Fabrication of Metallic Charge Transfer Channel between Photoanode Ti/Fe$_2$O$_3$ and Cocatalyst CoO$_x$: An Effective Strategy of Promoting Photoelectrochemical Water Oxidation

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ADDITIONAL EXPERIMENTAL SECTION

1. Additional Preparation of Samples

Preparation of various amount of metal Co modified Ti/Fe₂O₃ photoanodes: 1 mg, 2 mg, 4 mg and 8 mg cobalt (III) 2,4-pentanedionate was dispersed in 30 ml N,N-Dimethylformamide, respectively. The obtained solution was then transferred into a teflon-lined autoclave. A Ti/Fe₂O₃ film was placed in the teflon-liner and maintained at 200 °C for 10 h. The film was washed with absolute ethanol and then dried at 80 °C under N₂ flow. The obtained electrodes were denoted as Co1-Ti/Fe₂O₃, Co2-Ti/Fe₂O₃, Co4-Ti/Fe₂O₃, Co8-Ti/Fe₂O₃. The obtained films were annealed at 250 °C in air for 1 h to obtain core-shell Co/CoOₓ modified Ti/Fe₂O₃ electrodes (respectively denoted as Co1-250-Ti/Fe₂O₃, Co2-250-Ti/Fe₂O₃, Co4-250-Ti/Fe₂O₃, Co8-250-Ti/Fe₂O₃), and annealed at 550 °C in air for 2 h to obtain CoOₓ modified Ti/Fe₂O₃ electrodes (respectively denoted as Co1-550-Ti/Fe₂O₃, Co2-550-Ti/Fe₂O₃, Co4-550-Ti/Fe₂O₃, Co8-550-Ti/Fe₂O₃).

Note: If not specially indicated, the Co-Ti/Fe₂O₃, Co250-Ti/Fe₂O₃ and Co550-Ti/Fe₂O₃ represent Co2-Ti/Fe₂O₃, Co2-250-Ti/Fe₂O₃ and Co2-550-Ti/Fe₂O₃ in the manuscript and supporting information, respectively.

Synthesis of free metal Co, core-shell Co/CoOₓ (Co250) and CoOₓ (Co550) powder: The procedure is the same as that of preparing photoanodes. The only difference is that no Ti/Fe₂O₃ films were added during the synthesis.

2. Additional Characterization

Laser excited photocurrent transient measurements were carried out on home-made two-electrode system as schematically shown in Figure S1.

The crystal structure of the as-prepared samples was characterized by X-ray diffraction (XRD) using a Rigaku D/Max-2550 X-ray diffractometer with Cu–Kα radiation (λ = 1.5418 Å) at 50 kV and 200 mA in the 2θ range of 20–80° with a scanning rate of 5° min⁻¹. The optical absorption spectra of the samples were measured using a UV-vis-NIR spectrophotometer (Shimadzu UV-3600) over the range of 300–800 nm.
ADDITIONAL FIGURES AND DISCUSSION

Figure S2. Top-view SEM images of Ti/Fe$_2$O$_3$ (a), Co8-Ti/Fe$_2$O$_3$ (b), Co8-250-Ti/Fe$_2$O$_3$ (c), Co8-550-Ti/Fe$_2$O$_3$ (d) and EDX spectrum of Co8-Ti/Fe$_2$O$_3$ sample.

SEM in the Electronic Supplementary Information was carried out on a field-emission scanning electron microscope (SEM, SU8020; HITACHI)
Figure S3. Cyclic voltammograms of Ti/Fe$_2$O$_3$ and Co-Ti/Fe$_2$O$_3$ electrodes.
Figure S4. XRD patterns of FTO, Ti/Fe₂O₃, Co250-Ti/Fe₂O₃ and Co550-Ti/Fe₂O₃ electrodes.
Figure S5. XRD patterns of Co, Co250 and Co550 powder.
Figure S6. Raman spectra of Ti/Fe$_2$O$_3$, Co-Ti/Fe$_2$O$_3$, Co250-Ti/Fe$_2$O$_3$ and Co550-Ti/Fe$_2$O$_3$ electrodes.
Figure S7. UV-vis transmittance spectra (a) and the corresponding Tauc’s plots (b) of Ti/Fe$_2$O$_3$, Co250- Ti/Fe$_2$O$_3$ and Co550- Ti/Fe$_2$O$_3$ electrodes.
Figure S8. SPV phase spectra of Ti/Fe$_2$O$_3$, Co250-Ti/Fe$_2$O$_3$ and Co550-Ti/Fe$_2$O$_3$ samples.
Figure S9. SPV spectra of Ti$_2$O$_3$ film, metal Co, core-shell Co/CoO$_x$ and CoO$_x$ powder collected by lock-in amplifier.
Figure S10. Photocurrent and dark current densities of Co-Ti/Fe$_2$O$_3$ electrode under 100 mW/cm$^2$ visible light illumination with scanning rate: 5 mV s$^{-1}$.

It is obvious that the photocurrent intensity is even lower than that of dark current. As the metal Co could be oxidized more easily than water, the merely Co modified electrode could not be favorably applied in the PEC water oxidation.
Figure S11. Photocurrent and dark current densities of Ti/Fe₂O₃, Co1-250-Ti/Fe₂O₃, Co2-250-Ti/Fe₂O₃, Co4-250-Ti/Fe₂O₃ electrodes under 100 mW/cm² visible light illumination with scanning rate: 5 mV s⁻¹.

The Co2-250-Ti/Fe₂O₃ electrode exhibited the best PEC water oxidation performance. Therefore, we select this electrode as the object to discuss in the main manuscript.
Figure S12. Photocurrent stability curves of Ti/Fe\(_2\)O\(_3\) and Co250- Ti/Fe\(_2\)O\(_3\) electrodes.
Figure S13. Chopped light J-V curves under 100 mW/cm² visible light illumination with scanning rate: 5 mV s⁻¹.
At 0.7 V vs. RHE: the semicircles diameter of the three electrodes are quite similar and all of the three electrodes exhibit strong transfer resistance of photogenerated holes. Actually, at this potential, all of the three electrodes could not drive PEC water oxidation reaction. Therefore, large impedance was with them.

At 1.0 V vs. RHE: the semicircles diameter of Ti/Fe$_2$O$_3$ becomes a little smaller, which is well consistent with the onset potential of Ti/Fe$_2$O$_3$ electrode. At this potential, the PEC water oxidation reaction of Ti/Fe$_2$O$_3$ electrode is just to start. As a contrast, the semicircles diameter of Co550-Ti/Fe$_2$O$_3$ becomes quit bigger. This phenomenon is because more photogenerated holes accumulated at the interface between Ti/Fe$_2$O$_3$ and CoO$_x$ compared with 0.7 V vs. RHE, and photogenerated holes also could not transfer to the surface to drive PEC water oxidation reaction. Therefore, we observe much larger impedance.

For comparison, the semicircles diameter of Co250-Ti/Fe$_2$O$_3$ becomes quit smaller. At this potential, photogenerated holes could transfer to the surface of CoO$_x$ cocatalyst across the metallic charge transfer channel to drive PEC water oxidation reaction. Therefore, we observe much smaller impedance.

At 1.3 V vs. RHE: the transfer resistance of Co550-Ti/Fe$_2$O$_3$ is still quite strong. While, the transfer resistance of Co250-Ti/Fe$_2$O$_3$ becomes further weakened.

These various changes of EIS curves of the three electrodes at different potentials indicate metal Co plays an important role in charge transfer and PEC reaction.