Supplementary Information (SI)

Cooperative Effects of Surface and Interface Treatments in Hematite (α-Fe_2O_3) Photo-Anode on Its Photo-Electrochemical Performance

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Figure S1 XRD patterns of the FTO substrate and the reference peaks of the SnO_2 powder

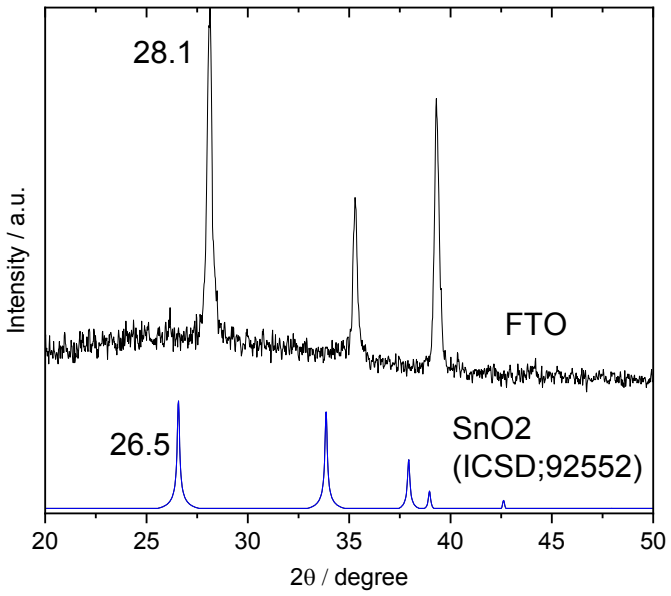


Figure S2 SEM section image of Hem/P@FTO/TiO_2

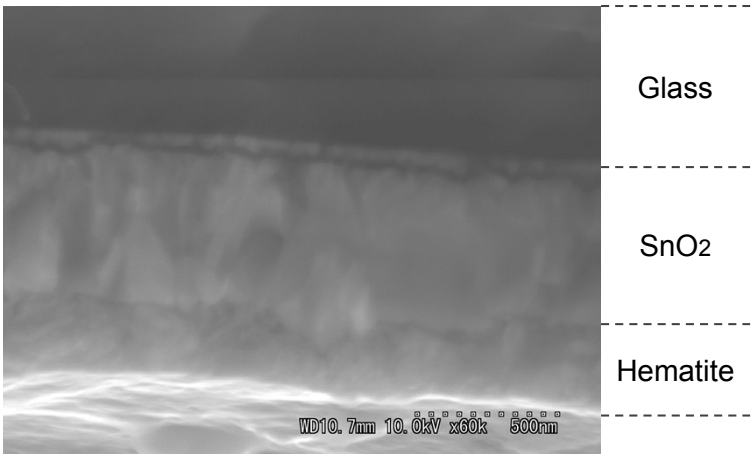


Figure S3 (a) UV-vis spectra of Hem@FTO (black), Hem@FTO/TiO_2 (green), Hem/P@FTO (red), and Hem/P@FTO/TiO_2 (blue)

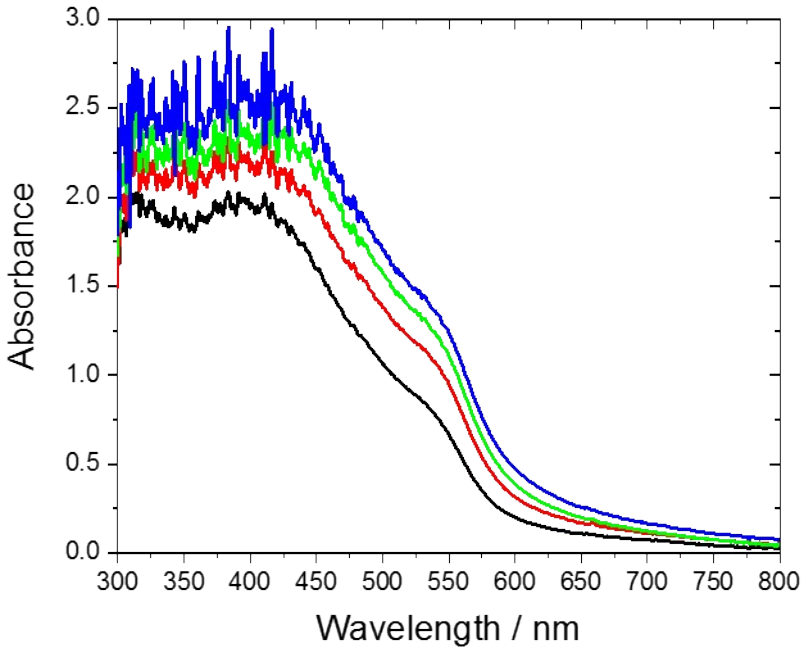
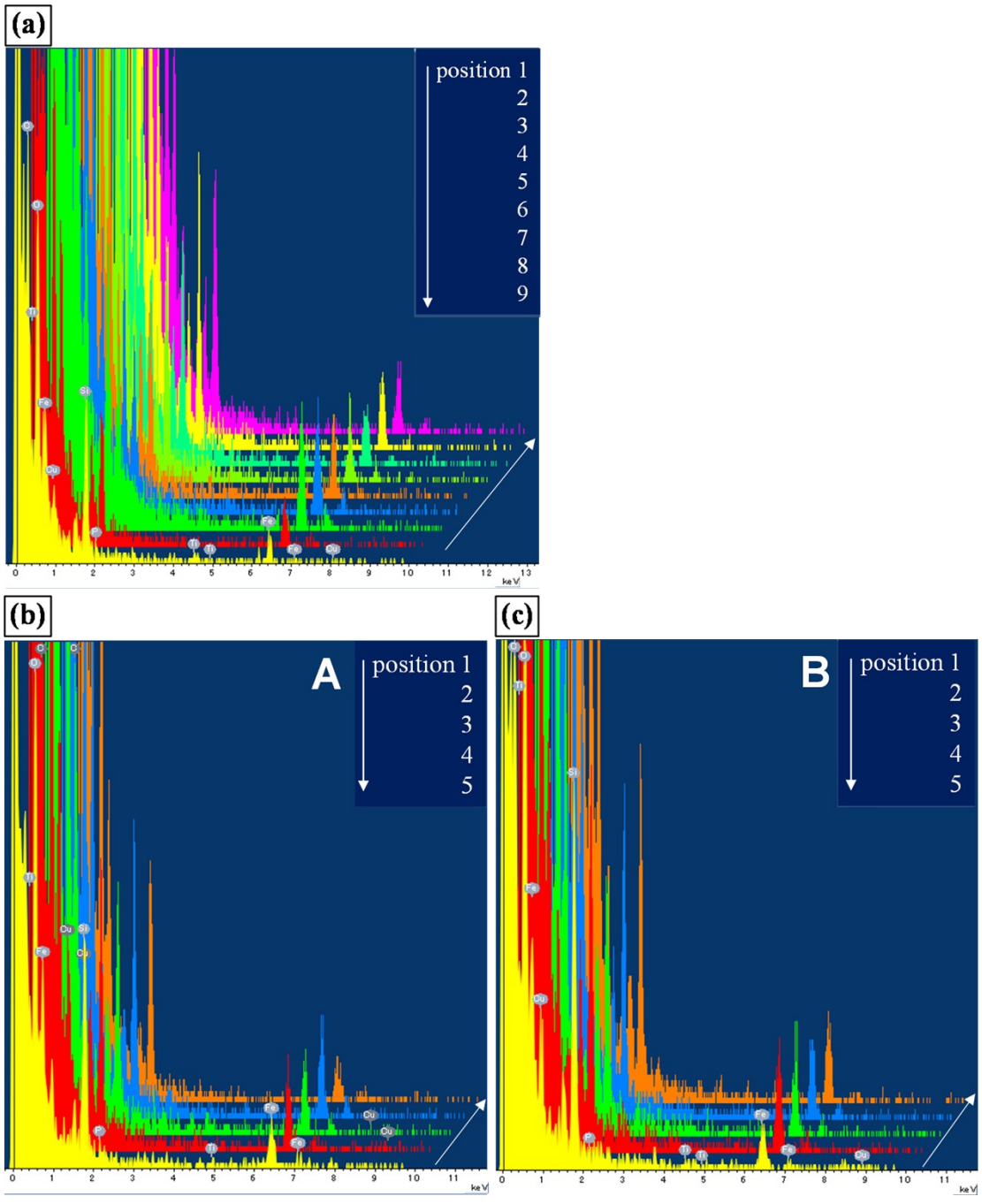


Figure S4 EDX spectra of (a) the positions of No.1-9 shown in Figure 3b, (b) No. A1-A5 and (c) No. B1-B5 shown in Figure 3c in Hem/P@FTO/TiO_2



(The presence of Cu in the pattern is due to the TEM grid. Si peak originated from the FTO substrate.)

Figure S5 XPS spectra of (a) P 2p, (b) O 1s, and (c) Fe 2p in Hem@FTO and Hem/P@FTO

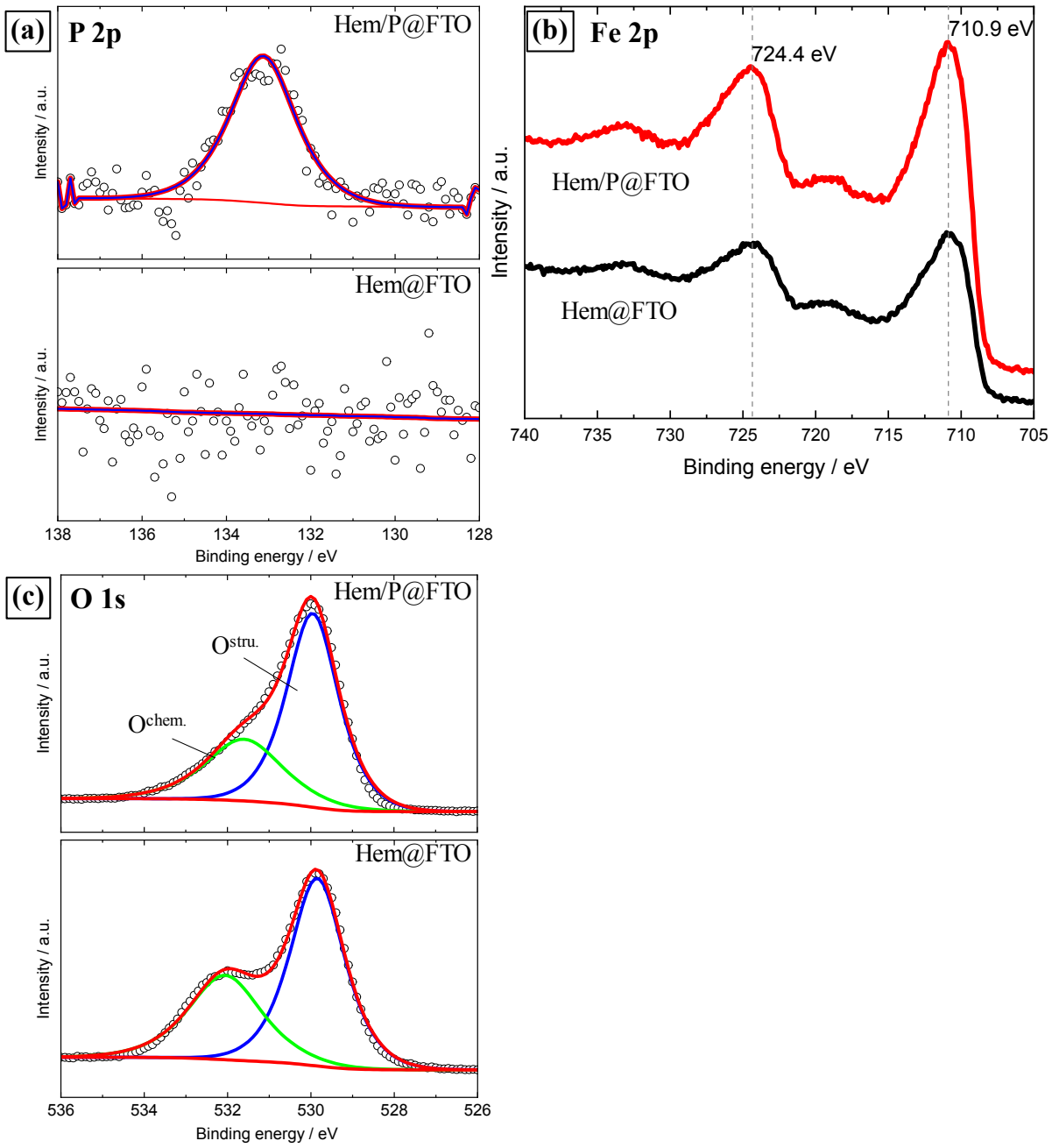
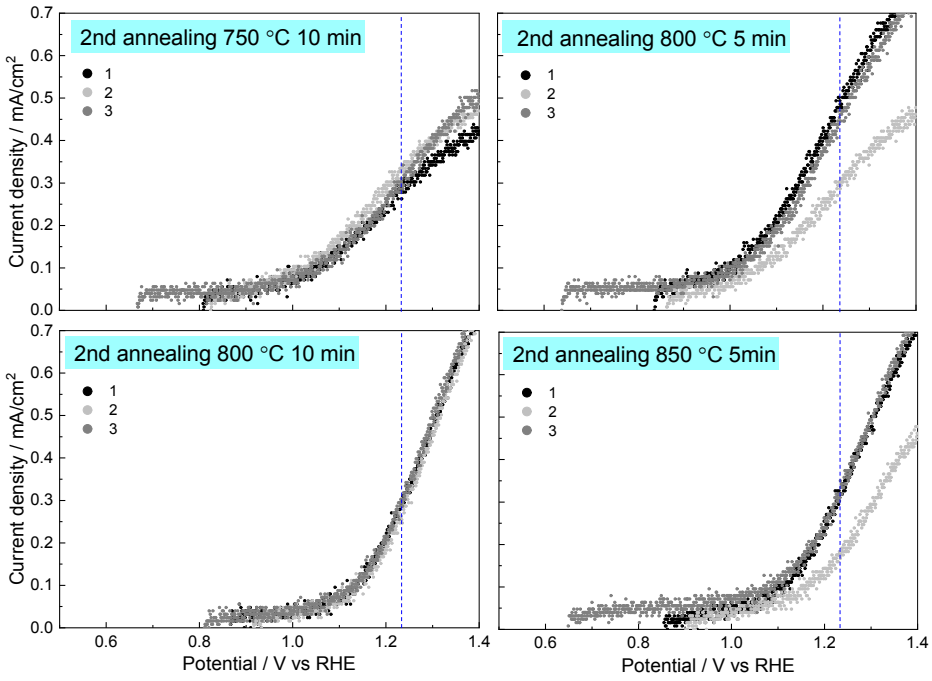


Figure S6 I-V curves of Hem/P@FTO/TiO_2 annealed at different temperatures and duration after 500 °C for 2 h annealing. Three times measurements were conducted in each condition to confirm the reproducibility.



The principle of the heterodyne transient grating (HD-TG) method

When a pump beam is incident on a transmission grating; an intensity pattern of an optical fringe is formed close to the grating. When a sample is placed near the transmission grating, it can be excited by the fringe pattern of the pump light. The refractive index of the sample changes giving the same pattern as the optical fringe because of photochemical or photothermal processes; the pattern of refractive index change is called a transient grating. When another light beam (probe light) is incident on the transient grating, a part of the probe is transmitted (reference), or another part of the probe is once diffracted by the transmission grating and refracted by the transient grating into the same direction with the reference (signal). The intensity of the mixture of the signal and reference (heterodyne signal) was monitored as the time passes.

In principle, the heterodyne signal intensity is expressed as follows:

$$I(t) = I_{ref} + ((\Delta n(t))^2 + (\Delta k(t))^2)I_{pr} + 2E_{ref}E_{pr}(\Delta n(t) \times \cos(\phi + \phi_0) + \Delta k(t) \times \sin(\phi + \phi_0))$$

where I_{ref} and I_{pr} represent the intensities of the reference and probe, respectively; E_{ref} and E_{pr} represent the electric field of the reference and probe, respectively; ϕ, the phase difference between the signal and the reference. ϕ_0 is the initial phase difference and ϕ is given by $\phi = (2\pi / \lambda_{pr})\Delta l$, where Δl is the optical path difference between the signal and reference fields. The first term in this expression is a constant background and the second term (homodyne signal) is usually significantly smaller than the third term (heterodyne signal). The fringe pattern is gradually lost by the intrinsic lifetime of the physical phenomena in the perpendicular direction to the fringe.

Figure S7 Schematic diagram of the heterodyne transient grating method

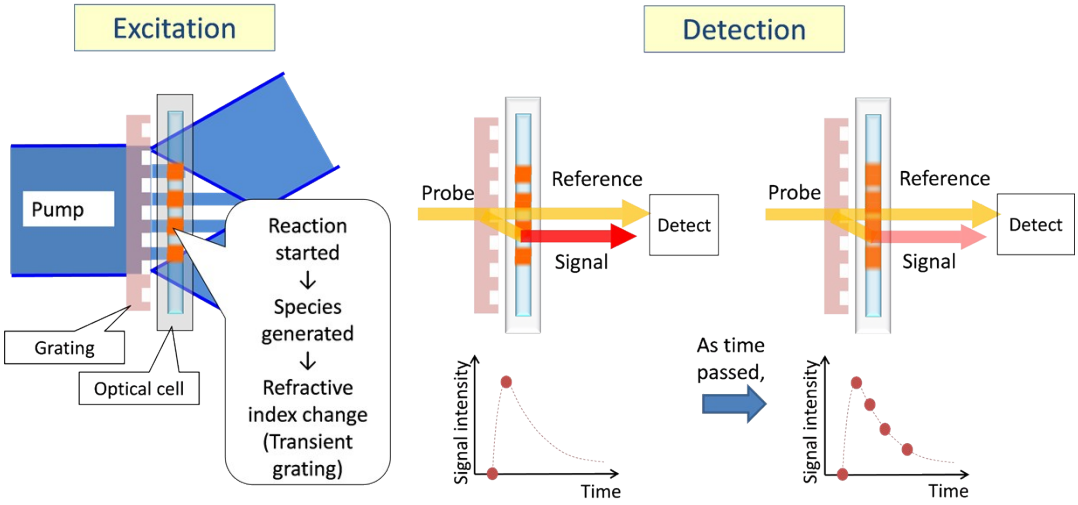


Figure S8 HD-TG responses of Hem@FTO in aqueous solution under strong pump light irradiation (1.3 mJ), depending on the applied bias voltage, 0.00 V (black), 0.8 V (blue) and 1.2 V (Green)

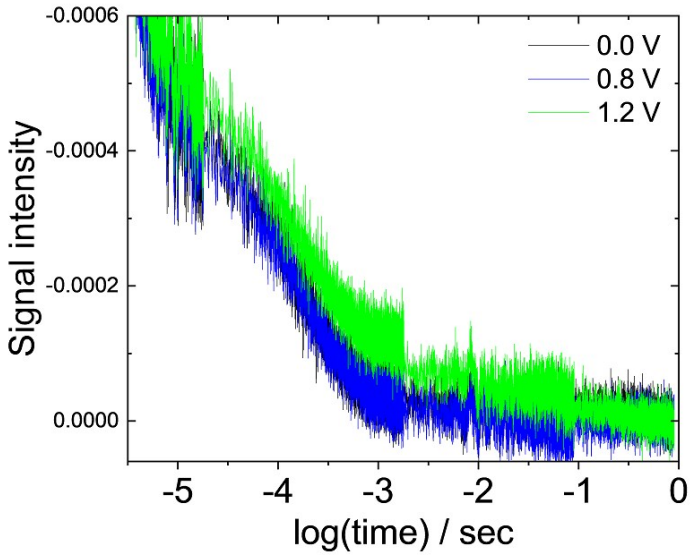


Figure S8 clearly shows that the signal intensity of the components arising from the trapped holes increased at 1.2 V, meaning that the dependence of the signal intensity on the applied bias voltage in Figure 5a is just very weak due to the weak pump light intensity.

Table S1 Time constant distributions in the HD-TG responses of Hem@FTO, Hem@FTO/TiO_2, Hem/P@FTO and Hem/P@FTO/TiO_2 in aqueous solution, depending on the applied bias voltage (vs RHE), obtained by MEM analysis

	Hem@FTO		Hem@FTO/TiO2		Hem/P@FTO		Hem/P@FTO/TiO2	
	Hole / us	Long - lived hole / ms	Hole / us	Long - lived hole / ms	Hole / us	Long - lived hole / ms	Hole / us	Long - lived hole / ms
0.00 V	230	–	270	–	160	–	340	–
1.20 V	330	–	190	–	120	230	170	220
2.00 V	300	–	170	220	140	–	160	370