Fabrication of Metallic Charge Transfer Channel between Photoanode Ti/Fe_2O_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/Fe_2O_3 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 telfon-lined autoclave. A Ti/Fe_2O_3 film was placed in the teflon-liner and maintained at 200 ºC for 10 h. The film was washed with absolute ethanol and then dried at 80 ºC under N_2 flow. The obtained electrodes were denoted as Co1-Ti/Fe_2O_3, Co2-Ti/Fe_2O_3, Co4-Ti/Fe_2O_3, Co8-Ti/Fe_2O_3. The obtained films were annealed at 250 ºC in air for 1 h to obtain core-shell Co/CoO_x modified Ti/Fe_2O_3 electrodes (respectively denoted as Co1-250-Ti/Fe_2O_3, Co2-250-Ti/Fe_2O_3, Co4-250-Ti/Fe_2O_3, Co8-250-Ti/Fe_2O_3).and annealed at 550 ºC in air for 2 h to obtain CoO_x modified Ti/Fe_2O_3 electrodes (respectively denoted as Co1-550-Ti/Fe_2O_3, Co2-550-Ti/Fe_2O_3, Co4-550-Ti/Fe_2O_3, Co8-550-Ti/Fe_2O_3).

Note: If not specially indicated, the Co-Ti/Fe_2O_3, Co250-Ti/Fe_2O_3 and Co550-Ti/Fe_2O_3 represent Co2-Ti/Fe_2O_3, Co2-250-Ti/Fe_2O_3 and Co2-550-Ti/Fe_2O_3 in the manuscript and supporting information, respectively.

Synthesis of free metal Co, core-shell Co/CoO_x (Co250) and CoO_x (Co550) powder: The procedure is the same as that of preparing photoanodes. The only difference is that no Ti/Fe_2O_3 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.

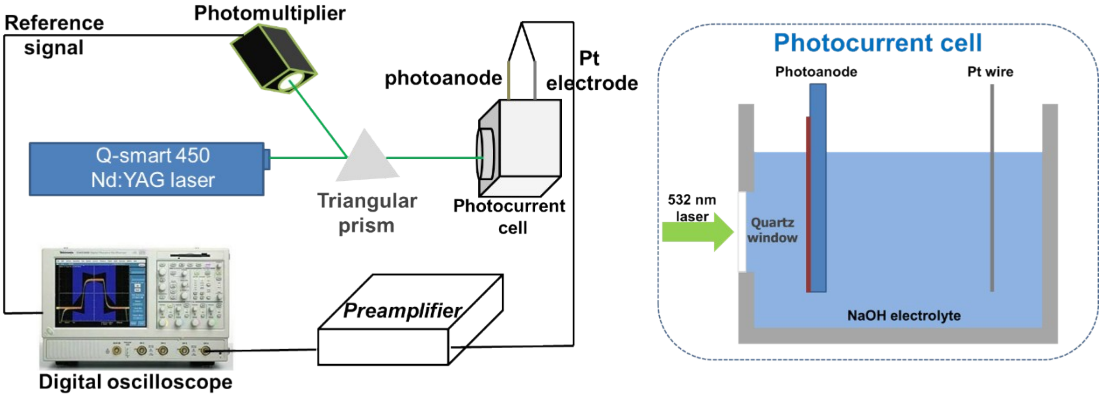

Figure S1. Scheme of the laser excited photocurrent transient measurement setup.

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 ($\lambda = 1.5418$ 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

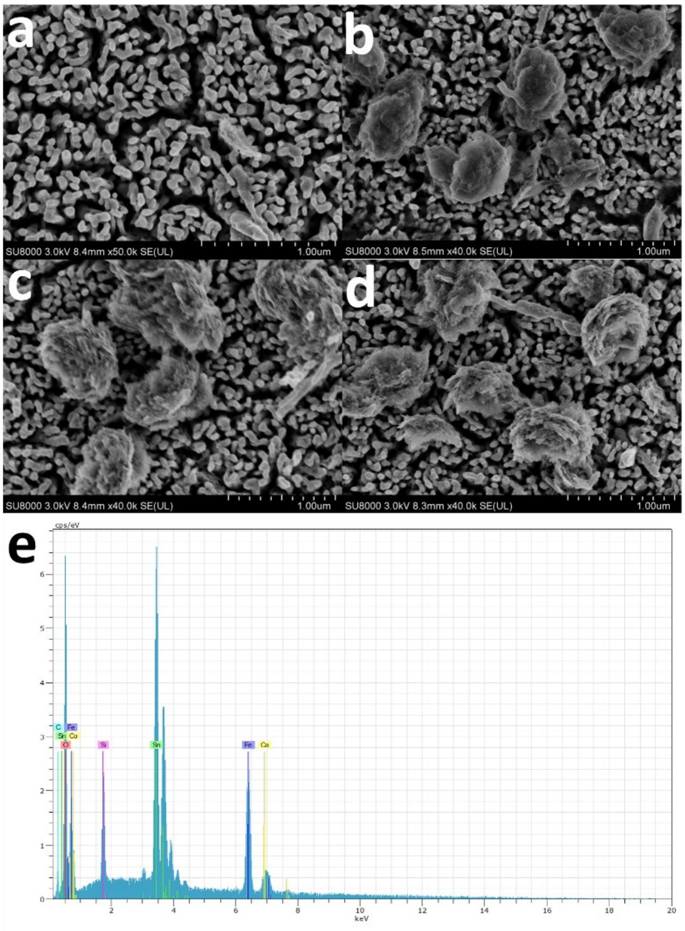

Figure S2. Top-view SEM images of Ti/Fe_2O_3 (a), Co8-Ti/Fe_2O_3 (b), Co8-250-Ti/Fe_2O_3 (c), Co8-550-Ti/Fe_2O_3 (d) and EDX spectrum of Co8-Ti/Fe_2O_3 sample.

SEM in the Electronic Supplementary Information was carried out on a field-emission scanning electron microscope (SEM, SU8020; HITACHI)

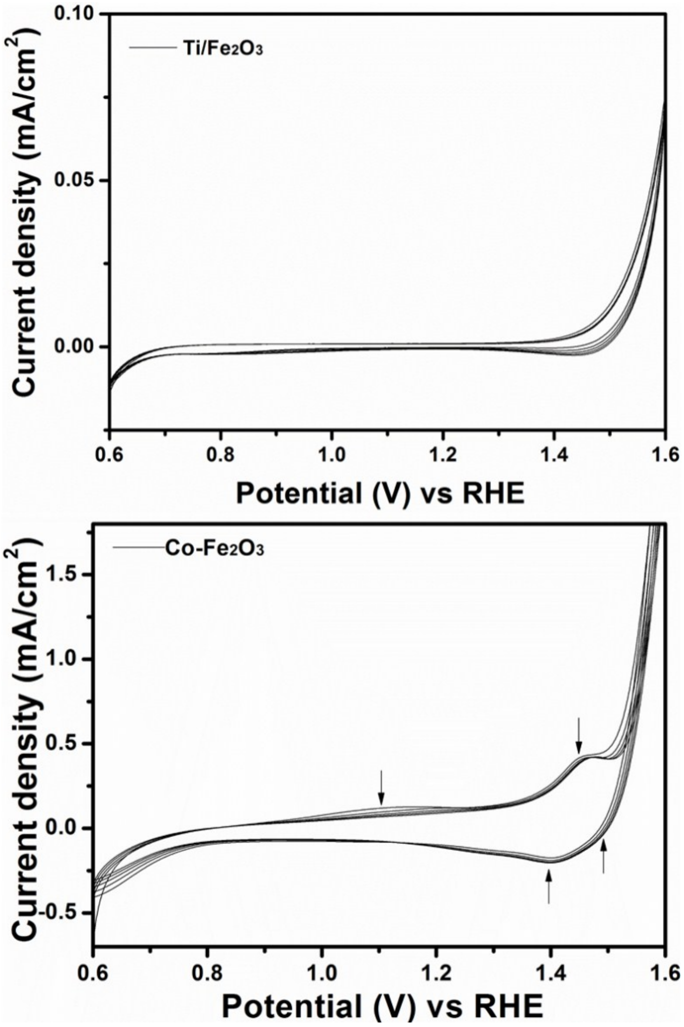

Figure S3. Cyclic voltammograms of Ti/Fe_2O_3 and Co-Ti/Fe_2O_3 electrodes.

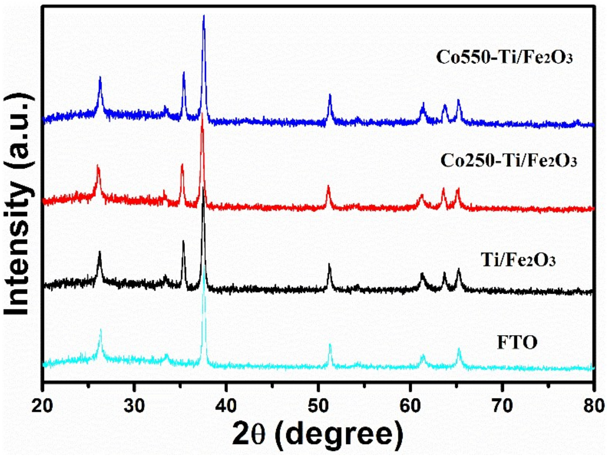

Figure S4. XRD patterns of FTO, Ti/Fe_2O_3, $Co250\text{-}Ti/Fe_2O_3$ and $Co550\text{-}Ti/Fe_2O_3$ electrodes.

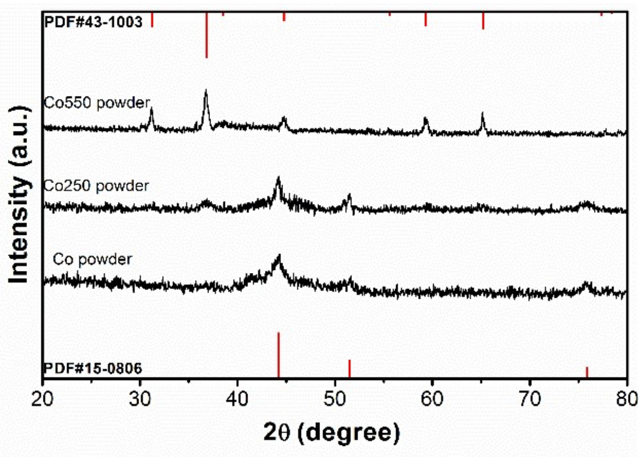

Figure S5. XRD patterns of Co, Co250 and Co550 powder.

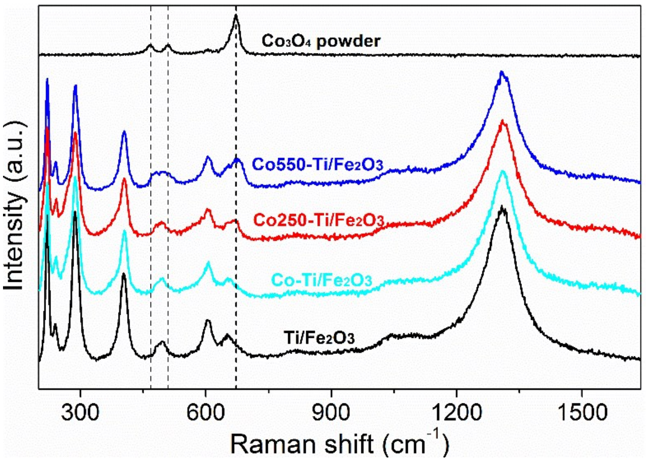

Figure S6. Raman spectra of Ti/Fe_2O_3, $Co-Ti/Fe_2O_3$, $Co250-Ti/Fe_2O_3$ and $Co550-$ Ti/Fe_2O_3 electrodes.

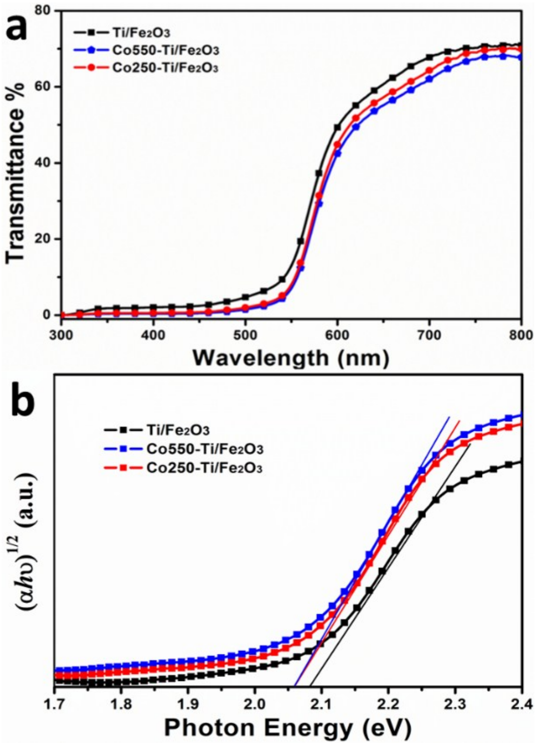

Figure S7. UV-vis transmittance spectra (a) and the corresponding Tauc's plots (b) of Ti/Fe_2O_3, Co250- Ti/Fe_2O_3 and Co550- Ti/Fe_2O_3 electrodes.

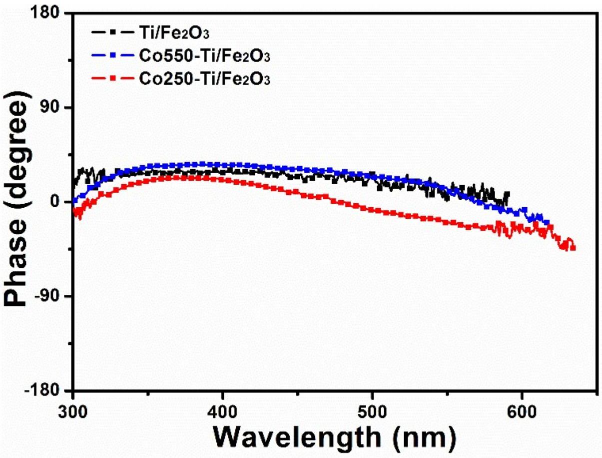

Figure S8. SPV phase spectra of Ti/Fe_2O_3, $Co250\text{-}Ti/Fe_2O_3$ and $Co550\text{-}Ti/Fe_2O_3$ samples.

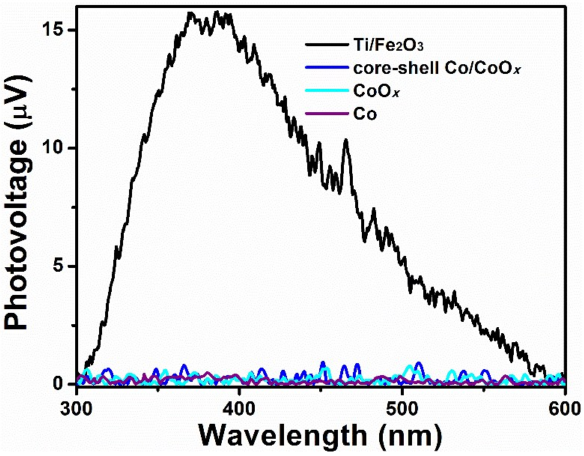

Figure S9. SPV spectra of Ti/Fe_2O_3 film, metal Co, core-shell Co/CoO_x and CoO_x powder collected by lock-in amplifier.

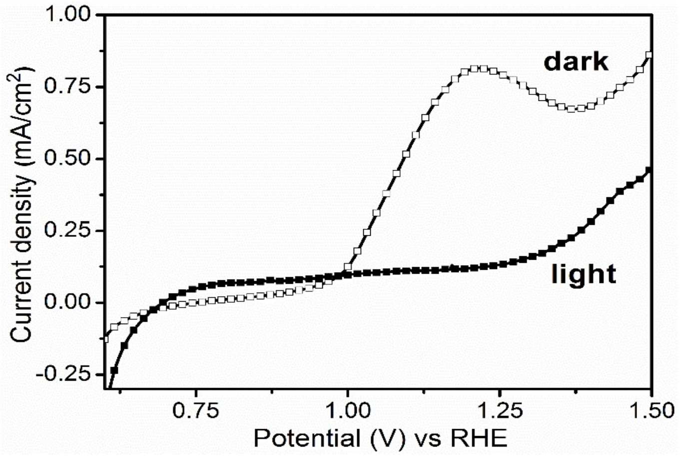

Figure S10. Photocurrent and dark current densities of Co-Ti/Fe_2O_3 electrode under 100 mW/cm^2 visible light illumination with scanning rate: 5 mV s^{-1}.

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.

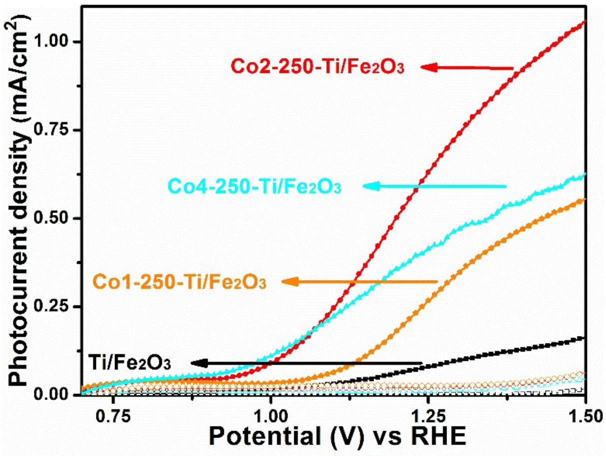

Figure S11. Photocurrent and dark current densities of Ti/Fe_2O_3, Co1-250-Ti/Fe_2O_3, Co2-250-Ti/Fe_2O_3, Co4-250-Ti/Fe_2O_3 electrodes under 100 mW/cm^2 visible light illumination with scanning rate: 5 mV s^{-1}.

The Co2-250-Ti/Fe_2O_3 electrode exhibited the best PEC water oxidation performance. Therefore, we select this electrode as the object to discuss in the main manuscript.

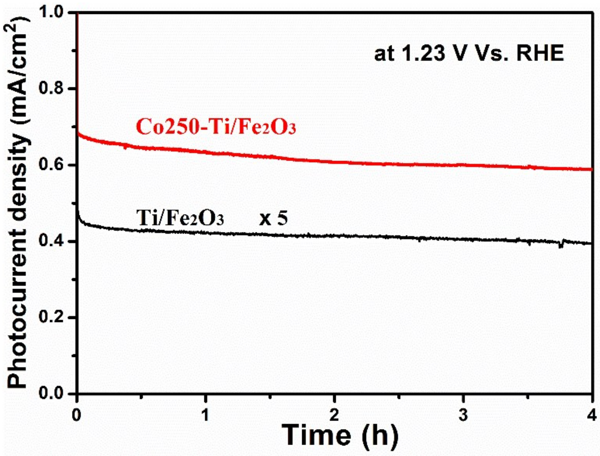

Figure S12. Photocurrent stability curves of Ti/Fe_2O_3 and Co250- Ti/Fe_2O_3 electrodes.

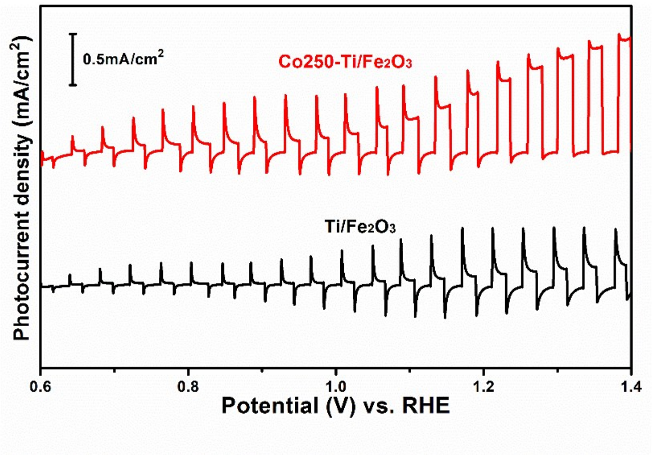

Figure S13. Chopped light J-V curves under 100 mW/cm^2 visible light illumination with scanning rate: 5 mV s^{-1}.

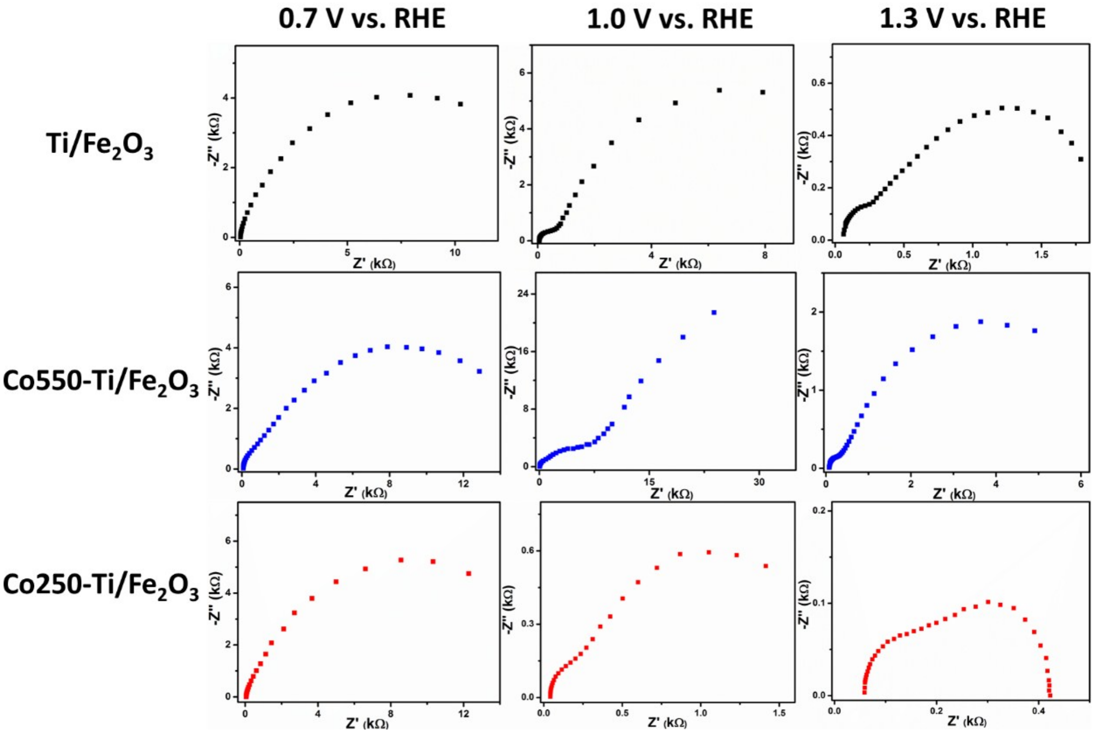

Figure S14. Nyquist plots of Ti/Fe_2O_3 Co250-Ti/Fe_2O_3 and Co550-Ti/Fe_2O_3 electrodes at various potential under 100 mW/cm^2 visible light illumination.

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_2O_3 becomes a little smaller, which is well consistent with the onset potential of Ti/Fe_2O_3 electrode. At this potential, the PEC water oxidation reaction of Ti/Fe_2O_3 electrode is just to start.

As a contrast, the semicircles diameter of Co550-Ti/Fe_2O_3 becomes quit bigger. This phenomenon is because more photogenerated holes accumulated at the interface between Ti/Fe_2O_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_2O_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_2O_3 is still quite strong. While, the transfer resistance of Co250-Ti/Fe_2O_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.