

Electronic Supporting Information (ESI)

**Calcium containing iron oxide as an efficient and robust catalyst in
(photo-)electrocatalytic water oxidation at neutral pH**

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Experimental Section

General consideration. Starting materials for this work were of the highest available purity and used as received from commercial suppliers. Fluorine-doped tin oxide coated glass (FTO; sheet resistance 7 ohm sq^{-1} , TEC Glass™ 7) was used as the electrode substrate and cleaned with an ammonia-hydrogen peroxide-deionized water mixture (volume ratio: 1:1:5) at 70 °C for 30 min before the deposition of catalytic material. Deionized water was used throughout the work.

Preparation of CaFeO_x thin film modified electrodes. CaFeO_x thin film modified electrodes were prepared by spin-coating an ethanolic precursor solutions onto the FTO substrate and subsequent annealing at 400 °C for 30 min. The resultant electrode was designated as FTO| CaFeO_x . The precursor solution contains 0.2 M iron(III) nitrate, 0.3 M ethanolamine, and calcium acetate of various concentrations (from 0 to 0.12 M). The content of Ca in the CaFeO_x thin film was controlled by adjusting the molar ratio of $\text{Ca}^{2+}/\text{Fe}^{3+}$ (r) in the precursor solution.

Preparation of Co-phosphate (Co-Pi) thin film modified electrodes. Co-Pi thin film modified electrodes were by electrochemical deposition onto the FTO substrate using the similar procedure reported previously.¹ Briefly, Co-Pi was electrodeposited onto the FTO substrate (with exposed area of $\sim 1.0 \text{ cm}^2$) from phosphate buffer solution (0.1 M, pH 7) containing 0.5 mM $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%, Sigma-Aldrich) at an applied potential of $\sim 1.1 \text{ V}$ (vs. Ag/AgCl) till a charge of 1.0 C cm^{-2} was passed.

Preparation of FeO_x thin film modified electrodes. FeO_x thin film modified electrodes were by electrochemical deposition onto the FTO substrate using the similar procedure reported previously.² Briefly, FeO_x was electrodeposited onto the FTO substrate (with exposed area of $\sim 1.0 \text{ cm}^2$) from HEPES buffer solution (0.1 M, pH 7) containing 1.0 mM $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (99%, Sigma-Aldrich) using cyclic voltammetry at a scan rate of 50 mV s^{-1} in the potential range between 0.61 to 1.76 V vs. RHE for 25 cycles. Note that the solution was entirely bubbled with nitrogen for at least 30 min to remove dissolved oxygen before the dissolution of FeSO_4 .

Preparation of iron phosphate modified electrodes. Iron phosphate modified electrodes were prepared by electrochemical deposition onto the FTO substrate in phosphate buffer (0.1 M, pH 7) containing 0.5 mM $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (99%, Sigma-Aldrich) under constant applied current density of 1 mA cm^{-2} for 1000 s under N_2 purge. Note that the solution was entirely bubbled with nitrogen for at least 30 min to remove dissolved oxygen before the dissolution of FeSO_4 .

Preparation of pristine and CaFeO_x modified BiVO_4 photoanodes. Before the fabrication of the pristine and CaFeO_x modified BiVO_4 photoanodes, BiOI nanosheets (*nanoBiOI*), as the template for the synthesis of BiVO_4 , was firstly prepared by electrochemical deposition onto the FTO substrate using the similar procedure reported previously.³ Briefly, *nanoBiOI* was electrodeposited onto the FTO substrate (with exposed area of $1.0\text{-}1.5 \text{ cm}^2$) from an aqueous plating solution containing 40 mM $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$

(98%, Sigma-Aldrich), 400 mM KI (99.5%, Sigma-Aldrich), and 50 mM p-benzoquinone (98%, Sigma-Aldrich) at an applied potential of -0.1 V (vs. Ag/AgCl) for 4 min. Thereafter, the BiVO₄ photoanode was fabricated by drop-coating 100 ml dimethyl sulfide solution containing 0.2 M vanadyl acetylacetonate (98%, Sigma-Aldrich) onto the *nano*BiOI modified electrode, followed by thermal treatment at 450 °C for 2 h. Finally, the annealed electrode was subjected to an etching process in 1 M NaOH solution under gentle stirring to remove excess V₂O₅. The obtained BiVO₄ electrode is designated as FTO|BiVO₄. The CaFeO_{x(r=0.6)} modified BiVO₄ photoanode (FTO|BiVO₄|CaFeO_{x(r=0.6)}) was prepared by spin-coating a precursor solution contains 0.2 M iron(III) nitrate, 0.3 M ethanolamine, and 0.12 M calcium acetate onto FTO|BiVO₄ and follow-up thermal annealing at 400 °C for 30 min.

Physical Characterization. The surface morphology of the electrodes was characterized using a Hitachi SU-8010 scanning electron microscope (SEM). X-ray diffraction (XRD) analyses were carried out using an Ultima IV (Rigaku Co., Japan) X-ray diffractometer. The amount of Fe, Ca, Co species in the catalysts of interests was determined by using Horiba Jobin Yvon JY 2000-2 ICP optical emission spectrometer. The surface composition of the films was verified by X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe system, ULVAC-PHI, Chigasaki, Japan), using a microfocused (100 μm, 25 W) Al X-ray beam, with a photoelectron take off angle of 45°. The Ar⁺ ion source for XPS (FIG-5CE) was controlled by using a floating voltage of 0.2 kV. The binding energies obtained in the XPS analyses were corrected for specimen charging, by referencing the C 1s peak to 285.0 eV. The local coordination of Fe in FTO|CaFeO_x samples was characterized with Fe K-edge extended X-ray-absorption fine-structure (EXAFS) spectra. The FTO|CaFeO_x samples were fixed on a holder (Kapton tape); data were collected at Taiwan Light Source (TLS) beamline BL17C1 in National Synchrotron Radiation Research Center. Data of Ca K-edge X-ray-absorption near-edge structure (XANES) were collected at TLS beamline BL16A1. The spectra of samples and reference materials were collected in a fluorescence mode with a Lytle detector.

Electrochemical and photoelectrochemical characterization. Electrochemical experiments were performed in a two-compartment, separated with a Nafion[®] 117 film, three-electrode electrochemical cell with a CHI 760 electrochemical workstation (CH Instruments, Inc., USA) at room temperature under N₂, artificial gas (70% CO₂, 10% CO, 10% CH₄, and 10% H₂), or CO₂ atmosphere and all potentials (E) are reported against the reversible hydrogen electrode (RHE) by using the equation Eq. 1:

$$E \text{ (V vs. RHE)} = E \text{ (V vs. Ag/AgCl)} + 0.197 + 0.059 \times \text{pH} - iR_u,$$

where R_u is the uncompensated resistance, measured at open circuit potential, and i is the current flowing through the cell. FTO|CaFeO_x, with various calcium contents, were used as the working electrode connected to a Pt foil counter electrode and a Ag/AgCl_{sat} reference electrode. The electrocatalytic properties, in terms of Tafel slope, exchange current density (i₀), overpotential (η), and stability, of the

modified electrodes (all with exposed area of $\sim 1.0 \text{ cm}^2$) were evaluated using linear sweep voltammetry (LSV), at a scan rate of 10 mV s^{-1} , and controlled-current electrolysis (CCE), at an applied current density of 1 or 5 mA cm^{-2} , in phosphate buffer solution (0.1 M) of various pHs ranging from 6 to 10. η is defined as the difference between the applied potential (V vs. RHE) to the thermodynamic potential of water oxidation, which is 1.23 V vs. RHE, and for the reliable comparison, initial overpotential (η_0) is defined as the one obtained at the first 0.5 minute during 2-h CCE, whereas final overpotential (η_f) is defined as the one obtained in the end of 2-h CCE.

Photoelectrochemical (PEC) properties of FTO|BiVO₄ and FTO|BiVO₄|CaFeO_{x(t=0.6)} (exposed area of $\sim 1.0 \text{ cm}^2$) in phosphate buffer (1.0 M, pH 7) were examined in a two-compartment, separated with a Nafion[®] 117 film, three-electrode electrochemical cell using LSVs, at a scan rate of 10 mV s^{-1} , and chronoamperometry at an applied potential of 1.23 V vs. RHE under light illumination (AM 1.5 G 100 mW cm^{-2}) provided by a solar light simulator (XES-40S2-CE, SAN-EI Electric)

Oxygen measurement. The amount of O₂ generated from the two-compartment three-electrode electrochemical systems was detected and quantified by headspace gas analysis with an Ocean Optics fluorescence O₂ probe (FOSPOR-R). The O₂ probe was inserted in an anodic compartment through a tightly sealed septum and continuous O₂ readings (O₂ partial pressure) at 1 s intervals throughout the experiment. The three-electrode electrochemical cell was operated with the sequence: at an applied current density of 0 mA cm^{-2} for a period of 30 min (control experiment), followed by 2-h CCE of water at 5 mA cm^{-2} and another 30 min at zero applied current density.

Table S1 The actual $\text{Ca}^{2+}/\text{Fe}^{3+}$ atomic ratio, Tafel slope, and exchange current density (i_0) of $\text{FTO}|\text{CaFeO}_x$ prepared with various nominal $\text{Ca}^{2+}/\text{Fe}^{3+}$ molar ratios (r).

	Nominal $\text{Ca}^{2+}/\text{Fe}^{3+}$ molar ratio (r)				
	0	0.05	0.25	0.5	0.6
Actual $\text{Ca}^{2+}/\text{Fe}^{3+}$ atomics ratio ^a	0	0.12	0.42	0.64	0.74
Tafel slope (mV dec^{-1})	65.3 ± 1.4	64.1 ± 0.1	74.5 ± 2.1	79.9 ± 2.5	77.0 ± 3.2
i_0 (pA cm^{-2})	1.8 ± 1.0	3.5 ± 1.3	83.6 ± 8.1	206.1 ± 106.7	244.5 ± 79.6

^a: determined by XPS

Table S2 Atomic ratios, measured by XPS, of P/Fe and Ca/Fe of $\text{FTO}|\text{CaFeO}_{x(r=0)}$ and $\text{FTO}|\text{CaFeO}_{x(r=0.6)}$ before and after 2-h treatment in phosphate buffer (0.1 M, pH 7).

	Sample							
	$\text{FTO} \text{CaFeO}_{x(r=0)}$				$\text{FTO} \text{CaFeO}_{x(r=0.6)}$			
	as-prepared	after 2-h immersion	after 2-h CCE at 1 mA cm^{-2}	after 2-h CCE at 5 mA cm^{-2}	as- prepared	after 2-h immersion	after 2-h CCE at 1 mA cm^{-2}	after 2-h CCE at 5 mA cm^{-2}
P/Fe (At%/At%)	0	0.13	0.17	0.20	0	0.43	0.37	0.52
Ca/Fe (At%/At%)	0	0	0	0	0.74	0.14	0.13	0.08

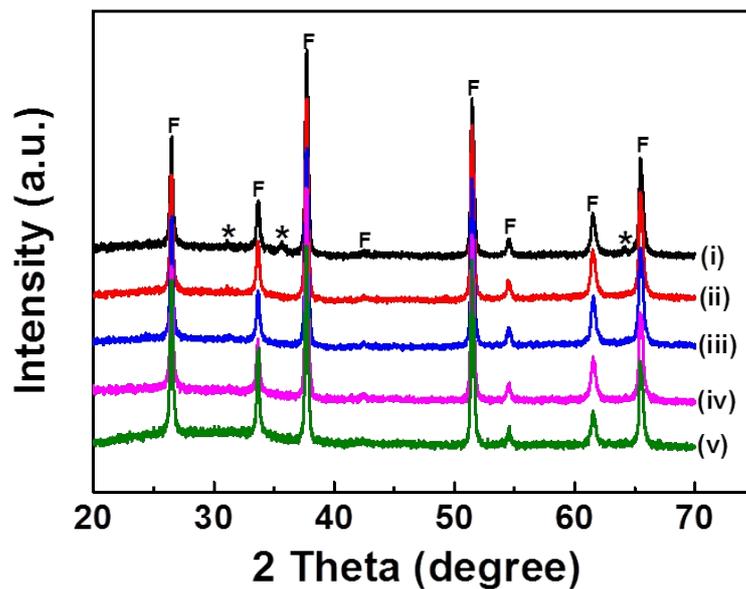


Figure S1 XRD patterns of FTO|CaFeO_x prepared with various different nominal Ca²⁺/Fe³⁺ molar ratios (r), ranging from (i) 0, (ii) 0.05, (iii) 0.25, (iv) 0.5, to (v) 0.6. F and * stand for the diffraction peaks belonging to FTO substrate and γ-Fe₂O₃, respectively.

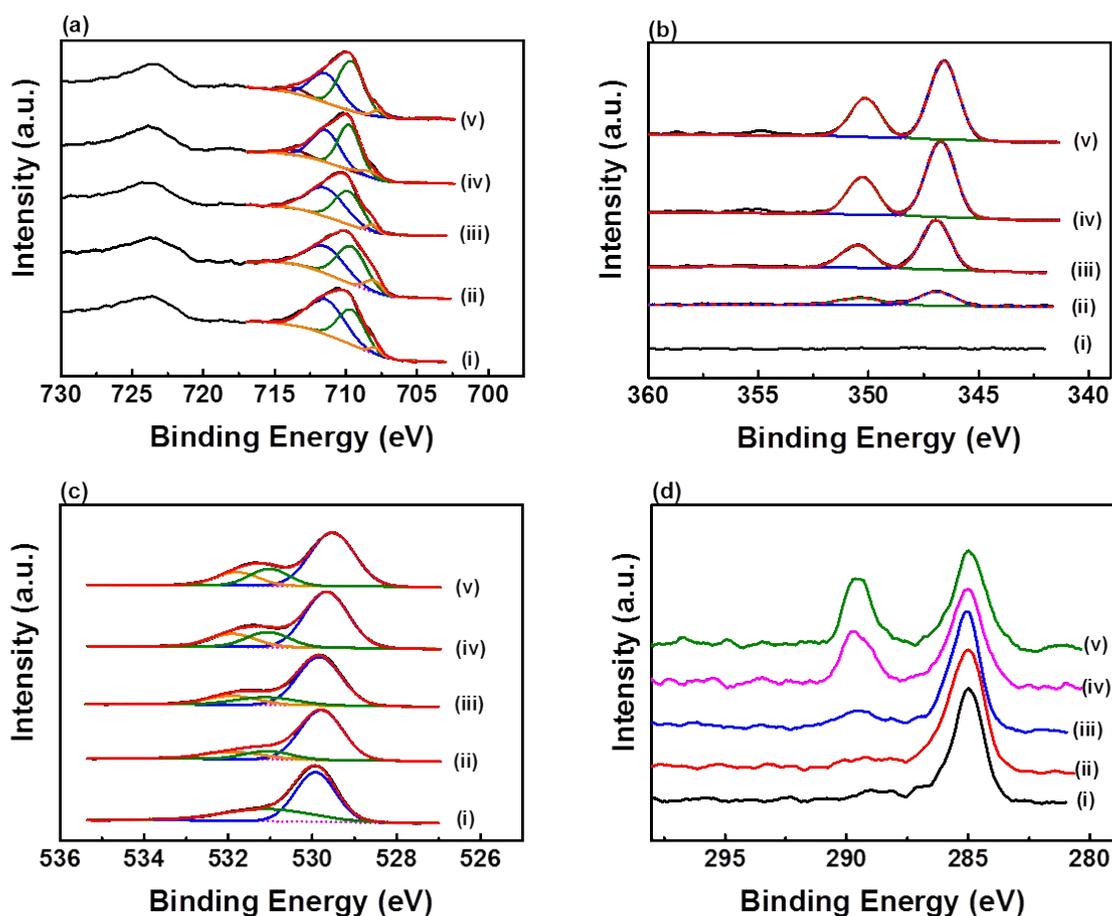


Figure S2 XPS spectra of FTO|CaFeO_x prepared with varied nominal Ca²⁺/Fe³⁺ molar ratios (*r*): (i) 0, (ii) 0.05, (iii) 0.25, (iv) 0.5, to (v) 0.6. (a) Fe 2p region. (b) Ca 2p region. (c) O 1s region. (d) C 1s region.

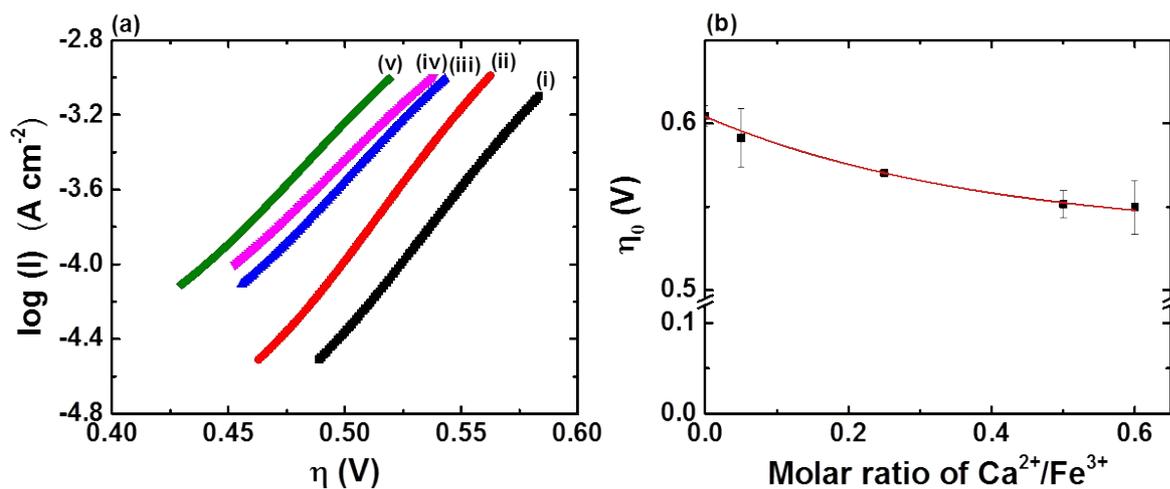


Figure S3 (a) Tafel plot, obtained using linear sweep voltammetry at a scan rate 10 mV s⁻¹, and (b) η_0 , recorded in the beginning of controlled-current electrolysis at applied current density of 1 mA cm⁻² in phosphate buffer (0.1 M, pH 7), of FTO|CaFeO_x prepared with various different nominal Ca²⁺/Fe³⁺ molar ratios (*r*), ranging from (i) 0, (ii) 0.05, (iii) 0.25, (iv) 0.5, to (v) 0.6.

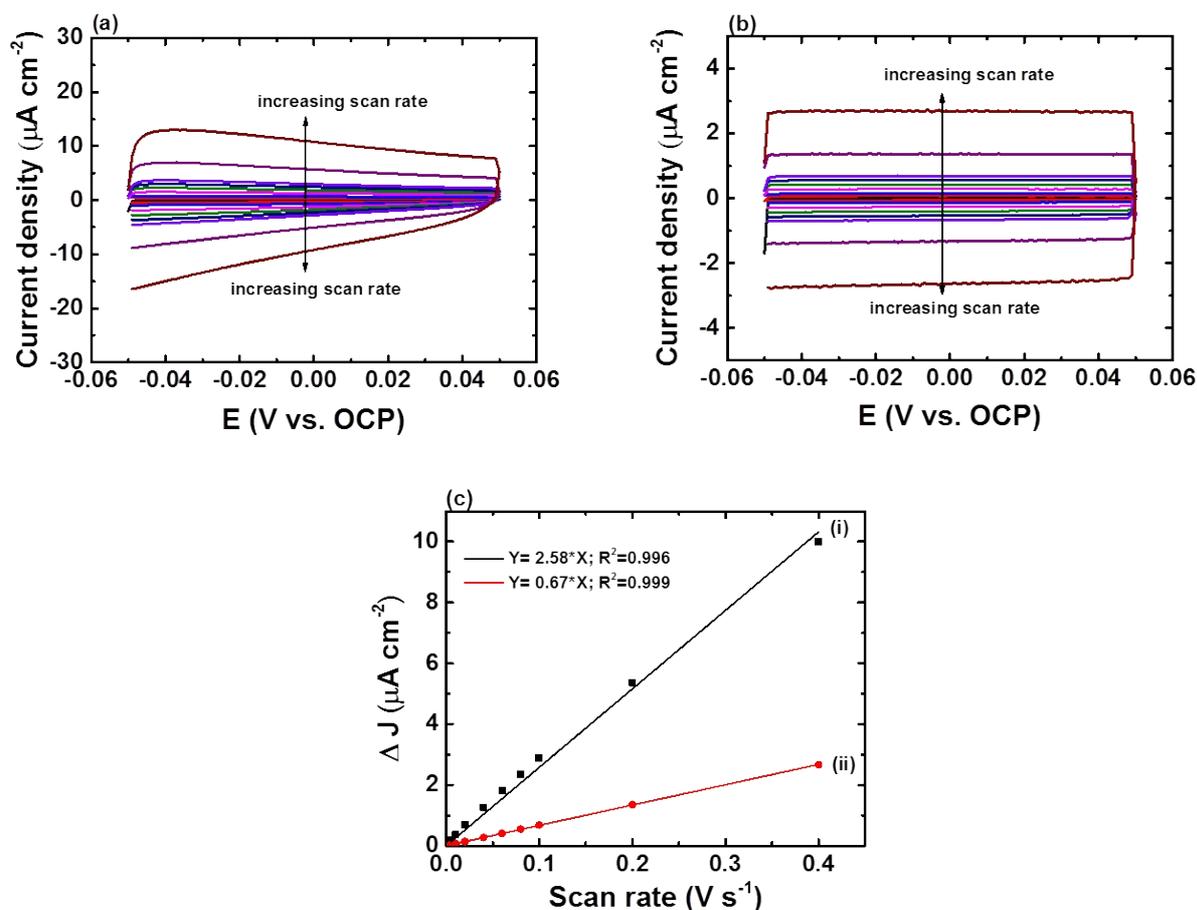


Figure S4 CVs of (a) FTO|CaFeO_{x(r=0)} and (b) FTO|CaFeO_{x(r=0.6)} recorded at various scan rates (ν), including 5, 10, 20, 40, 60, 80, 100, 200 and 400 mV s^{-1} , in phosphate buffer (0.1 M, pH 7). The plots of ΔJ vs. ν , where the ΔJ is the sum of the anodic current and cathodic current measured at open-circuit potential (OCP) from (a) and (b), are shown in (c). The capacitances of FTO|CaFeO_{x(r=0)} and FTO|CaFeO_{x(r=0.6)} were estimated from the slope of the curve of charging current density vs. ν (c), where the slope is equal to $2C_{dl}$. However, since the area-averaged capacitance of CaFeO_x is unknown, the relative effective surface area is calculated instead of actual effective surface area. As revealed in (c), the effective surface area of FTO|CaFeO_{x(r=0)} is about 3.9 times higher than that of FTO|CaFeO_{x(r=0.6)}.

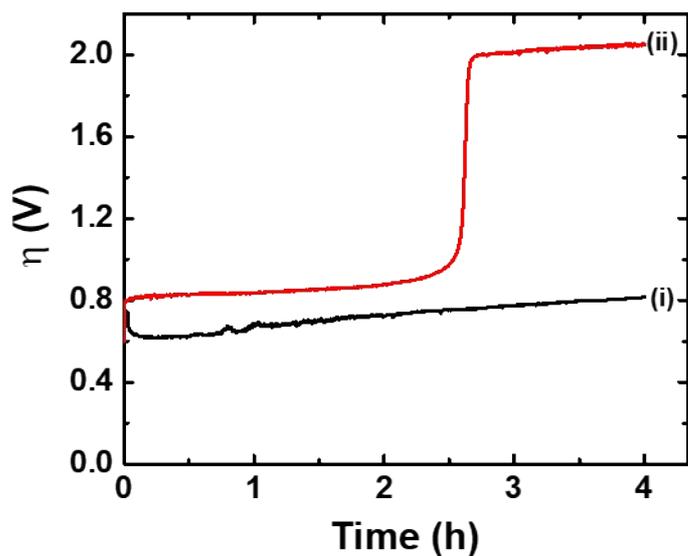


Figure S5 Overpotential (η) transients of (i) $\text{CaFeO}_{x(r=0.6)}$ and (ii) FeO_x measured at an applied current density of 5 mA cm^{-2} in phosphate buffer (0.1 M, pH 7).

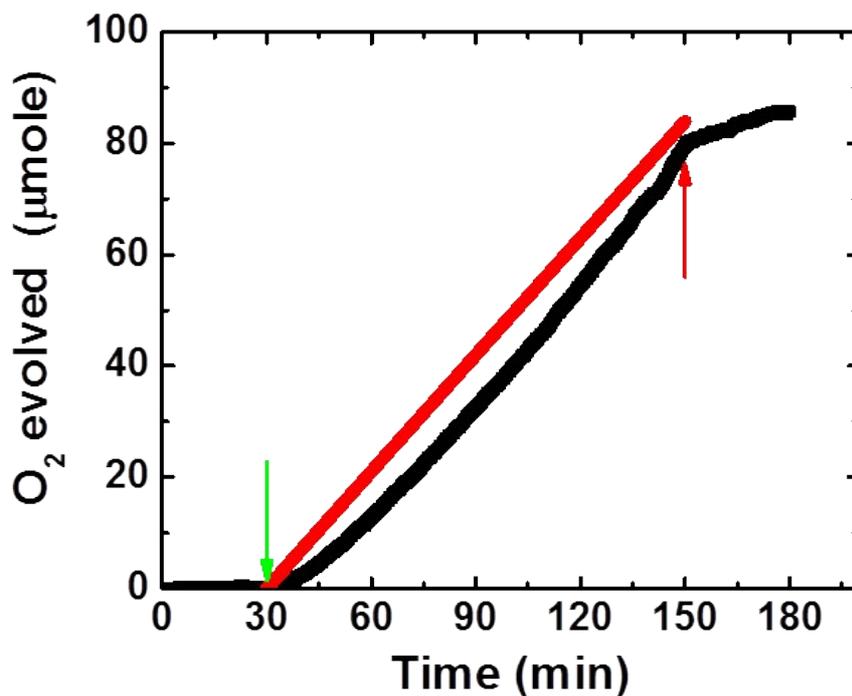


Figure S6 Evolution of O_2 at $\text{FTO}|\text{CaFeO}_{x(r=0.6)}$ during CCE in phosphate buffer (0.1 M, pH 7). Current density 5 mA cm^{-2} was applied only between 30 and 150 min (green and red arrows indicate the beginning and end of CCE, respectively). The amount of O_2 was quantified with an O_2 fluorescence probe (black trace); the theoretical amount of O_2 with 100 % Faradaic efficiency is shown as a red trace.

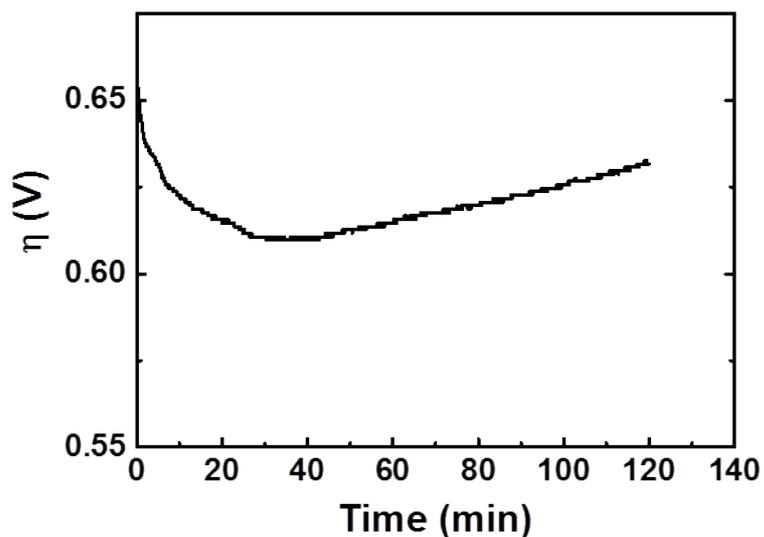


Figure S7 Overpotential (η) transient of FTO|CaFeO_{x(r=0.6)} measured at an applied current density of 5 mA cm⁻² in phosphate buffer (1.0 M) under CO₂ atmosphere. Solution pH of phosphate buffer shifted from 7.0 to 6.7 under purge of CO₂ gas.

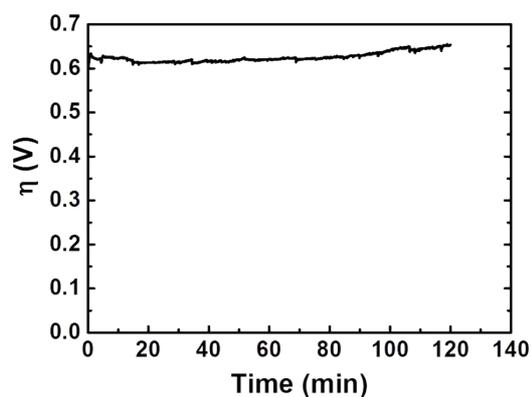


Figure S8 Overpotential (η) transients of CaFeO_{x(r=0.6)} measured at an applied current density of 5 mA cm⁻² in sodium bicarbonate (1.0 M)-sodium carbonate (0.1 M) electrolyte solution (pH 8.7) under N₂ atmosphere.

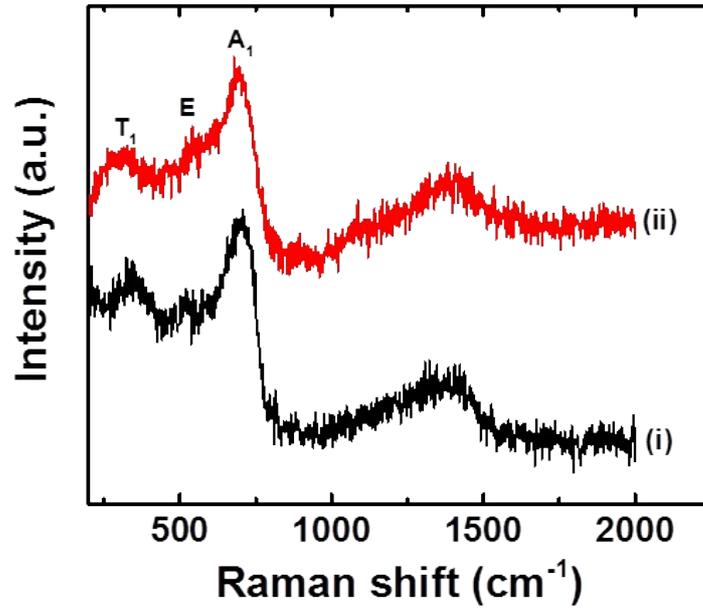


Figure S9 Raman spectra of (i) FTO|CaFeO_{x(r=0)} and (ii) FTO|CaFeO_{x(r=0.6)}.

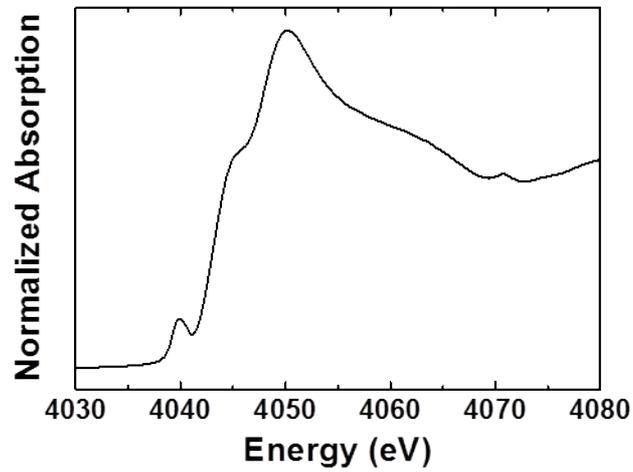


Figure S10 Ca K-edge XANES spectra for FTO|CaFeO_{x(r=0.6)}.

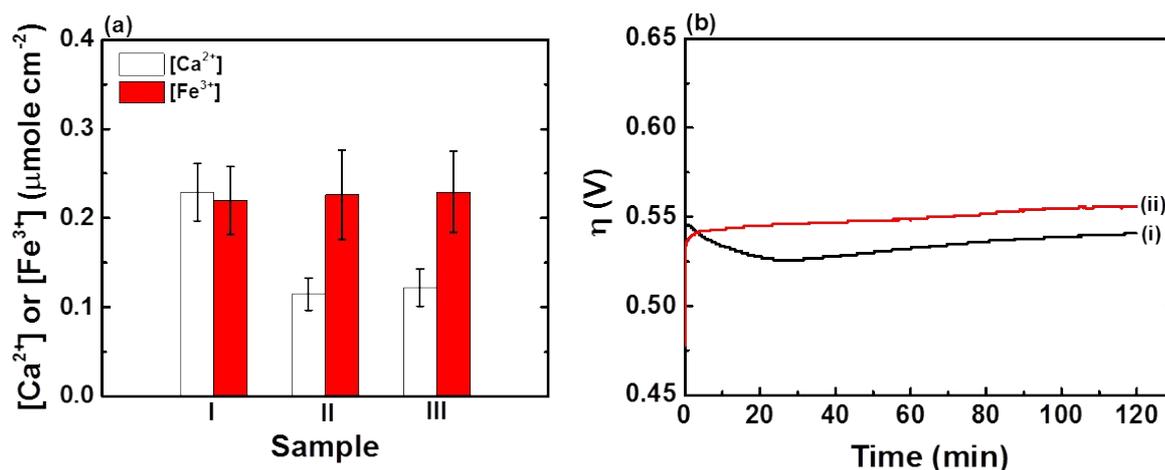


Figure S11 (a) The content of Ca^{2+} and Fe^{3+} , quantified by using ICP, in (I) as-prepared $\text{FTO}|\text{CaFeO}_{x(r=0.6)}$, (II) $\text{FTO}|\text{CaFeO}_{x(r=0.6)}$ after 2-h CCE at 1 mA cm^{-2} in phosphate buffer (1.0 M, pH 7), and (III) $\text{FTO}|\text{CaFeO}_{x(r=0.6)}$ after two times 2-h CCE at 1 mA cm^{-2} in phosphate buffer (1.0 M, pH 7). (b) η transients of $\text{FTO}|\text{CaFeO}_{x(r=0.6)}$ during (i) 1st and (ii) 2nd CCE at 1 mA cm^{-2} in phosphate buffer (1.0 M, pH 7).

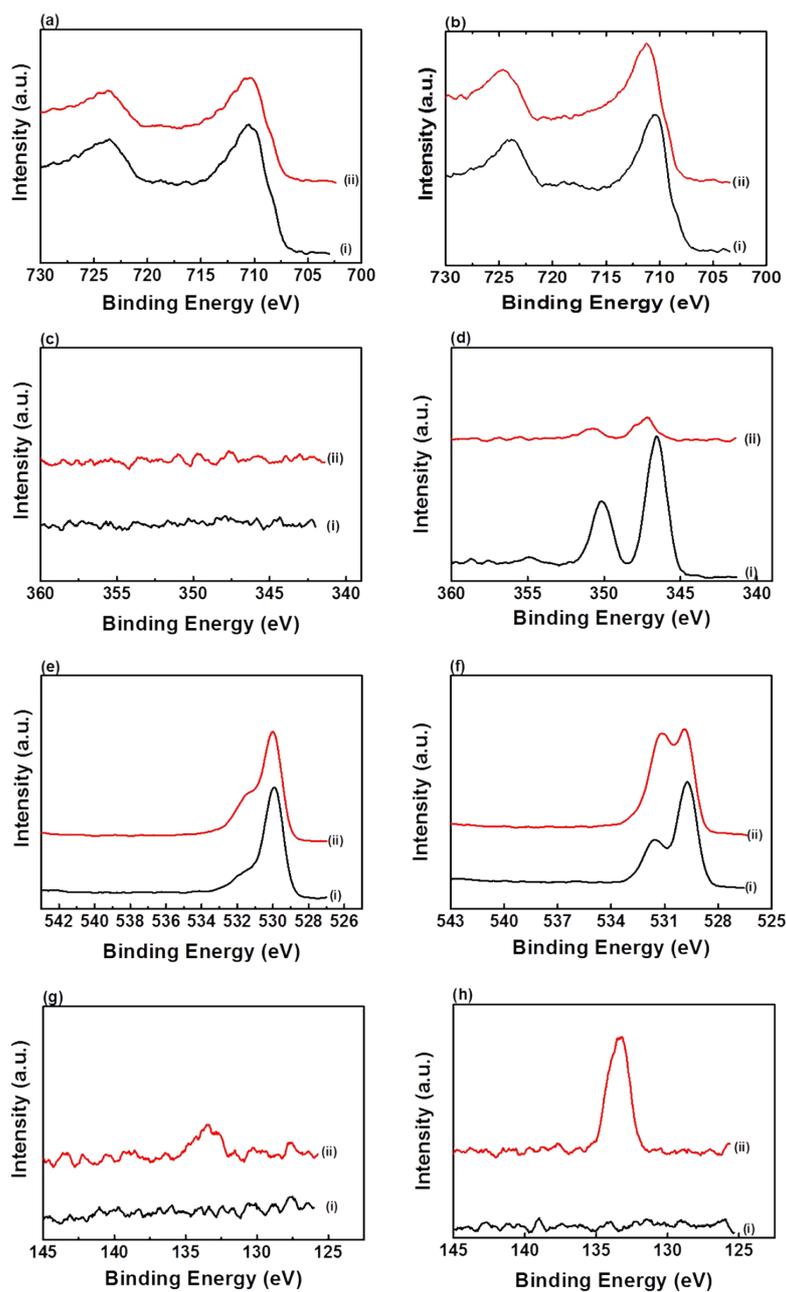


Figure S12 XPS spectra of (a, c, e, g) FTO|CaFeO_{x(r=0)} and (b, d, f, h) FTO|CaFeO_{x(r=0.6)} before (i) and after (ii) 2-h CCE at an applied current density of 1 mA cm⁻² in phosphate buffer (0.1 M, pH 7). (a, b) Fe 2p region. (c, d) Ca 2p region. (e, f) O 1s region. (g, h) P 2p region.

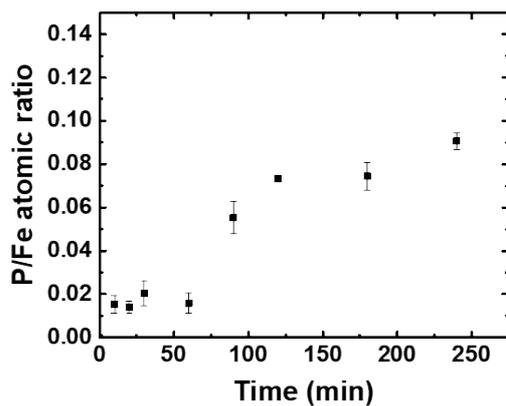


Figure S13 P/Fe atomic ratios for $\text{CaFeO}_{x(r=0.6)}$ measured using EDX after different periods of electrolysis at an applied current of 5 mA cm^{-2} in phosphate buffer (0.1 M, pH 7).

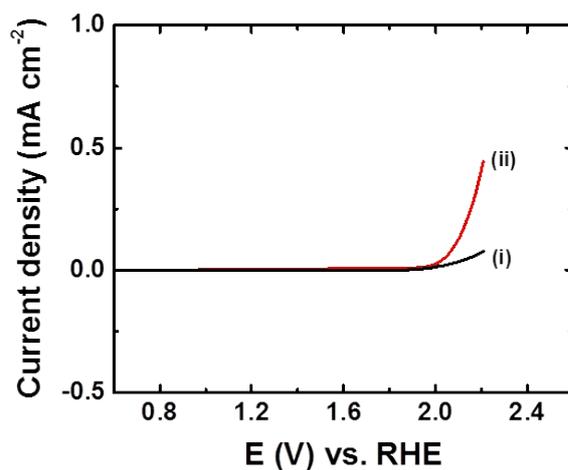


Figure S14 Linear sweep voltammetry, recorded at a scan rate of 10 mV s^{-1} , of (i) unmodified and (ii) iron phosphate modified FTO in phosphate buffer (0.1 M, pH 7).

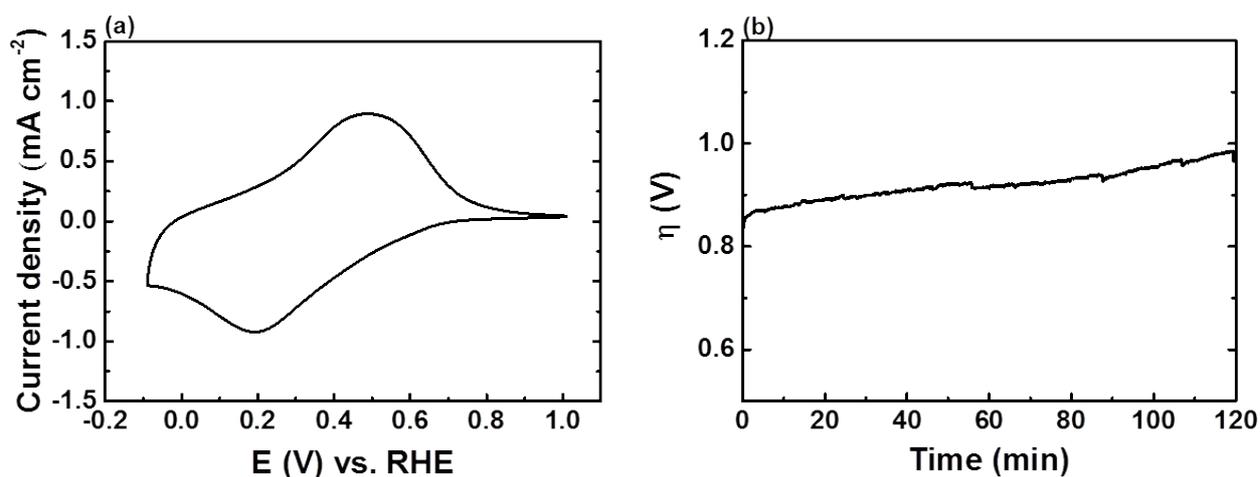


Figure S15 (a) CV, recorded at a scan rate of 50 mV s^{-1} and (b) η transients, recorded at an applied current density of 5 mA cm^{-2} , of CV pretreated FTO| $\text{CaFeO}_{x(r=0)}$ in phosphate buffer (0.1 M , pH 7).

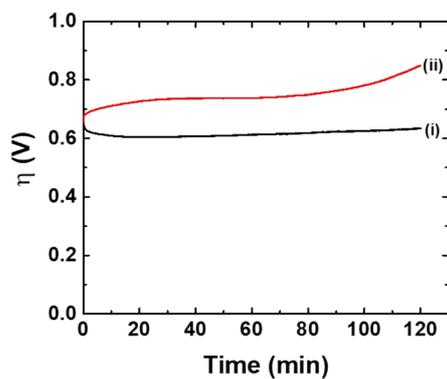


Figure S16 Overpotential (η) transients of (i) $\text{CaFeO}_{x(r=0.6)}$ and (ii) FeO_x measured at an applied current density of 10 mA cm^{-2} in phosphate buffer (1.0 M , pH 7).

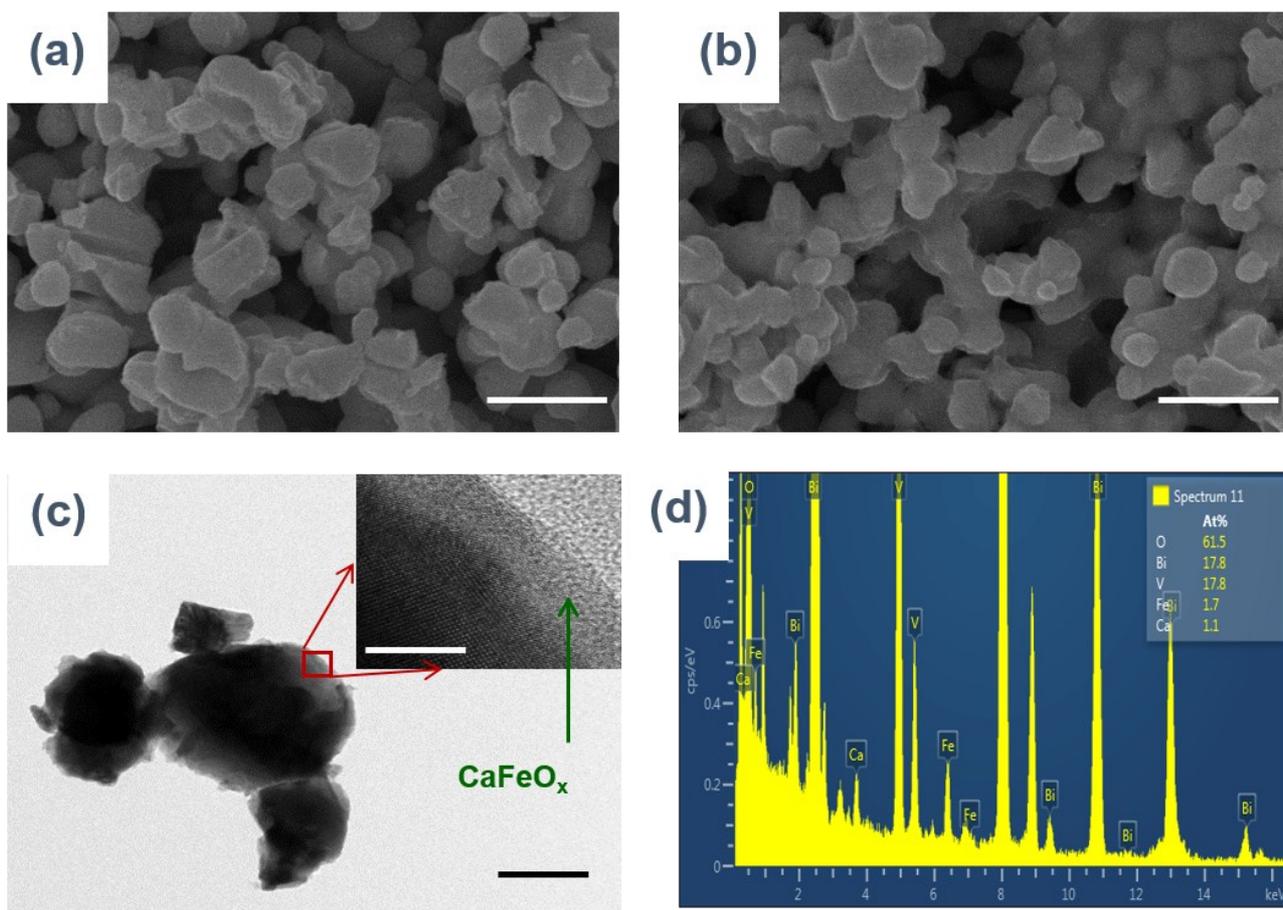


Figure S17 (a, b) SEM images, with scale bar 500 nm, of FTO|BiVO₄ (a) and FTO|BiVO₄|CaFeO_{*x*(*r*=0.6)} (b). (c) TEM and HRTEM images (inset), and (d) EDS of FTO|BiVO₄|CaFeO_{*x*(*r*=0.6)}. Scale bars in TEM and HRTEM images are 200 and 10 nm, respectively.

Reference

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