Revealing Long-lived Electron-hole Migration in Core-Shell α/γ-Fe_2O_3/FCP for Efficient Photoelectrochemical Water Oxidation

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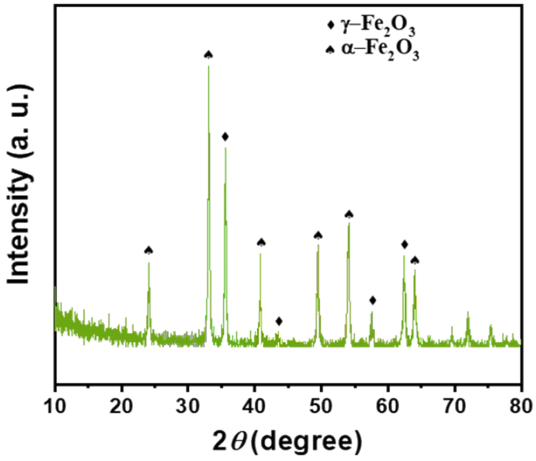

Fig. 1. (a) XRD patterns of γ-Fe_2O_3/α-Fe_2O_3 powder.

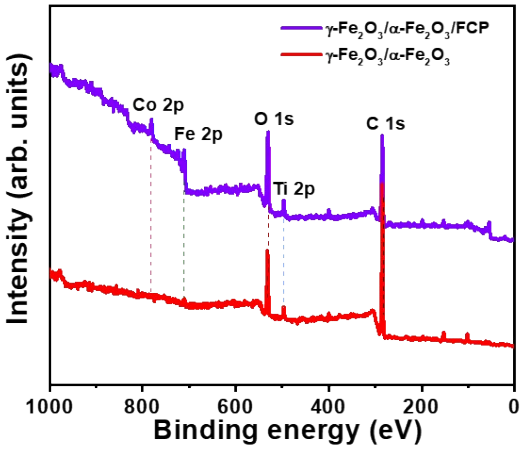

Fig. S2: XPS survey spectra of γ-Fe_2O_3/α-Fe_2O_3/FCP and γ-Fe_2O_3/α-Fe_2O_3.[1]

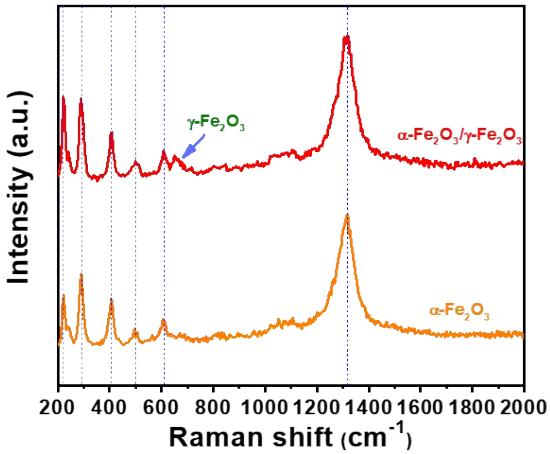

Fig. S3: Raman spectra of γ-Fe_2O_3/α-Fe_2O_3 and α-Fe_2O_3.

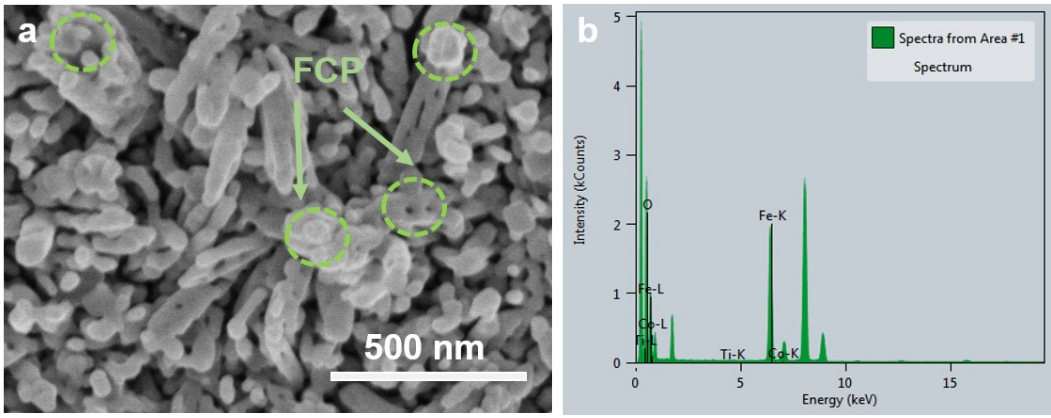

Fig. S4: (a) SEM images of α-Fe_2O_3/FCP. (b) EDS spectra of γ-Fe_2O_3/α-Fe_2O_3/FCP.

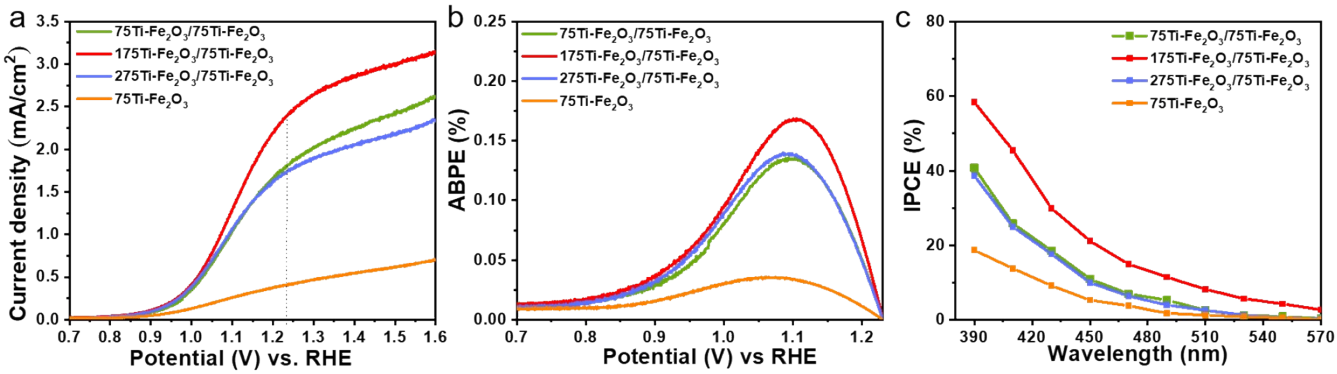

Fig. S5. Ti-Fe_2O_3, 75Ti-Fe_2O_3/75Ti-Fe_2O_3, 175Ti-Fe_2O_3/75Ti-Fe_2O_3, and 225Ti-Fe_2O_3/75Ti-Fe_2O_3: (a) Current density-potential curves; (b) ABPE spectra; (c) IPCE plots.

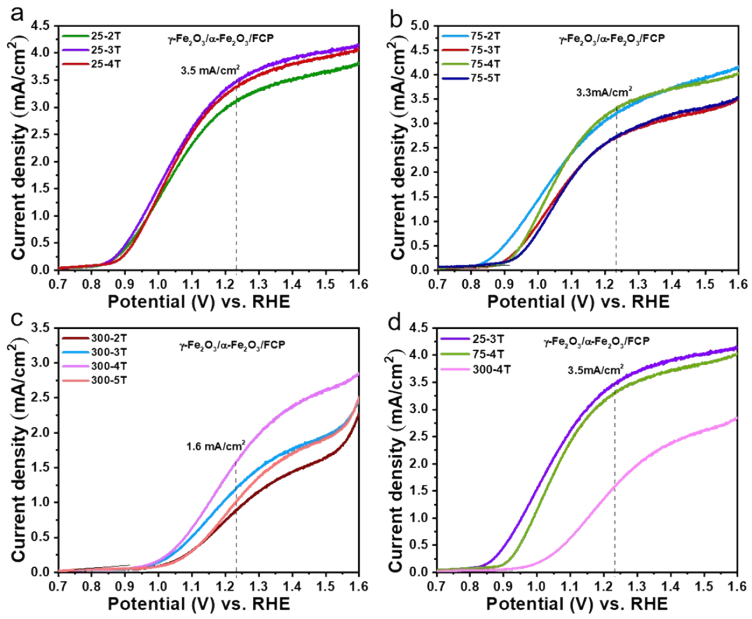

Fig. S6. LSV plots of γ-Fe_2O_3/α-Fe_2O_3/FCP: (a) dipping times (2, 3, or 4) under 25°; (b) dipping times (2, 3, 4, or 5) under 75°; (c) dipping times (2, 3, 4, or 5) under 300°. (d) comparison under optimal conditions.[2]

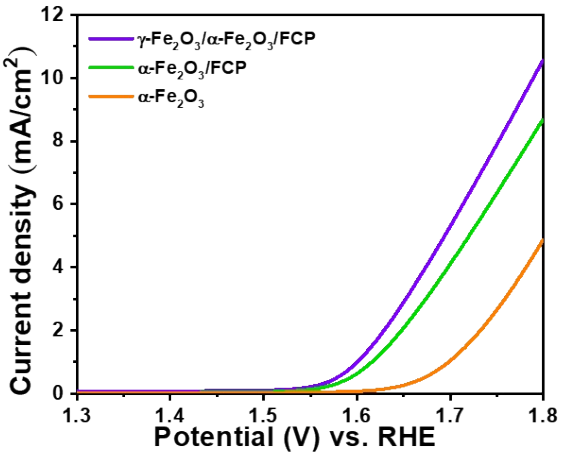

Fig. S7. LSV curves of α-Fe_2O_3 and phase junction measured without AM 1.5G irradiation.

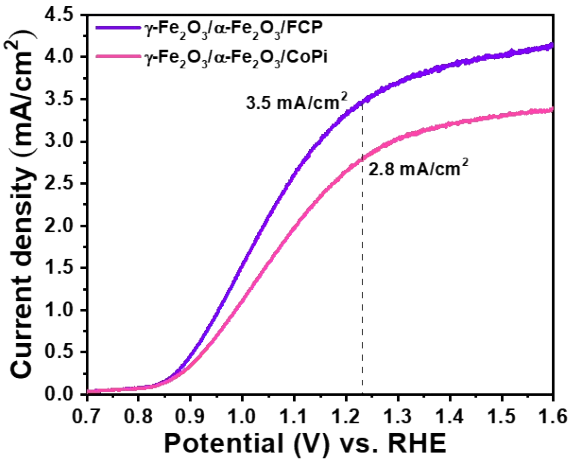

Fig. S8. LSV plots of γ-Fe_2O_3/α-Fe_2O_3/FCP and γ-Fe_2O_3/α-Fe_2O_3/CoPi in KOH electrolyte.

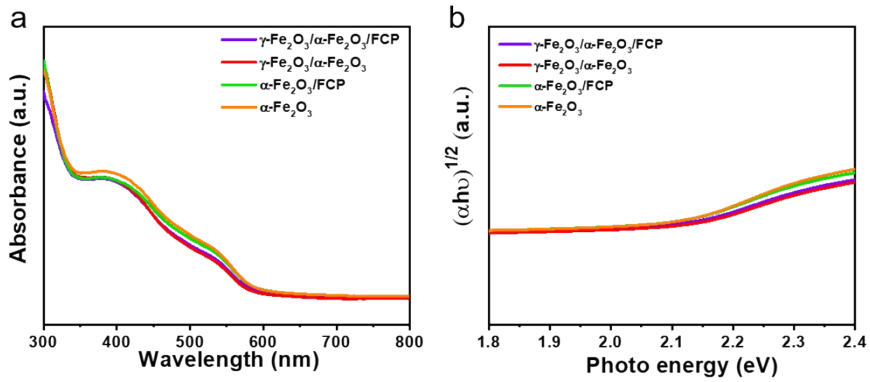

Fig. S9. (a) UV-vis absorption spectra of α-Fe_2O_3 and phase junction. (b) Tauc's plots of α-Fe_2O_3 and phase junction.

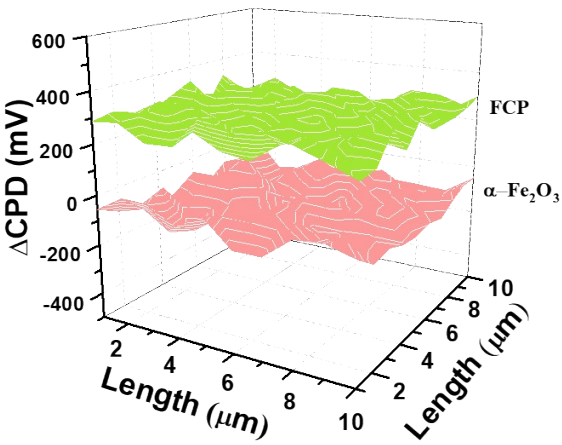

Fig. S10: Work Function measurement of pure α-Fe_2O_3 and FCP.

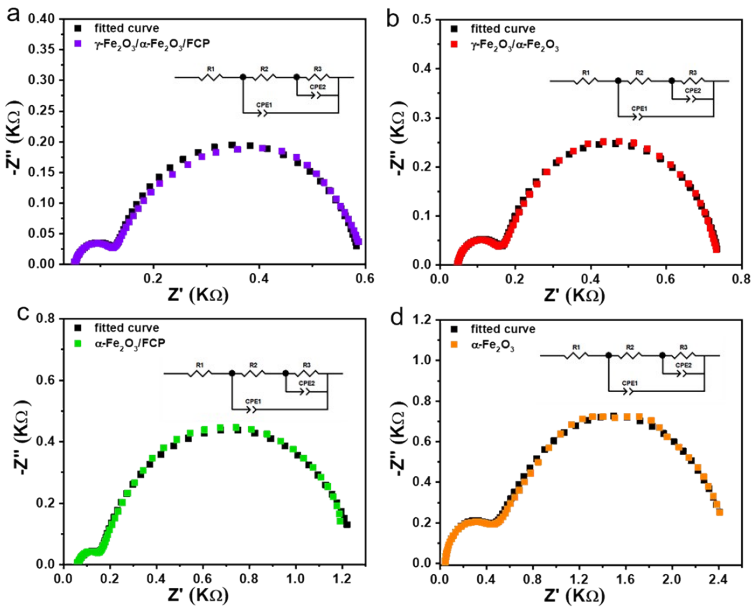

Fig. S11: Equivalent circuit diagram and the fitted Nyquist plots for α-Fe_2O_3 and phase junction.

Samples	R_1 (Ω)	R_2 (Ω)	R_3 (Ω)
α-Fe_2O_3	**45.12**	**461.9**	**2036**
α-Fe_2O_3/FCP	**61.74**	**129.9**	**1096**
γ-Fe_2O_3/α-Fe_2O_3	**46.62**	**111.9**	**564.8**
γ-Fe_2O_3/α-Fe_2O_3/**FCP**	**51.93**	**83.8**	**454.9**

Table S1. The fitted results of Nyquist plots for α-Fe_2O_3 and phase junction. Here, we named FeCo Prussian Blue as FCP.

In this work, the surface photovoltage (SPV) spectroscopic measurement was performed based on the system consisted of a lock-in amplifier (SR830-D SP) with a light chopper (SR540), a computer, a sample cell together with a source of monochromatic light provided by a 500 W xenon lamp (CHF-XM-500 W, Global Xenon Lamp Power) coupled with a grating monochromator (Omni-5007, Zolix). A low chopping frequency of 24 Hz was used. Before measurement, the system was calibrated by a DSI200 UV enhanced silicon detector to eliminate the possible phase

shift which was not correlated to the SPV response, so that any phase retardation reflected the kinetics of SPV response. The transient photovoltage (TPV) measurement was taken under a laser radiation pulse with the wavelength of 355 nm and pulse width of 5 ns from a third-harmonic Nd:YAG laser (Polaris II, New Wave128 Research, Inc.). The TPV signals were recorded by a 500 MHz digital phosphor oscilloscope (TDS 5054, Tektronix). Both SPV and TPV measurements are conducted in air at room temperature.

	A_1	τ_1 (ps)	A_2	τ_2 (ps)
α-Fe_2O_3	**0.81 ± 0.020**	**0.81 ± 0.019**	**0.22 ± 0.002**	**21.00 ± 0.58**
α-Fe_2O_3/FCP	**0.90 ± 0.011**	**0.80±0.010**	**0.24 ± 0.002**	**29.59 ± 0.59**
γ-Fe_2O_3/α-Fe_2O_3	**0.66 ± 0.009**	**0.94 ± 0.014**	**0.18 ± 0.001**	**33.45 ± 0.50**
γ-Fe_2O_3/α-Fe_2O_3/**FCP**	**0.56 ± 0.009**	**1.31 ± 0.029**	**0.18 ± 0.004**	**50.64 ± 0.78**

Table S2. Kinetic parameters of TAS decays of α-Fe_2O_3 and phase junction under 400 nm excitation with time profiles of absorption probed at 580 nm.[3] Here, we named FeCo Prussian Blue as FCP.

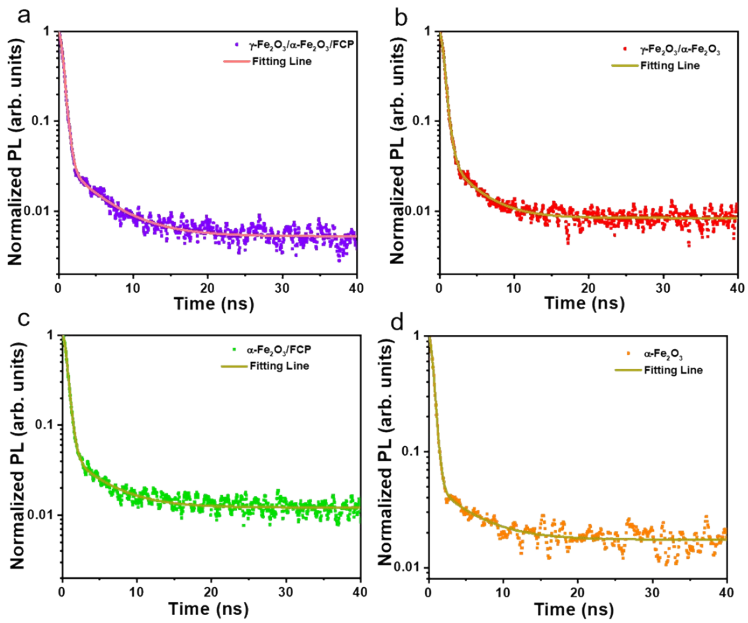

Fig. S12. Experimental decay kinetics fitted under 485 nm: a) γ-Fe_2O_3/α-Fe_2O_3/FCP, b) γ-Fe_2O_3/α-Fe_2O_3, c) α-Fe_2O_3/FCP, d) α-Fe_2O_3.

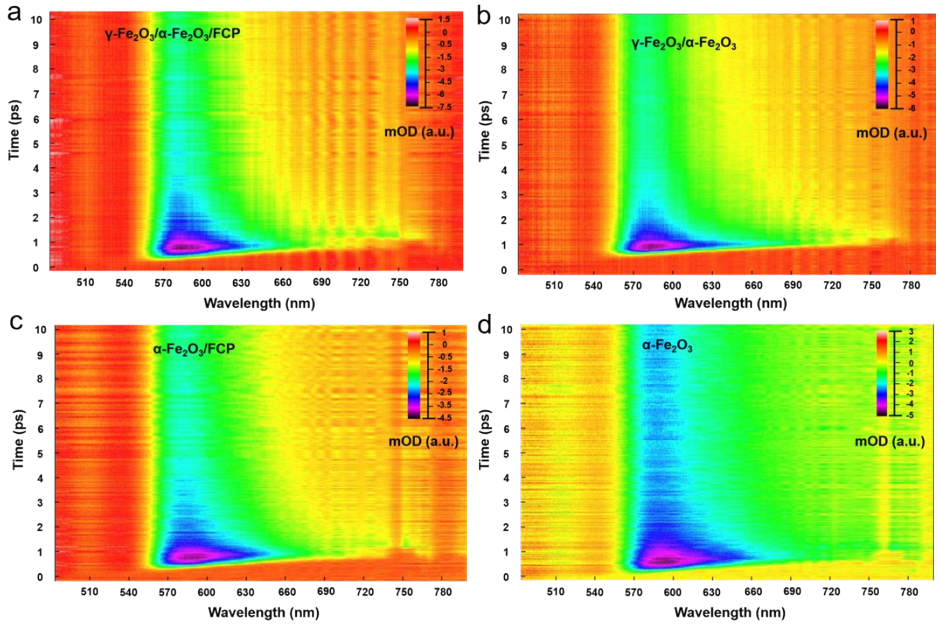

Fig. S13. Pseudocolor TA plots of α-Fe_2O_3-based photoanodes under femtosecond laser pulses excitation with ~0.8 mJ fluence at 1 kHz repetition rate: a) γ-Fe_2O_3/α-Fe_2O_3/FCP, b) γ-Fe_2O_3/α-Fe_2O_3, c) α-Fe_2O_3/FCP, d) α-Fe_2O_3.

Reference

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3. F. Liu, R. Shi, Z. Wang, Y. Weng, C. M. Che and Y. Chen, *Angew. Chem. Int. Ed.,* 2019, **58**, 11791-11795.