***Electronic Supplementary Information (ESI)***

# A bifunctional lead–iron oxyfluoride, $PbFeO_2F$, that functions as a visible-light-responsive photoanode and an electrocatalyst for water oxidation

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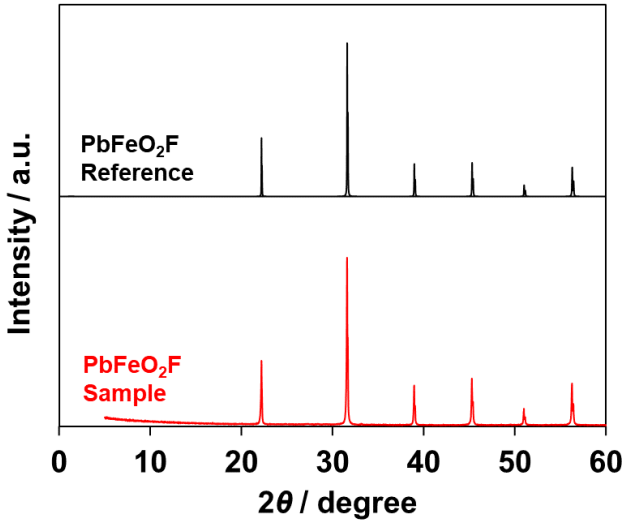


**Fig. S1.** XRD patterns of the synthesized $PbFeO_2F$ and the reference. The pattern of the reference was drawn using a CIF file available from the literature.[1]

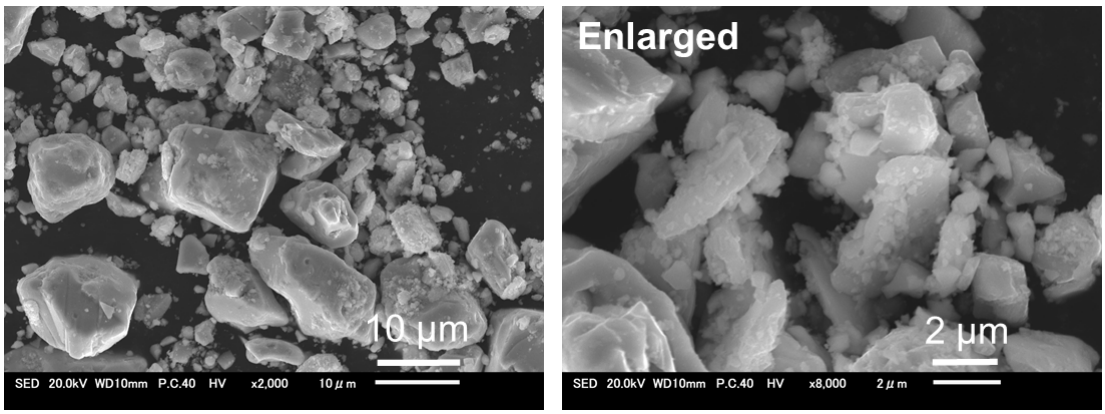


**Fig. S2.** SEM images of the synthesized $PbFeO_2F$ powder.

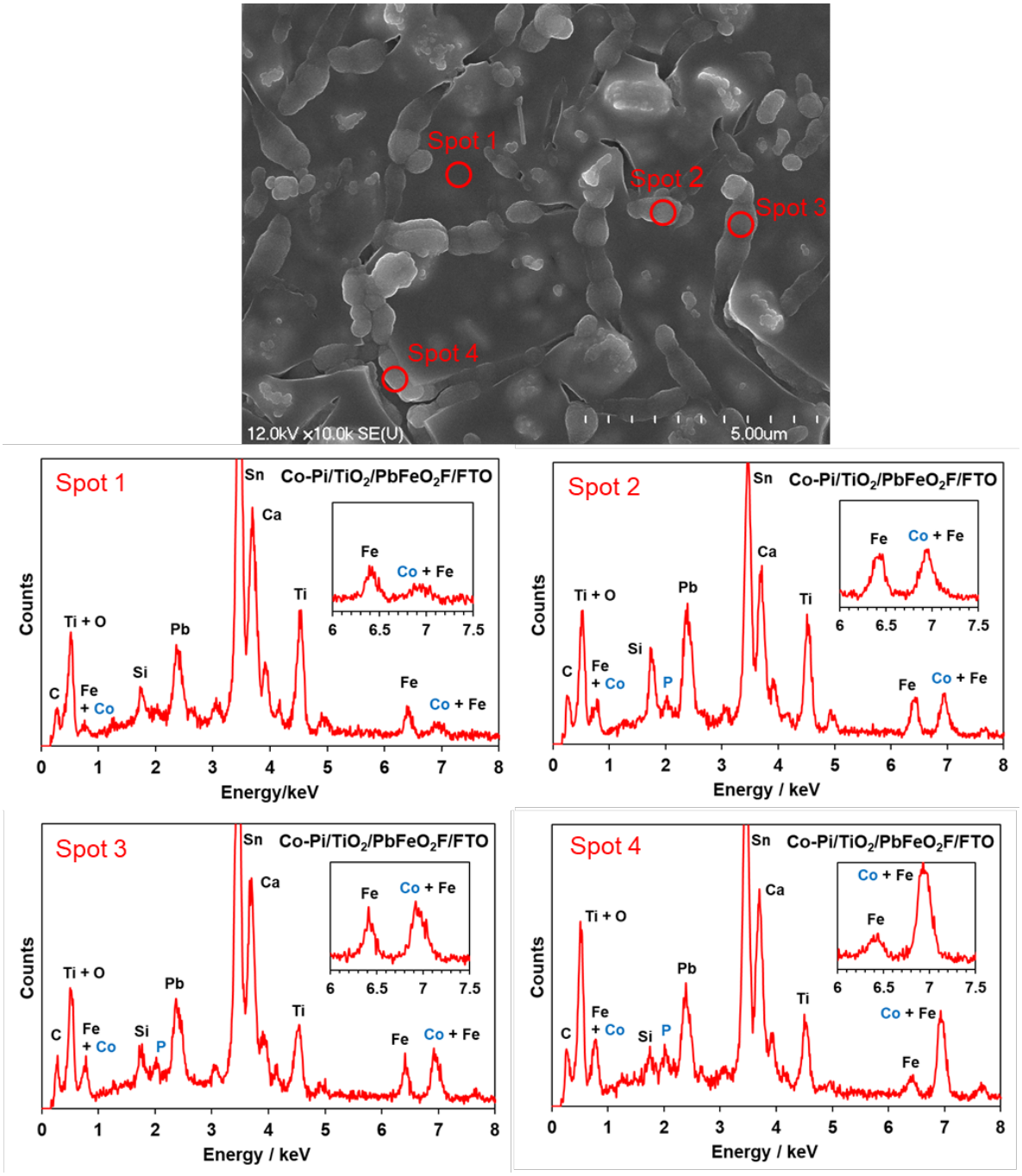


**Fig. S3.** EDS spectra for the Co-Pi/$TiO_2$/$PbFeO_2F$/FTO electrode. Spot 1 in the flat area shows a weak signal of Co at 6.9 keV. By contrast, spots 2, 3 and 4 in "islands" show an obvious contribution of P with an energy at ~2.0 keV as well as a stronger Co signal.

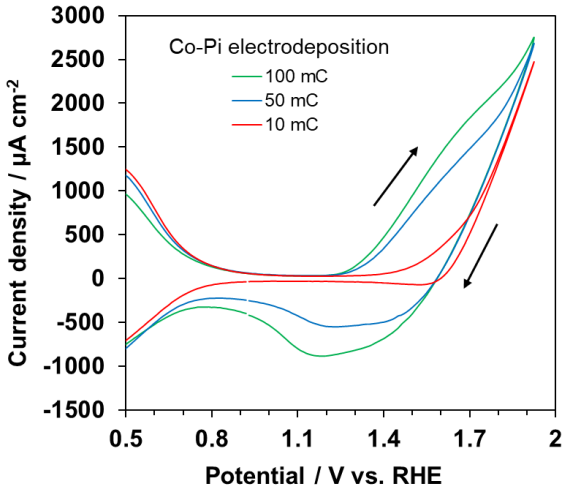


**Fig. S4.** Current-potential curves in aqueous 0.1 M $K_3PO_4$ solution (pH 12.4) for Co-Pi/$TiO_2$/$PbFeO_2F$/FTO electrodes. Scan rate: 100 mV $s^{-1}$. Co-Pi was loaded by applying +1.0 V *vs* Ag/AgCl for the $TiO_2$/$PbFeO_2F$/FTO electrodes in 0.1 M potassium phosphate buffered solution containing 0.5 mM cobalt nitrate (pH 7). The total charge that flowed was varied from 10 to 100 mC.

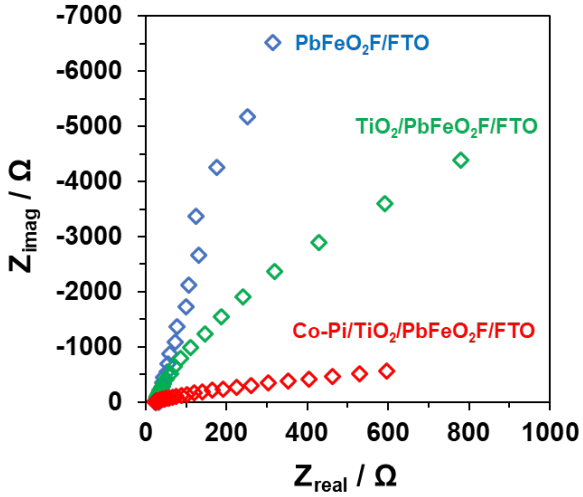


**Fig. S5.** Nyquist plots for the modified $PbFeO_2F$/FTO electrodes (3 $cm^2$) at +1.0 V *vs* RHE in aqueous 0.1 M $K_3PO_4$ solution (pH 12.4) under visible-light irradiation. Light source: 300 W xenon lamp fitted with an L42 cutoff filter ($\lambda$ > 400 nm). The amplitude of the modulation potential was 10 mV. The frequency of the modulation potential was lowered from 10 kHz to 1 Hz.

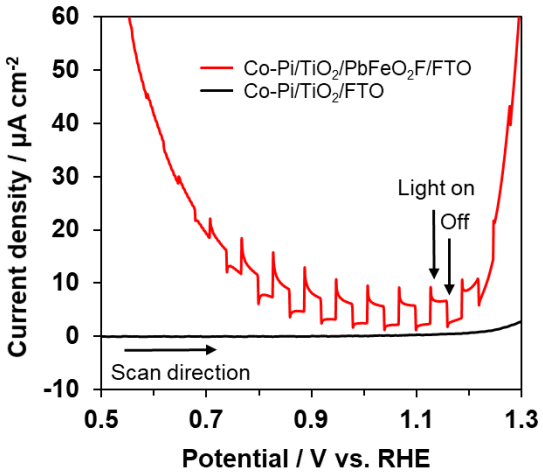


**Fig. S6.** Current–potential curves for the Co-Pi/$TiO_2$/$PbFeO_2F$/FTO and Co-Pi/$TiO_2$/FTO electrodes in aqueous 0.1 M $K_3PO_4$ solution (pH 12.4), as recorded at a sweep rate of 10 mV $s^{-1}$ under intermittent visible-light irradiation. Light source: 300 W xenon lamp fitted with a Y48 cutoff filter ($\lambda > 460$ nm, 0.26 W $cm^{-2}$).

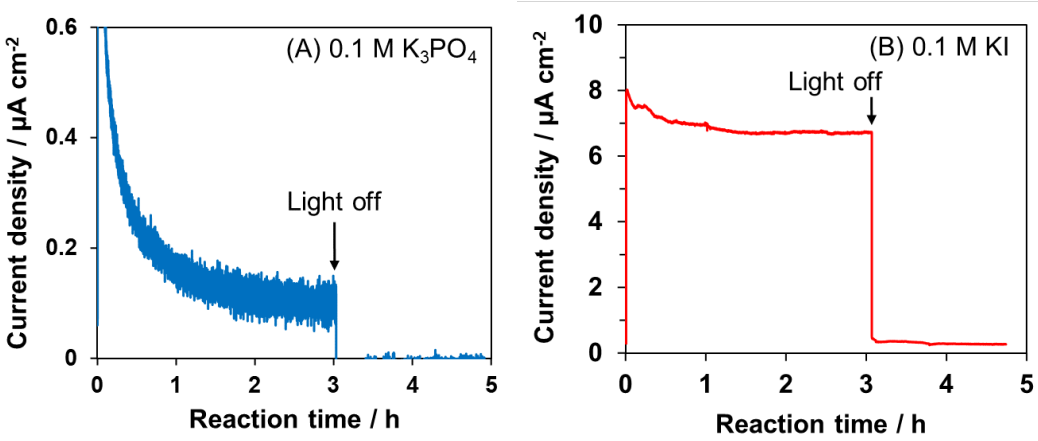


**Fig. S7.** Current–time curves in controlled-potential photoelectrolysis at +1.0 V *vs* RHE under visible-light irradiation. The experiments were conducted (A) in 0.1 M $K_3PO_4$ solution (pH 12.9) using the Co-Pi/$TiO_2$/$PbFeO_2F$/FTO electrode and (B) in 0.1 M KI solution (pH 6.3) using the $TiO_2$/$PbFeO_2F$/FTO electrode, respectively. Light source: 300 W xenon lamp fitted with an L42 cutoff filter ($\lambda > 400$ nm).

## References

S1. Y. Inaguma, J.-M. Greneche, M.-P. Crosnier-Lopez, T. Katsumata, Y. Calage and J.-L. Fourquet, Structure and Mössbauer Studies of F−O Ordering in Antiferromagnetic Perovskite $PbFeO_2F$, *Chem. Mater.*, 2005, **17**, 1386-1390.