

## Supporting Information

### Effect of Preparation Conditions and Co-Pi Groups as Noble Metal-free Redox Mediator and Hole Extractor to Boost Photoelectrochemical Water Oxidation for 1D Nanorod $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>

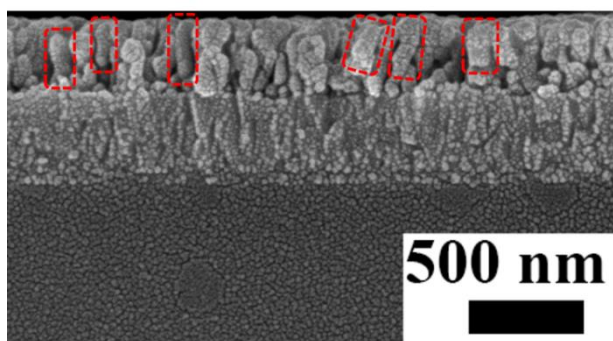
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**Figure S1 SEM image of cross-section of Fe<sub>2</sub>O<sub>3</sub> at 600°C calcination temperature photoanodes.**

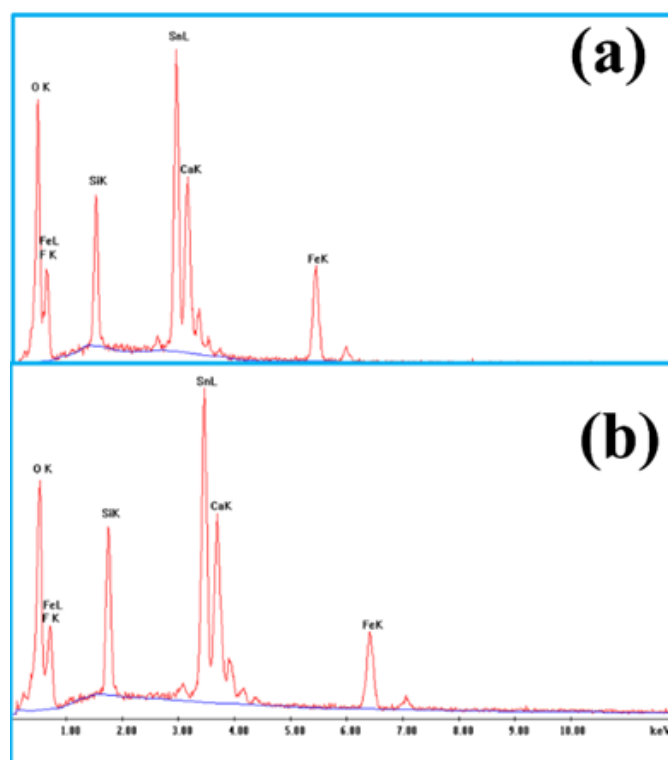


Figure S2 EDS scanning spectra of (a) $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and (b) $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Co-Pi photoanodes.

Table S1 Contents of corresponding elements in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Co-Pi photoanodes obtained from EDS.

| Element | Wt%                                      |                                                 | At%                                      |                                                 |
|---------|------------------------------------------|-------------------------------------------------|------------------------------------------|-------------------------------------------------|
|         | $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> | $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /Co-Pi | $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> | $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /Co-Pi |
| O K     | 6.21                                     | 5.97                                            | 21.29                                    | 20.71                                           |
| F K     | 3.10                                     | 3.13                                            | 8.96                                     | 9.15                                            |
| Si k    | 7.47                                     | 8.32                                            | 14.58                                    | 16.45                                           |
| Sn K    | 54.03                                    | 57.17                                           | 24.95                                    | 26.73                                           |
| Ca K    | 4.09                                     | 4.37                                            | 5.60                                     | 6.05                                            |
| Fe K    | 25.08                                    | 21.04                                           | 24.62                                    | 20.91                                           |

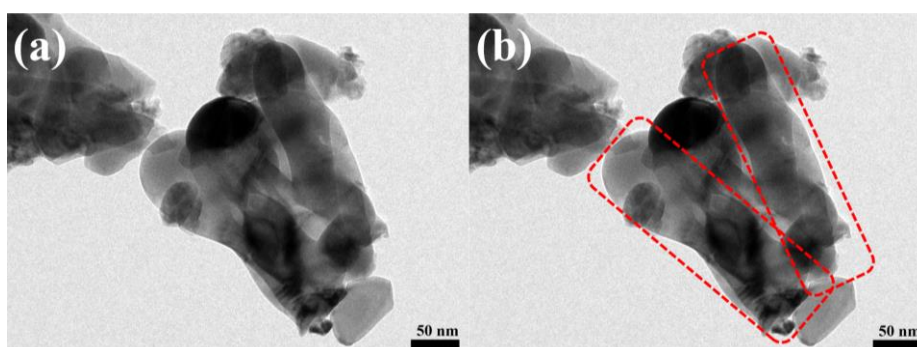


Figure S3 TEM image with 50000x magnification of  $\text{Fe}_2\text{O}_3$  (a) without or (b) with dashed frame. Inside the dashed frame was  $\text{Fe}_2\text{O}_3$  with short nanorod morphology.

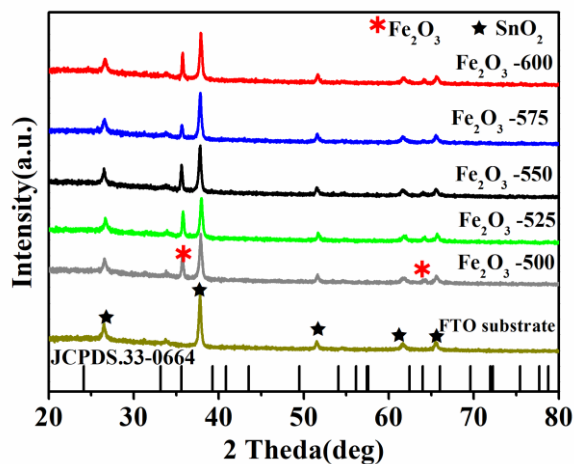


Figure S4 XRD for FTO substrate,  $\text{Fe}_2\text{O}_3$  calcined at various temperatures of 500, 525, 550, 575, and 600°C,  $\text{SnO}_2$ (black five-pointed star),  $\alpha\text{-Fe}_2\text{O}_3$ (red snowflake).

Table S2 The content of each element in  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3/\text{Co-Pi}$  photoanodes obtained from XPS.

| Sample |          | $\text{Fe}_2\text{O}_3$ |          | $\text{Fe}_2\text{O}_3/\text{Co-Pi}$ |  |
|--------|----------|-------------------------|----------|--------------------------------------|--|
| Name   | Atomic % | PP At. %                | Atomic % | PP At. %                             |  |
| C 1s   | 36.67    | 41.8                    | 35.76    | 44.28                                |  |
| Fe 2p  | 19.04    | 5.43                    | 14.02    | 4.71                                 |  |
| O 1s   | 44.28    | 52.77                   | 43.46    | 48.54                                |  |
| Co 2p  | 0        | 0                       | 4.74     | 1.09                                 |  |
| P 2p   | 0        | 0                       | 2.02     | 1.38                                 |  |

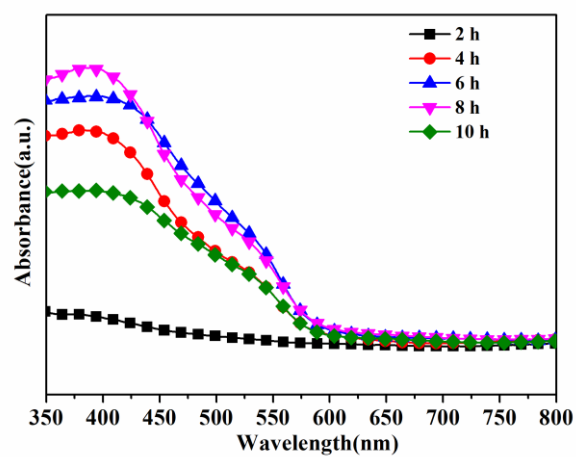


Figure S5 UV-vis absorption spectra of  $\text{Fe}_2\text{O}_3$  prepared with various hydrothermal time of 2, 4, 6, 8, and 10 h.

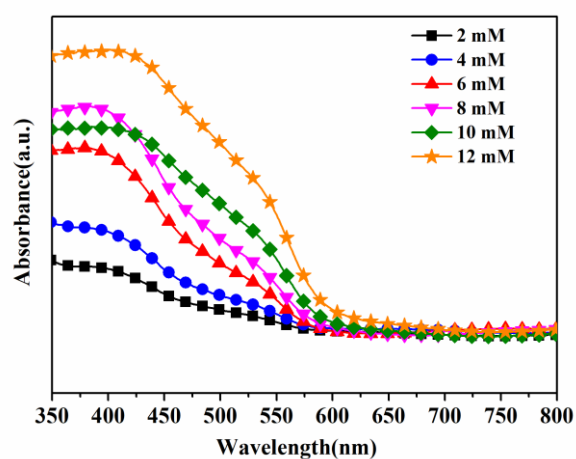


Figure S6 UV-vis absorption spectra of  $\text{Fe}_2\text{O}_3$  prepared with various concentration of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  precursor of 2, 4, 6, 8, 10, and 12 mM.

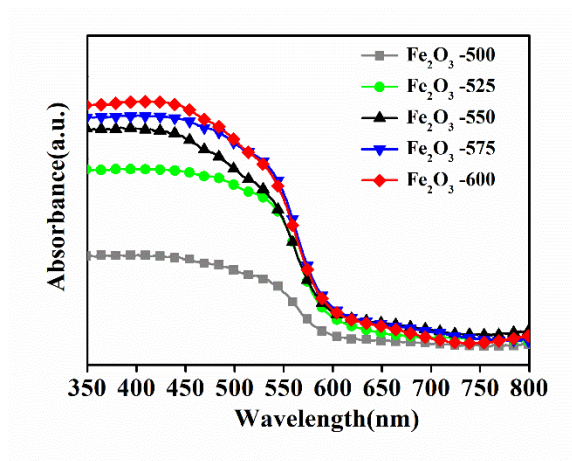


Figure S7 UV-vis absorption spectra of  $\text{Fe}_2\text{O}_3$  calcined at various temperatures of 500, 525, 550, 575, and 600°C.

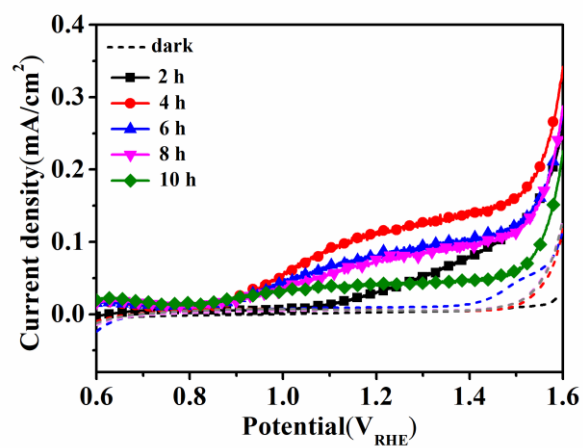
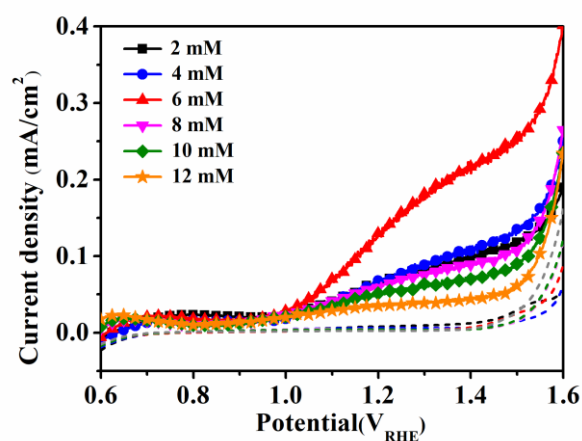
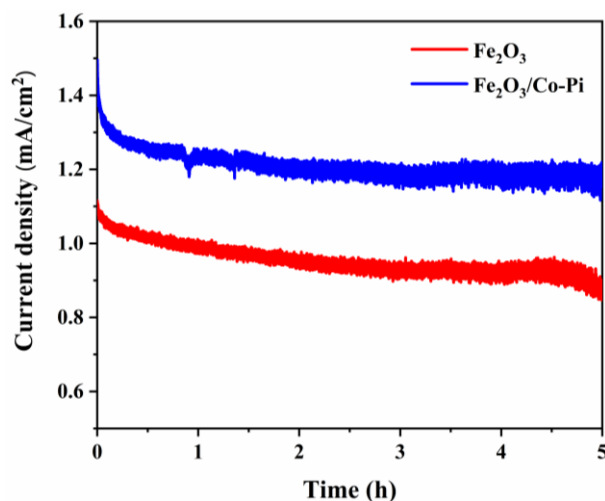


Figure S8 LSV curves of bare  $\alpha\text{-Fe}_2\text{O}_3$  prepared with various hydrothermal time of 2, 4, 6, 8, and 10 h. The dotted line represents the dark state current density.



**Figure S9** LSV curves of bare  $\alpha$ - $\text{Fe}_2\text{O}_3$  prepared with various concentration of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  precursor of 2, 4, 6, 8, 10, and 12 mM. The dotted line represents the dark state current density.



**Figure S10** PEC stability test of 5h of bare  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3/\text{Co-Pi}$ .

Fig. S10 is the PEC stability test of 5h of bare  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3/\text{Co-Pi}$ . It could be seen from the figure that after the PEC stability test for 5 hours at  $1.23\text{V}_{\text{RHE}}$ , the bare  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3/\text{Co-Pi}$  photoanodes both maintained the photocurrent density of 80% of the initial value.

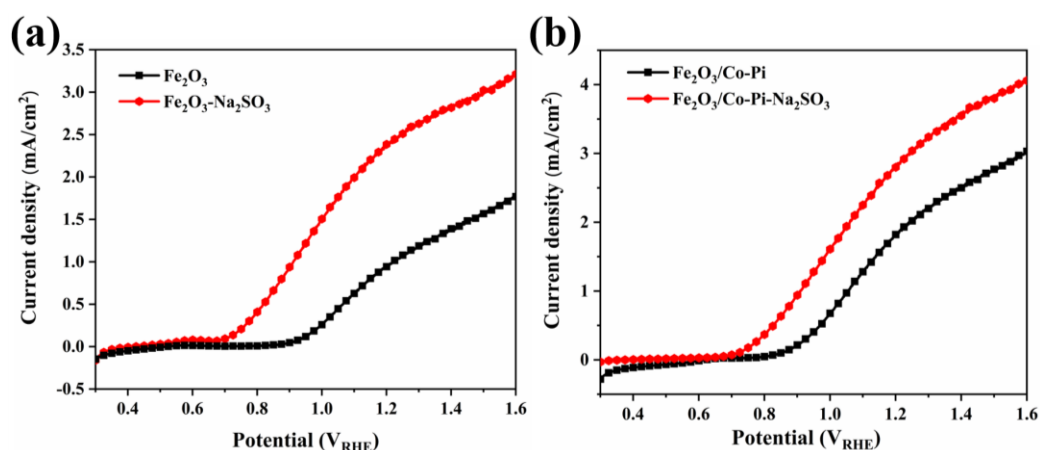


Figure S11 LSV curves of (a) bare  $\text{Fe}_2\text{O}_3$  and (b)  $\text{Fe}_2\text{O}_3/\text{CoPi}$  without and with  $\text{Na}_2\text{SO}_3$ .

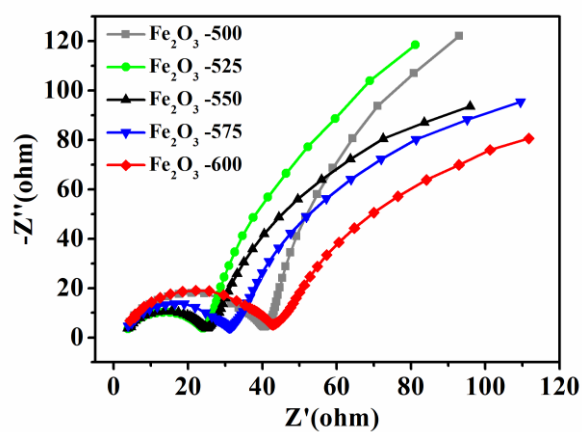


Figure S12 EIS Nyquist plots of  $\text{Fe}_2\text{O}_3$  calcined at various temperatures of 500, 525, 550, 575, and 600°C at a bias of 1.23  $\text{V}_{\text{RHE}}$  under simulated solar light illumination.

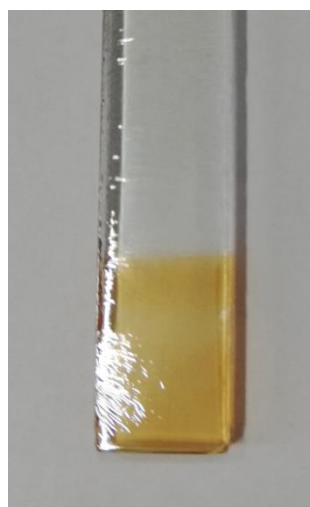
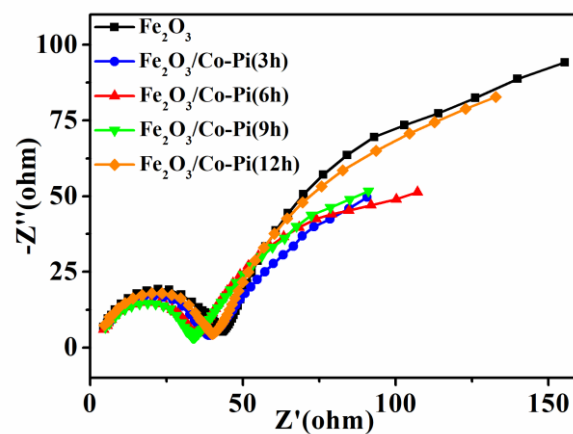


Figure S13 Digital photo of bare  $\text{Fe}_2\text{O}_3$  calcined at 600°C.



**Figure S14** EIS Nyquist plots for Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>/Co-Pi photoanodes after immersion in phosphate for various time of 3, 6, 9, and 12 h at a bias of 1.23 V<sub>RHE</sub> under simulated solar light illumination.