Supporting Information

Operando measurement of electrocatalyst potential on particulate photocatalyst for overall water splitting

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Fig. S1 – S16

Table S1 – S3

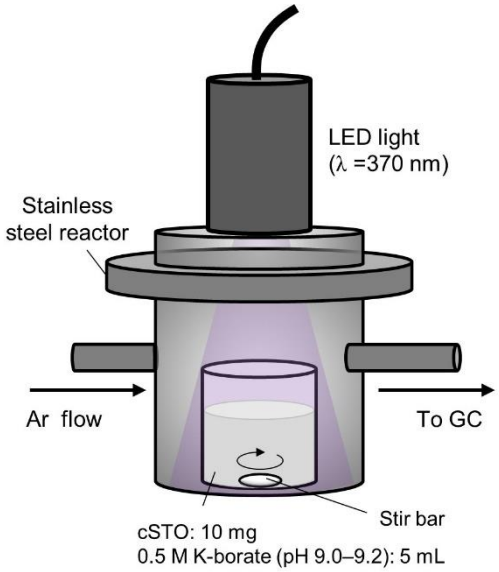

Fig. S1. Schematic illustration of a reactor for photocatalytic water splitting.

Table S1. The light intensity and the photon number of LED light used in this study.

Light intensity / mW cm^{-2}	Photon / μmol h^{-1} cm^{-2}	Photon number /photon h^{-1} cm^{-2}
12	1.3×10^2	8.0×10^{19}
30	3.3×10^2	2.0×10^{20}
59	6.7×10^2	4.0×10^{20}
94	1.1×10^3	6.4×10^{20}
1.2×10^2	1.3×10^3	8.1×10^{20}

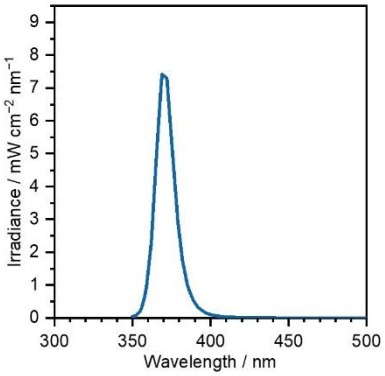

Fig. S2. The measured irradiance spectrum of the LED light used in this study. The integrated value is 1.2 × 10^2 mW cm^{-2}.

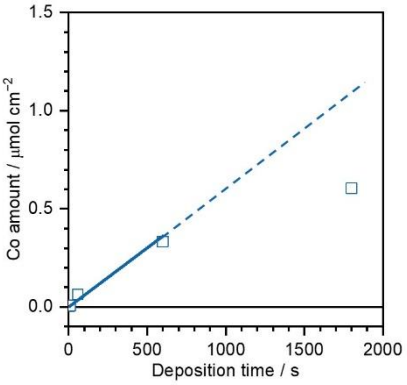

Fig. S3. The relationship between Co loading amount on FTO substrates and electrodeposition time. The CoOOH deposition on FTO substrates was conducted by CP at 0.5 mA cm^{-2} for 5, 10, 60, 600, or 1800 s in 0.1 M $Co(NO_3)_2$ aqueous solution. After deposition, CoOOH/FTO was immersed in 0.1 M HNO_3 (super special grade, Wako) and ultrasonicated to dissolve all Co species. Finally, the solution was diluted in 0.01 M HNO_3 for ICP–OES analysis.

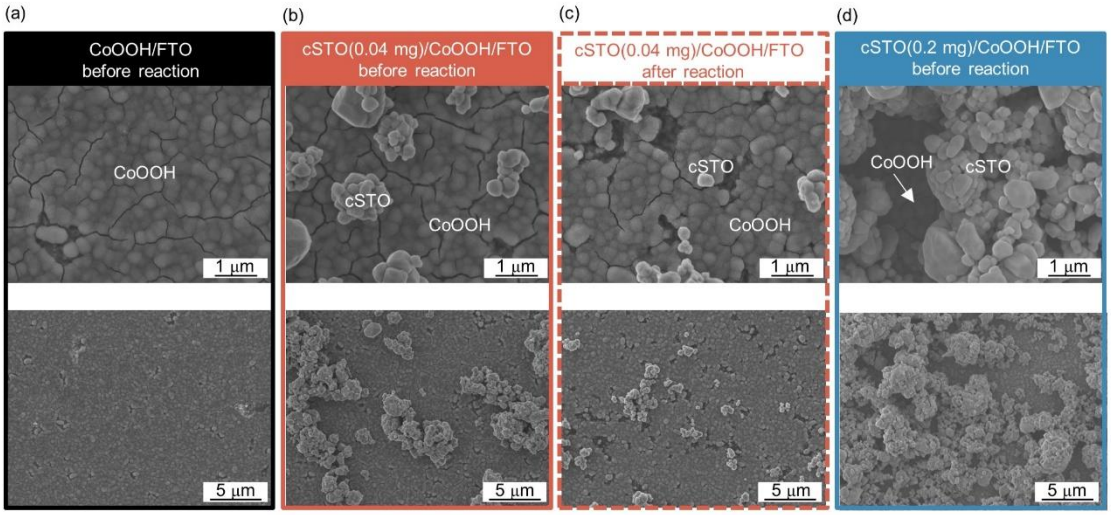

Fig. S4. Top-view SEM images of (a) CoOOH/FTO, (b) cSTO(0.04 mg)/CoOOH/FTO, (c) cSTO(0.04 mg)/CoOOH/FTO after the reaction, and (d) cSTO(0.2 mg)/CoOOH/FTO, respectively. The loading amount of CoOOH on FTO substrates is 0.4 μmol cm^{-2}.

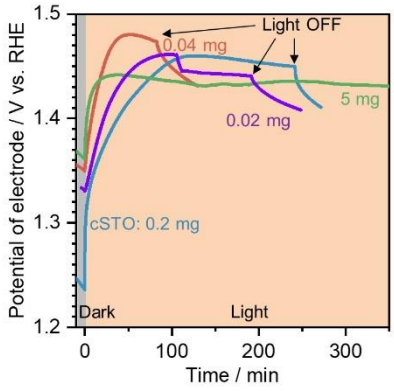

Fig. S5. OCP of 0.02, 0.04, 0.2, and 5 mg cSTO loaded on CoOOH electrode as a function of time. Light source was LED light (λ = 370 nm, 59 mW cm^{-2}).

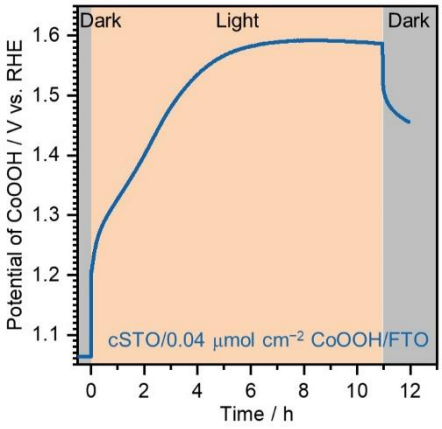

Fig. S6. Long-term measurement of OCP of cSTO/0.04 μmol cm^{-2} CoOOH/FTO electrode in 0.5 M K-borate (pH 9.0–9.2) under LED illumination (λ = 370 nm, 59 mW cm^{-2}). WE: cSTO/0.04 μmol cm^{-2} CoOOH/FTO electrode, RE: Hg/Hg_2Cl_2 (sat. KCl).

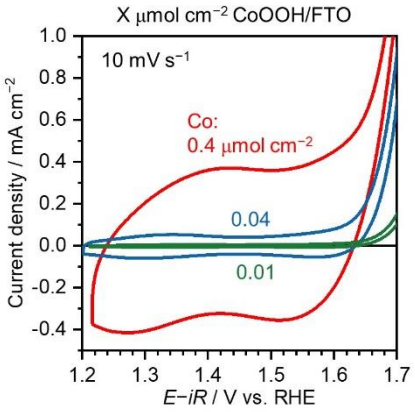

Fig. S7. The results of CV for CoOOH/FTO electrodes under dark condition. WE: CoOOH/FTO electrode, RE: Hg/Hg_2Cl_2 (sat. KCl), CE: Pt wire, electrolyte: 0.5 M K-borate (pH 9.0–9.2).

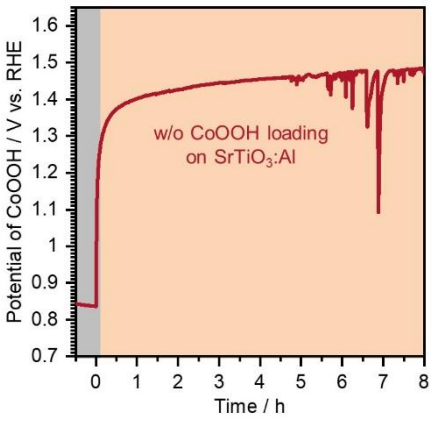

Fig. S8. OCP of Rh (0.1 wt%)/Cr_2O_3 (0.05 wt%)/$SrTiO_3$:Al (without CoOOH pre-loading)/CoOOH electrode in 0.5 M K-borate (pH 9.0–9.2) under LED illumination (λ = 370 nm, 59 mW cm^{-2}). RE: Hg/Hg_2Cl_2 (sat. KCl). It took over 7 h for the OCP to stabilize, a longer time than in **Fig. 3a**.

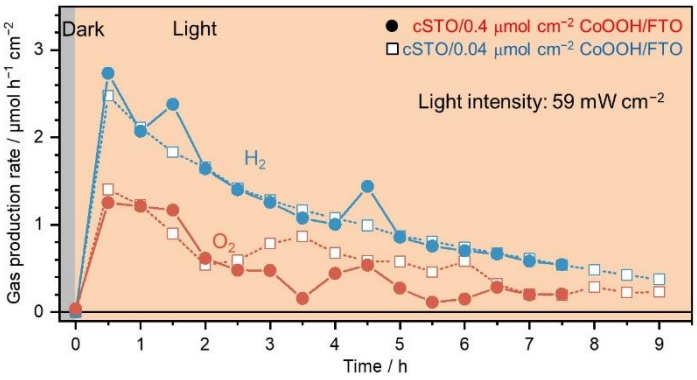

Fig. S9. Time course of detected gas production rate of cSTO/0.04 μmol cm^{-2} CoOOH/FTO or cSTO/0.4 μmol cm^{-2} CoOOH/FTO electrode in 0.5 M K-borate (pH 9.0–9.2) under LED light illumination (λ = 370 nm, 59 mW cm^{-2}). WE: cSTO/CoOOH/FTO electrode, RE: Hg/Hg_2Cl_2 (sat. KCl).

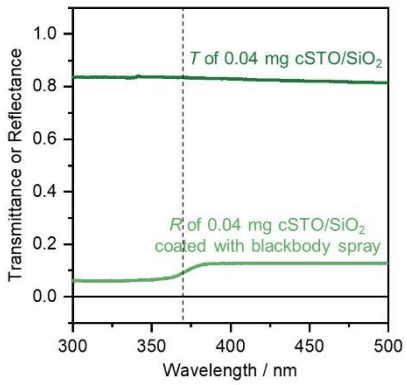

Fig. S10. UV–vis transmission and reflection spectra of 0.04 mg cSTO/SiO_2. Only for reflection spectrum, the SiO_2 substrate was coated with blackbody spray.

Table S2. Apparent quantum yield (AQY) and internal quantum yield (IQY) of attempted photocatalytic systems. All systems use 0.5 M K-borate (pH 9.0–9.2) as an electrolyte and LED light (λ: 370 nm, 59 mW cm^{-2}) as a light source.

Photocatalyst structure	AQY / %	IQY / %
cSTO powder	15	-
cSTO/0.04 μmol cm^{-2} CoOOH/FTO	0.7	11
cSTO/0.4 μmol cm^{-2} CoOOH/FTO	0.8	12

Table S3. Photocurrent density and measured surface hole quasi-Fermi level ($E_{f,h}$) using $SrTiO_3$.

Condition	Photocurrent density / μA cm^{-2}	$E_{f,h}$ / V vs. RHE	Electrolyte	Light source	
Open circuit	7*	1.56–1.59	0.5 M K-borate (pH 9.0–9.2)	LED light (λ: 370 nm, 59 mW cm^{-2})	This study
Open circuit	~0	~0.5	0.1 M K-phosphate (pH 7)	ultraviolet lamp (10 mW cm^{-2})	ref[S2]
Short circuit ($E_{f,e}$ = 0.3 V vs. RHE)	~100	~0.9			

*The photocurrent density is estimated from the measured OCP of cSTO/CoOOH/FTO electrode and the *j–E* curve of CoOOH/FTO electrode under dark condition.

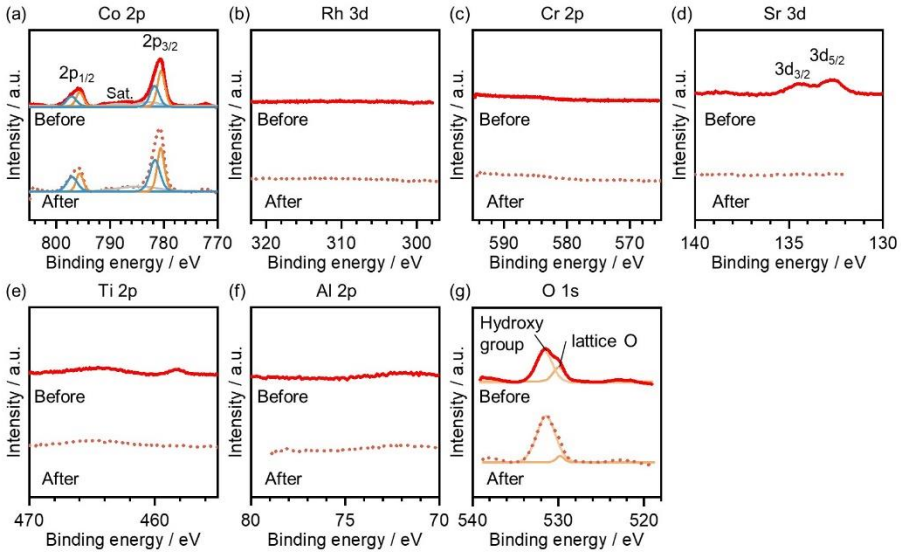

Fig. S11. XPS spectra of (a) Co 2p, (b) Rh 3d, (c) Cr 2p, (d) Sr 3d, (e) Ti 2p, (f) Al 2p, and (g) O 1s of cSTO/0.4 μmol cm^{-2} CoOOH/FTO before and after the reaction test. Co $2p_{1/2}$ and Co $2p_{3/2}$ peaks centered at the binding energy of 796 and 781 eV were observed. By the deconvolution of Co $2p_{3/2}$ spectra, two peaks centered at 780.5 and 781.7 eV were found. These peak positions are well consistent with previously reported CoOOH XPS spectra.[S3]

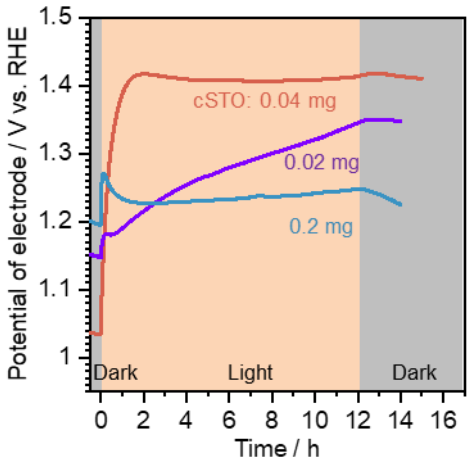

Fig. S12. OCP transients of cSTO (0.02, 0.04, and 0.2 mg) /0.4 μmol cm^{-2} CoOOH/FTO electrode measured in 0.5 M K-borate (pH 9.0–9.2). Light source was solar simulator equipped with AM1.5G filter (100 mW cm^{-2}, 1 sun). WE: cSTO (0.02, 0.04, and 0.2 mg)/ 0.4 μmol cm^{-2} CoOOH/FTO electrode, RE: Hg/Hg_2Cl_2 (sat. KCl).

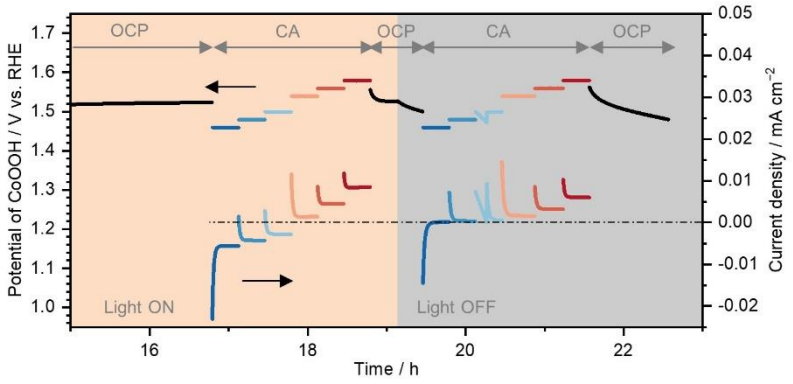

Fig. S13. The measured potential and produced current of cSTO/0.4 μmol cm^{-2} CoOOH/FTO in 0.5 M K-borate (pH 9.0–9.2) under open circuit condition and CA. WE: cSTO/CoOOH/FTO electrode, RE: Hg/Hg_2Cl_2 (sat. KCl), CE: coiled-Pt wire, light source: LED light (λ = 370 nm, 59 mW cm^{-2}).

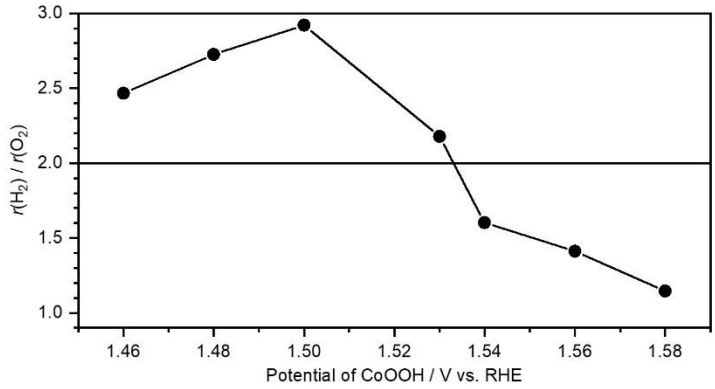

Fig. S14. The ratio of $r(H_2)$ to $r(O_2)$ at various electrode potentials. WE: cSTO/0.4 μmol cm^{-2} CoOOH/FTO electrode, RE: Hg/Hg_2Cl_2 (sat. KCl), CE: coiled-Pt wire, electrolyte: 0.5 M K-borate (pH 9.0–9.2), light source: LED light (λ = 370 nm, 59 mW cm^{-2}).

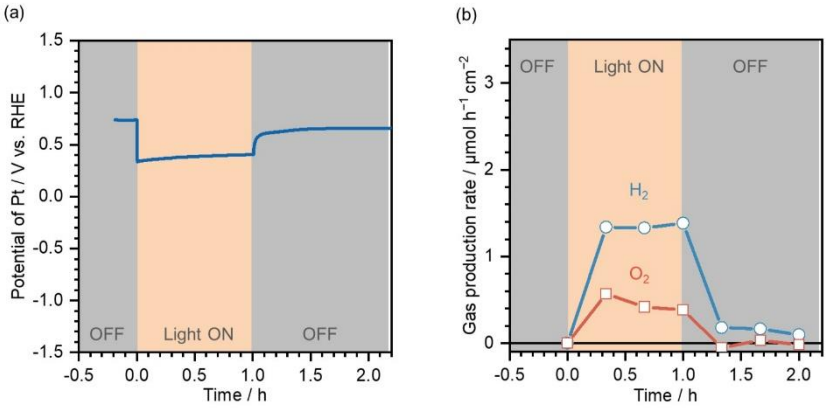

Fig. S15. (a) OCP and (b) gas production rate of CrO_x/cSTO/Pt electrode in 0.5 M K-borate (pH 9.0–9.2) under LED illumination (λ = 370 nm, 59 mW cm^{-2}). WE: CrO_x/cSTO/Pt electrode, RE: Hg/Hg_2Cl_2 (sat. KCl).

Pt foil (99.95%, *t* = 0.05 mm, The Nilaco Corporation) was cut to 10 mm × 30 mm and polished with 1 μm of diamond and with 0.05 μm of alumina (both purchased from BAS, Inc.). 0.04 mg of cSTO was drop-cast on a Pt foil (cSTO/Pt). cSTO/Pt was immersed in 50 mM K_2CrO_4 (FUJIFILM Wako Pure Chemical Corporation) aqueous solution for 30 min with H_2 bubbling to obtain CrO_x-coated cSTO/Pt (CrO_x/cSTO/Pt).[S1]

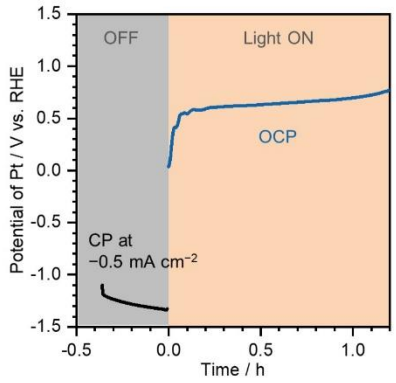

Fig. S16. The measured potential of CrO_x/cSTO/Pt electrode in 0.5 M K-borate (pH 9.0–9.2) under CP (at −0.5 mA cm^{-2}) and open circuit condition. WE: CrO_x/cSTO/Pt electrode, RE: Hg/Hg_2Cl_2 (sat. KCl), CE: coiled-Pt wire, light source: LED light (λ = 370 nm, 59 mW cm^{-2}).

Reference

[S1] M. Qureshi, T. Shinagawa, N. Tsiapis, and K. Takanabe, *ACS Sustainable Chem. Eng.* 2017, **5**, 8079−8088.

[S2] R. Chen, D. Zhang, Z. Wang, D. Li, L. Zhang, X. Wang, F. Fan and C. Li, J. Am. Chem. Soc., 2023, 145, 4667−4674.

[S3] J. Yang, H. Liu, W. N. Martens, and R. L. Frost, *J. Phys. Chem. C*, 2010, **114**, 111–119.