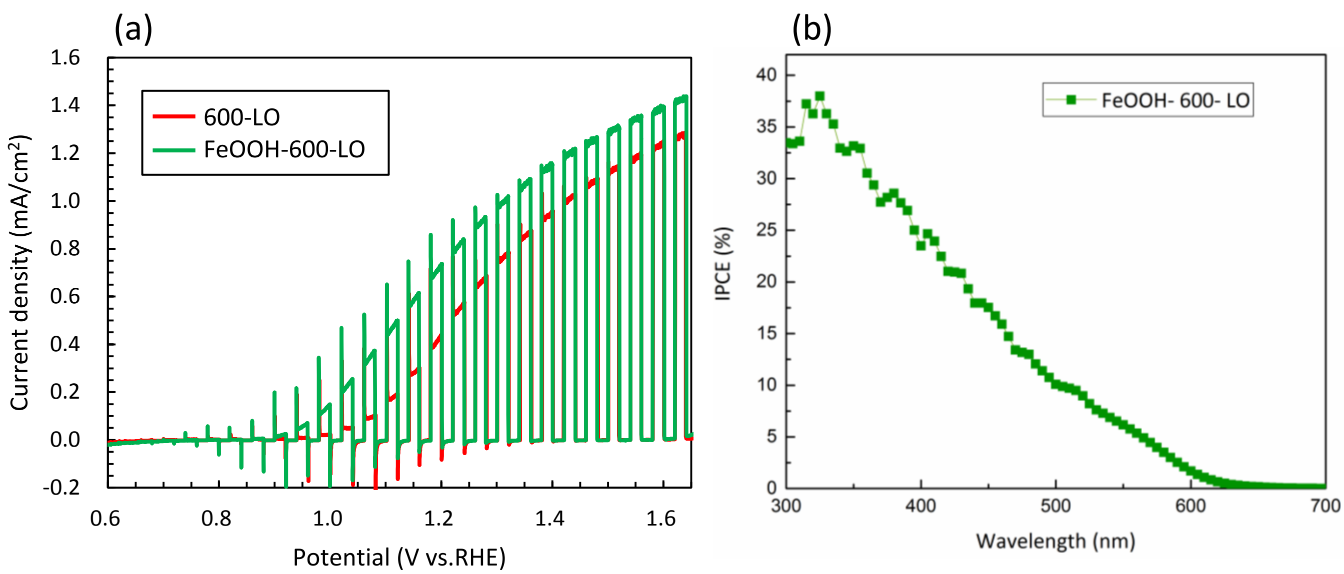


Figure S9. (a) Photocurrent-potential (*J*-*V*) curves with chopped light illumination (AM 1.5G, 100 mW/cm^2) and (b) IPCE spectra measurement at 1.5 V vs. RHE for α-Fe_2O_3 layer decorated with FeOOH. All samples were measured in 1.0 M KOH electrolyte.

Table S2. photocurrent densities of recent reports and present study on anodized α-Fe_2O_3 layer.

Fabrication technique	Substrate	Annealing		Material	Additional treatment	Electrolyte	Illumination	Photocurrent / mA cm^{-2}	Ref.
		Temp. / ℃	Atmosphere					at 1.5 V vs. RHE	
Two-step anodization	Fe foil	400	O2	Hematite	-	0.01 M $NaSO_4$	AM 1.5 G, 100 mW/cm^2	0.88 (at 0.6 V vs Ag/AgCl)	65
Anodization	FTO	500	10%H_2-Ar	Hematite	-	1 M KOH	Xe lamp, 100 mW/cm^2	0.6	66
Anodization	FTO	750	Ar	Hematite	-	1 M KOH	AM 1.5 G, 100 mW/cm^2	0.4	32
Anodization	FTO	550	Air	Hematite	-	1 M NaOH	NA	0.47	67
Anodization	FTO	750	Air	Hematite	-	1 M NaOH	AM 1.5 G, 100 mW/cm^2	0.2	33
Anodization	FTO	500	Air	Hematite	-	1 M NaOH	AM 1.5 G, 100 mW/cm^2	0.05	68
				Hematite/ Amorphous Ti-Oxide	-			0.2	
Anodization with rotation	Fe foil	500	Ar	Hematite Magnetite	-	1 M KOH	AM 1.5 G, 100 mW/cm^2	0.11	69
Anodization	Mild steel	450	Air	Hematite Magnetite	L-Cysteine treatment	1 M NaOH	AM 1.5 G, 100 mW/cm^2	0.8	70
					-			0.1	
Anodization with rotation	Fe rod	500	Ar	Hematite Magnetite	-	1 M KOH	AM 1.5 G, 100 mW/cm^2	0.11	71
Modulated anodization	Fe foil	600	NA	Hematite Magnetite	-	1 M KOH	AM 1.5 G, 100 mW/cm^2	0.32	72
					Sn-doped			0.67	
					Co-Pi / Sn-doped			0.73	
Anodization	FTO	600	0.03%O_2-Ar	Hematite	-	1 M KOH	AM 1.5 G, 100 mW/cm^2	1.1	This study
					FeOOH			1.3	