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Electronic Supplementary Information for

Self-activated Rh–Zr mixed oxide as a nonhazardous cocatalyst for photocatalytic hydrogen evolution

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Experimental details

Chemicals: The following chemicals were used as received without purification: $SrTiO_3$ (Wako), Al_2O_3 (Aldrich, nanopowder), $SrCl_2$ (Kanto), $RhCl_3{\cdot}3H_2O$ (Wako), $Rh(NO_3)_3{\cdot}xH_2O$ (Aldrich), $Cr(NO_3)_3{\cdot}9H_2O$ (Wako), $ZrOCl_2{\cdot}8H_2O$ (Wako), $ZrO(NO_3)_2{\cdot}6H_2O$ (Wako), $Fe(NO_3)_3{\cdot}9H_2O$ (Wako), $Ce(NO_3)_3{\cdot}6H_2O$ (Wako), $La(NO_3)_3{\cdot}6H_2O$ (Wako), Eu acetate$\cdot nH_2O$ (Wako), Er acetate$\cdot 4H_2O$ (Wako), $Al(NO_3)_3{\cdot}9H_2O$ (Wako), $Mn(NO_3)_2{\cdot}6H_2O$ (Aldrich), $Ni(NO_3)_2{\cdot}6H_2O$ (Wako), $Ga(NO_3)_3{\cdot}nH_2O$ (Aldrich), $Cu(NO_3)_2{\cdot}3H_2O$ (Wako), $Zn(NO_3)_2{\cdot}6H_2O$ (Aldrich), $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (Wako), $In(NO_3)_3{\cdot}3H_2O$ (Wako), $Co(NO_3)_2{\cdot}6H_2O$ (Kanto), $Cd(NO_3)_2{\cdot}4H_2O$ (Aldrich), $Pb(NO_3)_2$ (Wako), $Na_2WO_4{\cdot}2H_2O$ (Aldrich) and K_2IrCl_6 (Wako).

Synthesis of $SrTiO_3$:Al: $SrTiO_3$:Al was synthesized by the molten-salt synthesis (flux method). A mixture of $SrTiO_3$, Al_2O_3 and $SrCl_2$ at a molar ratio of 1:0.02:10 was heated in an alumina crucible (Nikkato, SSA-S) at 1150 °C for 10 h in air. The $SrTiO_3$:Al was subsequently separated from the flux by washing with deionized water three times.

Cocatalyst loading on $SrTiO_3$:Al: Cocatalyst was loaded on $SrTiO_3$:Al by impregnation method. Aqueous solution of desired amount of Rh and metal precursor was mixed with $SrTiO_3$:Al (50 mg) and dried on the glass dish with hot plate. Dried powder was collected and annealed at 350 °C for 1 h in air. Product was washed with water three times for water-washed sample for XPS measurement.

Photocatalysis measurements: $SrTiO_3$:Al based photocatalyst powder (10 mg) was dispersed in water (20 mL) in Pyrex glass reactor by sonication. Xe lamp (300 W) with a cold mirror, which reflects the light of 250-450 nm, was used, but Pyrex glass transmits only the light >300 nm. The power of 300 W Xe lamp was set to 10 A for experiments shown in Figs. S1 and S9, and 20 A for those shown in Figs. 1, 5, S4, S11, S15 and S16. The reactor was immersed in a water bath and connected to Ar-flow system GC (Shimadzu GC-2014). Evolved hydrogen and oxygen were automatically collected at every 30 min.

Apparent quantum yield (AQY) estimation: The AQY of water splitting reaction is given by the equation (1):

$$\mathrm{AQY} = 2 \times \gamma(\mathrm{H_2O})/\gamma(\mathrm{photon}) \qquad (1)$$

where $\gamma(H_2O)$ and γ(photons) denote the number of decomposed water molecules and the number of incident photons per unit time, respectively. The water splitting reaction was carried out using a closed circulation system equipped with a gas chromatograph with a thermal conductivity detector in an Ar carrier gas. The light source used was a 300 W Xe lamp equipped with a bandpass filter with central wavelength of 365 nm. The spatial distributions of the power spectra are measured using a grating spectroradiometer (EKO Instruments Co., Ltd., LS-100). γ(photons) and $\gamma(H_2O)$ were measured to be 3.2×10^{20} photon h^{-1} and 88 µmol h^{-1}, respectively. Based on the equation (1), the AQY was calculated to be 33%. For estimating solar-to-hydrogen efficiency (STH), a solar simulator (Asahi Spectra Co., Ltd., HAL-320) with an irradiation area of 2.9×2.9 cm^2 was used as a light source.

Electrocatalysis measurements: $RhZrO_x$/XC-72 catalyst was prepared by the impregnation method. An aqueous solution containing $RhCl_3\cdot3H_2O$ (0.1 wt% Rh vs. XC-72) and $ZrOCl_2\cdot8H_2O$ (0-0.7 wt% Zr vs. XC-72) was mixed with XC-72 (10 mg) and dried on the glass dish with hot plate. Dried powder was annealed at 350 °C for 1 h in air. We confirmed that XC-72 is not burnt out by annealing process with TG-DTA analysis (Fig. S12). $RhZrO_x$/XC-72 powder (1 mg), water (394 µL), 2-propanol (96 µL) and 5 wt% Nafion solution (10 µL) were mixed by sonication for 30 min to prepare homogeneous catalyst slurry. 10 µL of catalyst slurry was placed on a rotating disk glassy carbon electrode (5 mm in diameter), followed by rotating at 700 rpm until the catalyst layer was dried. HER was measured in Ar-saturated 1 M Na_2SO_4 aqueous solution at pH 7 at 3600 rpm at RT. ORR was measured in O_2-saturated 1 M Na_2SO_4 aqueous solution at pH 7 at 3600 rpm at RT.

Characterization: SEM observation and EDX analysis were carried out using HITACHI S-4800. HRTEM and STEM-EDS mapping measurements were conducted using JEOL JEM-ARM200F. ICP measurements were carried out using SHIMADZU ICPE-9820. XRD patterns were obtained using Panalytical X'Pert Pro MPD with CuKα radiation (λ = 1.542 Å) operated at 45 kV and 40 mA. TG-DTA measurements were conducted with Shimadzu DTG-60. X-ray photoelectron spectroscopy (XPS) was conducted in an ultrahigh vacuum combined system equipped with a hemispherical electron analyzer (Omicron model EA125) and a twin-anode (Mg/Al) X-ray source (Vacuum Generators).

In–situ XANES measurement: XANES measurements were conducted at BL01B2 beamline in SPring-8. $RhZrO_x/SrTiO_3$:Al (0.1 g) was suspended in distilled water (approximately 2 mL) in a Pyrex tube (inner diameter of 9 mm and outer diameter of 12 mm, transmittance of light >300 nm), and was vigorously stirred using a magnetic stirrer. The photocatalyst suspension was irradiated with UV light using a 300 W Xe lamp (250 nm < λ < 450 nm). Fluorescence X-rays were collected using semiconductor detector. XANES spectra of reference samples, Rh foil and Rh_2O_3 powder, were obtained in transmittance mode. For Rh_2O_3, a pellet was prepared using BN as a dispersion media.

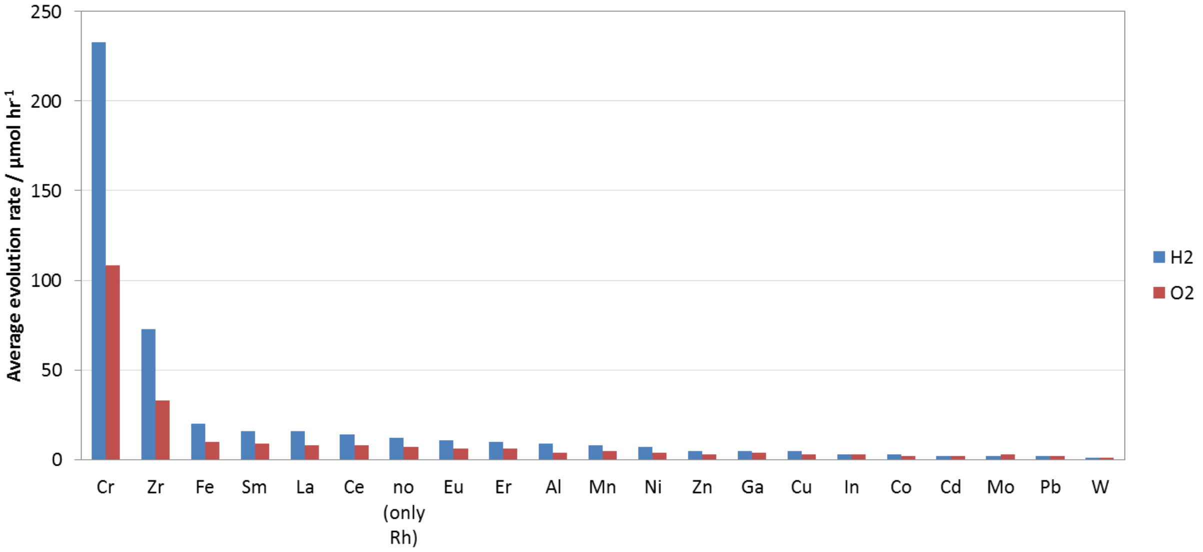

Fig. S1 Average evolution rates of H_2 and O_2 gases using $SrTiO_3$:Al with Rh-metal mixed oxide cocatalysts (Rh = 0.1 wt% and other metals = 0.5 wt% vs. $SrTiO_3$:Al). Reaction conditions: catalyst, 10 mg; solution, 20 mL of H_2O; light source, 300 W Xe lamp (λ = 300–450 nm).

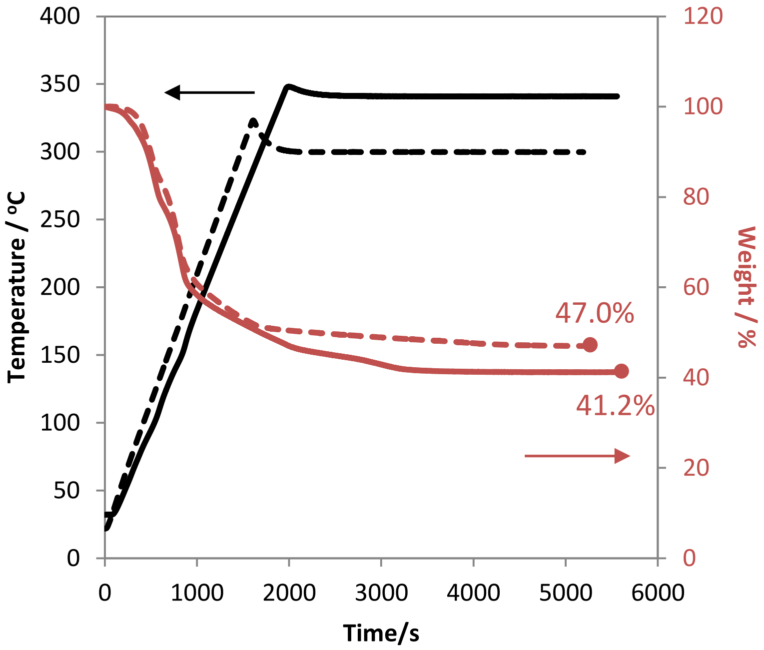

Fig. S2 TG analyses of $ZrOCl_2 \cdot 8H_2O$ at the holding temperatures of 300 (broken line) and 350 °C (solid line). If $ZrOCl_2 \cdot 8H_2O$ is completely converted into ZrO_2, the weight ratio is calculated to be 38.4%.

Table S1 Cl/Zr molar ratios in $ZrOCl_2 \cdot 8H_2O$ annealed at various temperature for 1 h in air (EDX analyses)

Annealing Temp. (°C)	Cl/Zr (mol/mol)
non-annealed	2.07
300	0.61
350	0.39
400	0.27
450	0.08

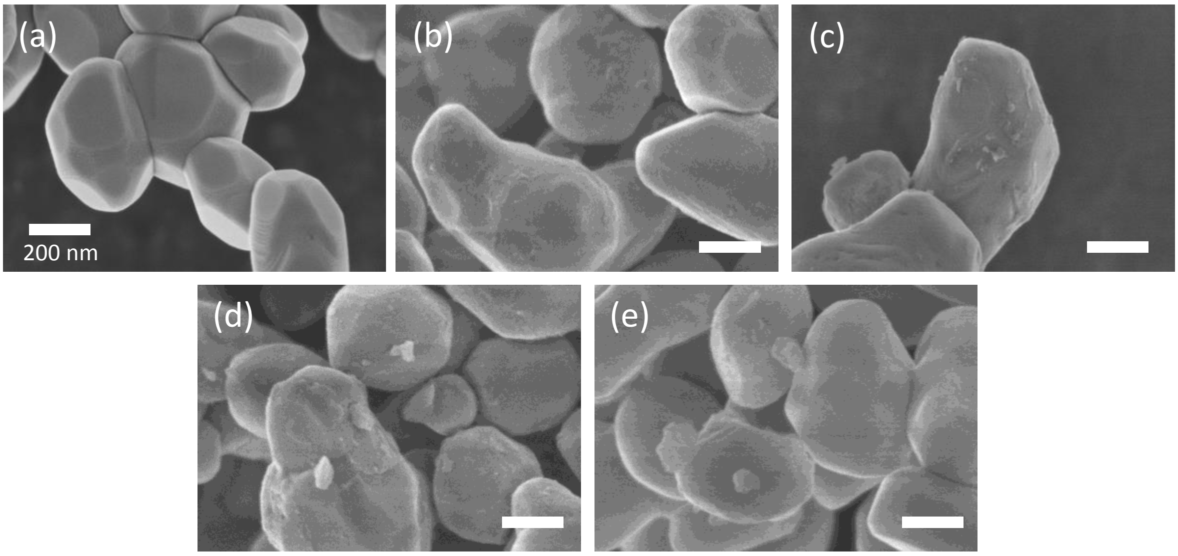

Fig. S3 SEM images of (a) pristine $SrTiO_3$:Al and (b–e) $RhZrO_x/SrTiO_3$:Al annealed at (b) 300, (c) 350, (d) 400 and (e) 450 °C. Scale bars are 500 nm.

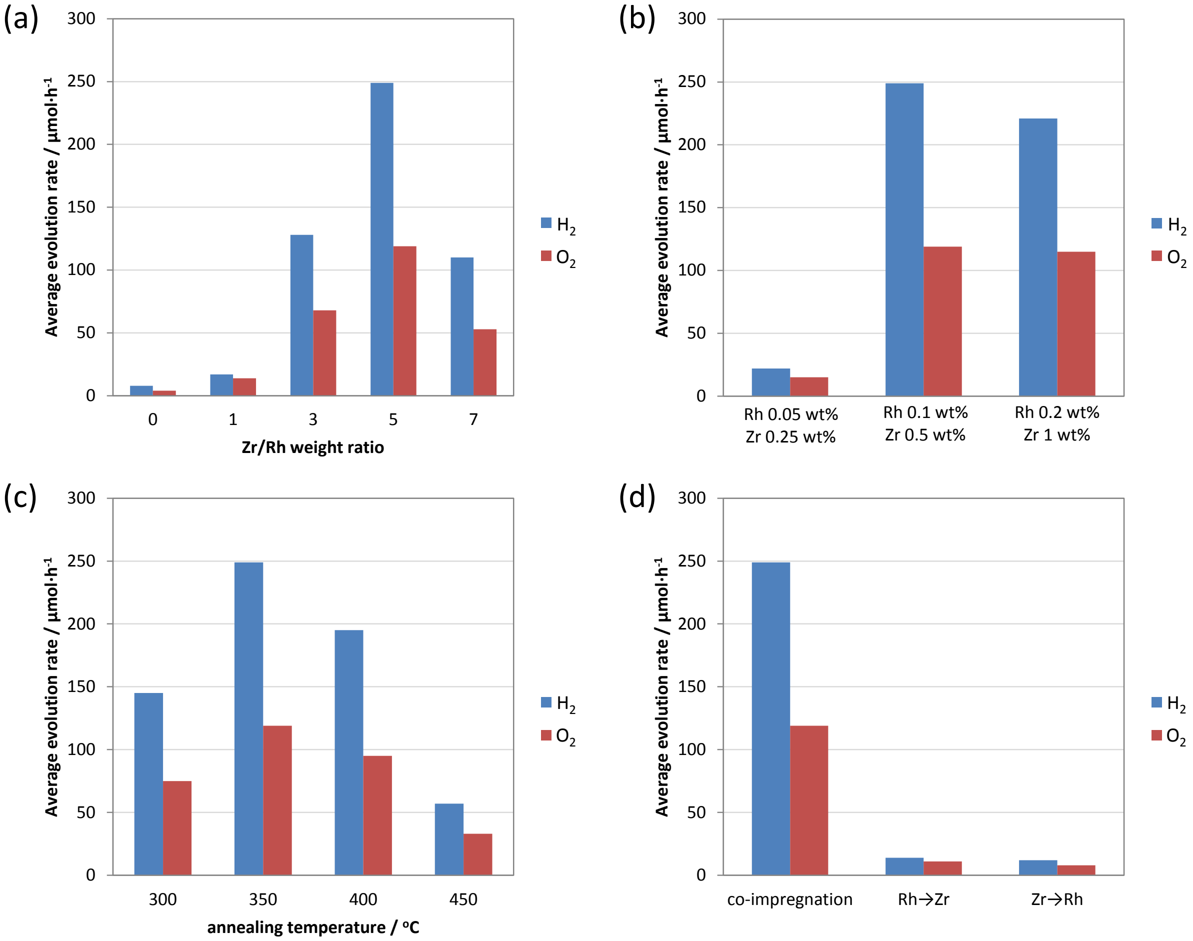

Fig. S4 Average evolution rates of H_2 and O_2 gases using $RhZrO_x/SrTiO_3$:Al preapred at various preparation conditions. Each graph corresponds to that of Fig.1.

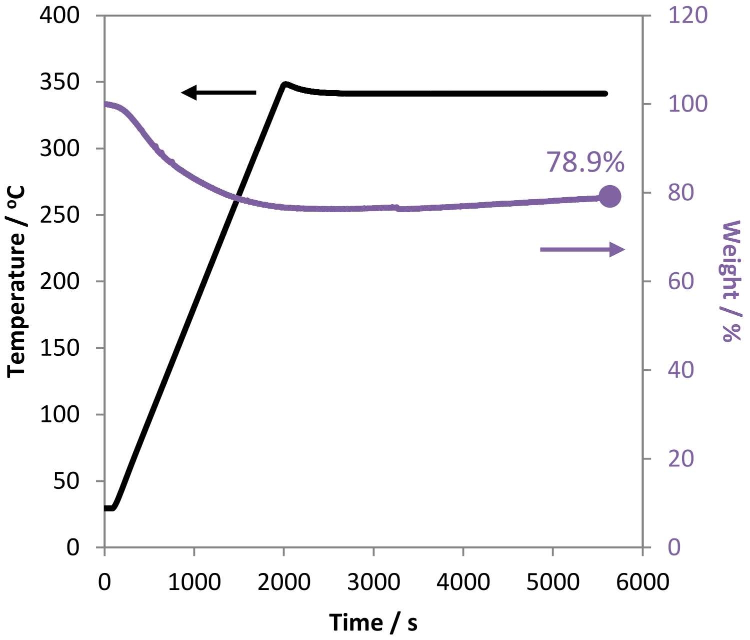

Fig. S5 TG analysis of $RhCl_3{\cdot}3H_2O$ at the same annealing conditions as impregnation. If $RhCl_3{\cdot}3H_2O$ is completely converted into $RhCl_3$ or Rh_2O_3, the weight ratio is calculated to be 79.5 or 48.2%, respectively.

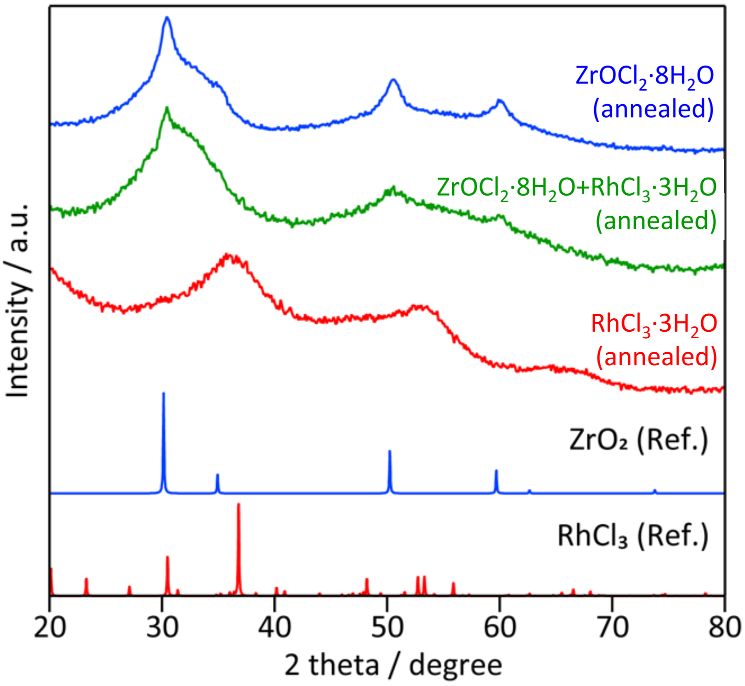

Fig. S6 XRD patterns of solids prepared by annealing RhCl$_3$·3H$_2$O and/or ZrOCl$_2$·8H$_2$O.

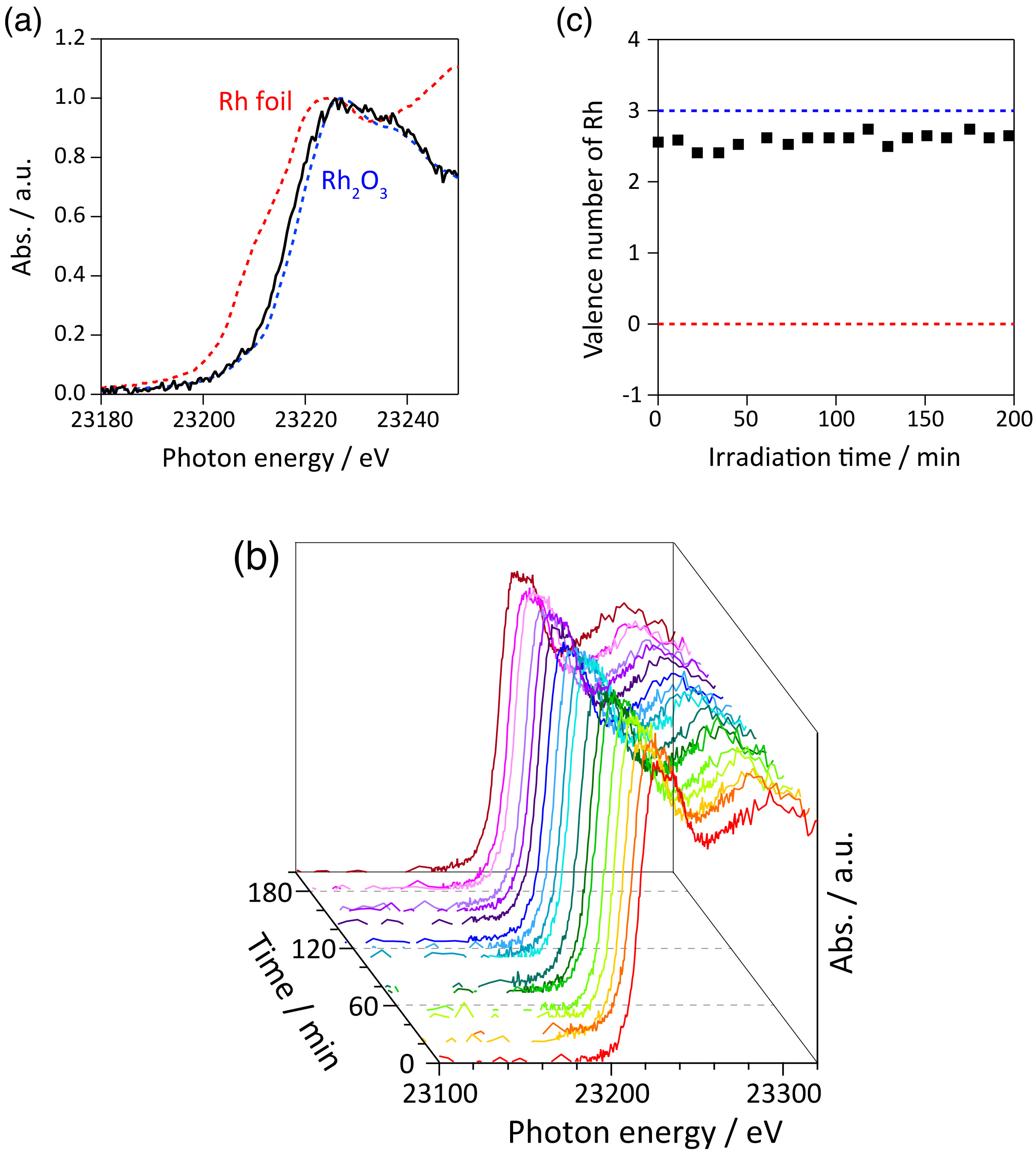

Fig. S7 (a) Rh XANES spectra of Rh foil (red), Rh_2O_3 (blue) and $RhZrO_x/SrTiO_3$:Al (black) before light irradiation. (b) Stacked in-situ Rh XANES spectra and (c) estimated valence state of Rh (black square) vs metal Rh (red) and Rh_2O_3 (blue) reference samples, assuming that Rh in Rh_2O_3 is trivalent.

Table S2 Amounts of Zr and Rh in $RhZrO_x/SrTiO_3:Al$ before and after photocatalytic reaction measured by ICP

	Before	After
Zr	0.57 wt%	0.54 wt%
Rh	0.10 wt%	0.09 wt%
Zr/Rh	5.77	5.84

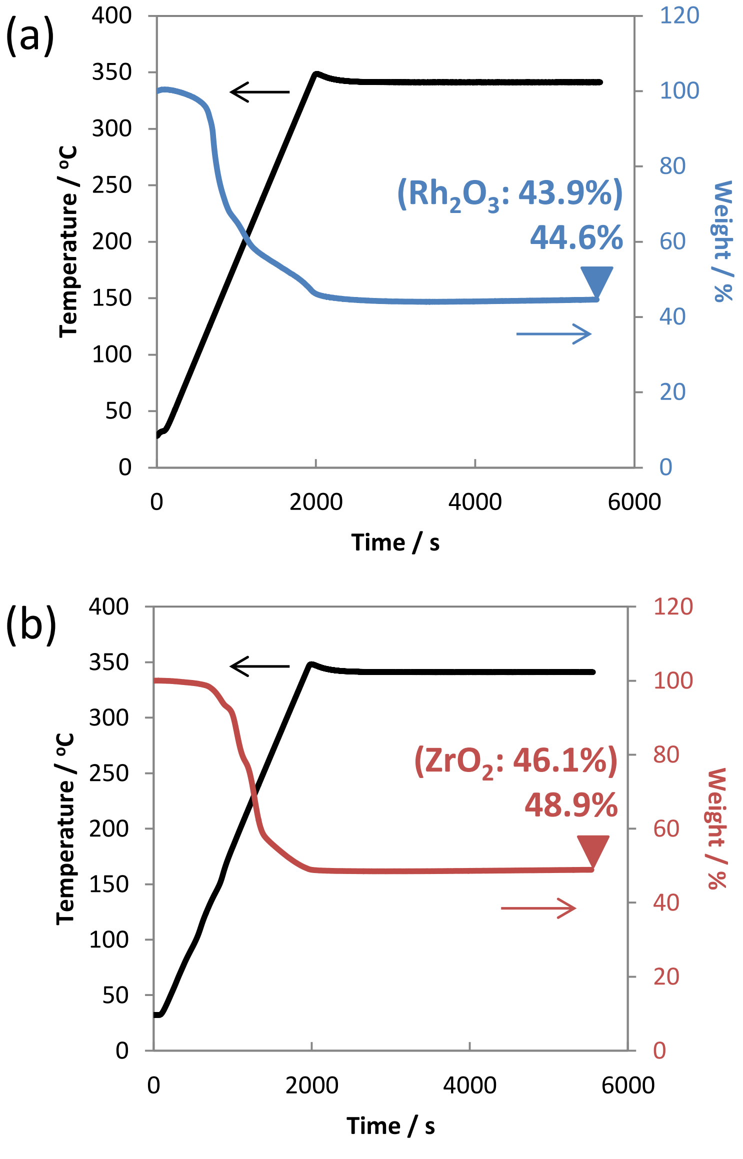

Fig. S8 TG analyses of (a) $Rh(NO_3)_3 \cdot xH_2O$ and (b) $ZrO(NO_3)_2 \cdot 6H_2O$ at the same heating conditions as the co-impregnation.

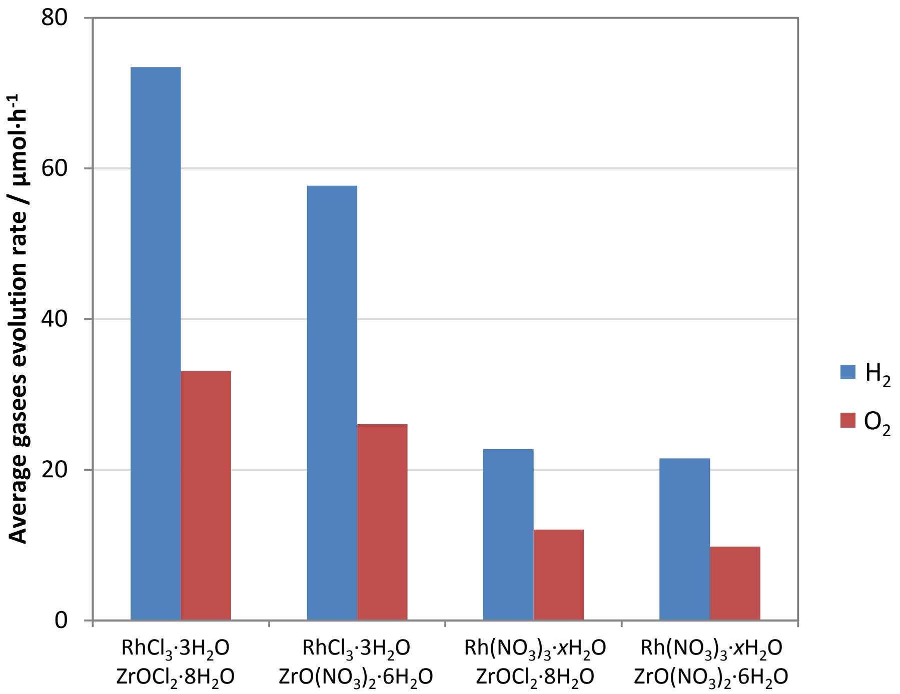

Fig. S9 Average evolution rates of H_2 and O_2 gases over $RhZrO_x/SrTiO_3:Al$ prepared from $RhCl_3·3H_2O$, $Rh(NO_3)_3·xH_2O$, $ZrOCl_2·8H_2O$ and $ZrO(NO_3)_2·6H_2O$. Reaction conditions: catalyst, 10 mg; solution, 20 mL of H_2O; light source, 300 W Xe lamp (λ = 300-450 nm).

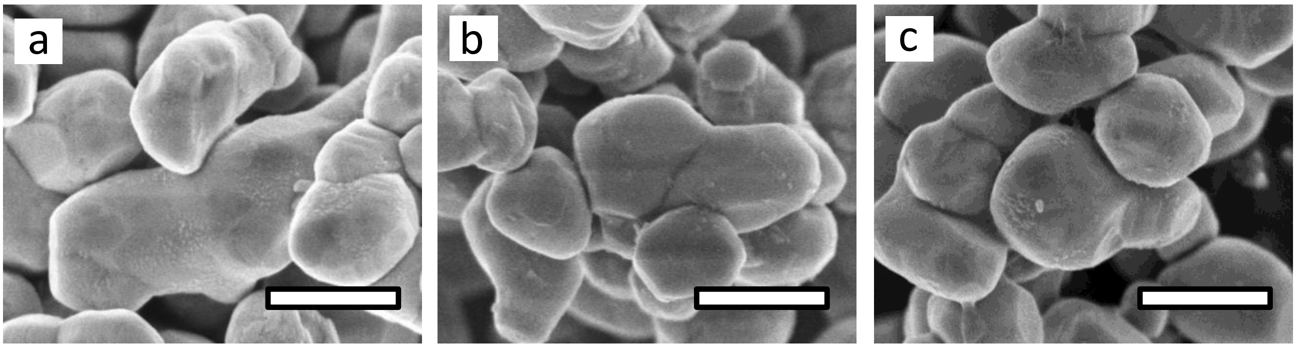

Fig. S10 SEM images of $RhZrO_x/SrTiO_3$:Al prepared from (a) $RhCl_3 \cdot 3H_2O$ and $ZrO(NO_3)_2 \cdot 6H_2O$, (b) $Rh(NO_3)_3 \cdot xH_2O$ and $ZrOCl_2 \cdot 8H_2O$ and (c) $Rh(NO_3)_3 \cdot xH_2O$ and $ZrO(NO_3)_2 \cdot 6H_2O$ (Zr/Rh weight ratio = 5). Scale bars are 500 nm.

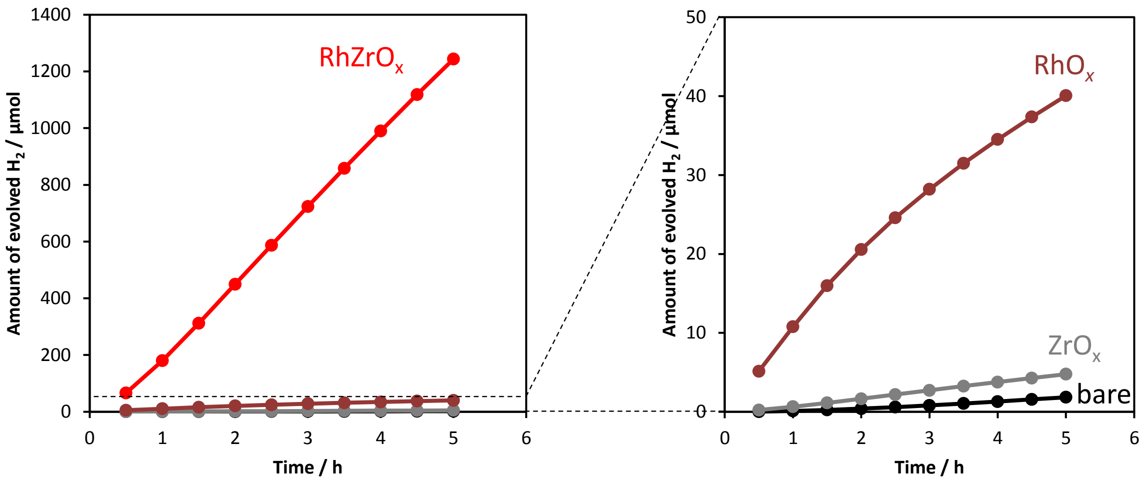

Fig. S11 Photocatalytic activities of $RhO_x/SrTiO_3$:Al (Rh = 0.1 wt% vs. $SrTiO_3$:Al), $ZrO_x/SrTiO_3$:Al (Zr = 0.5 wt% vs. $SrTiO_3$:Al) and $RhZrO_x/SrTiO_3$:Al (Rh = 0.1 wt% and Zr = 0.5 wt% vs. $SrTiO_3$:Al). Reaction conditions: catalyst, 10 mg; solution, 20 mL of H_2O; light source, 300 W Xe lamp (λ = 300-450 nm).

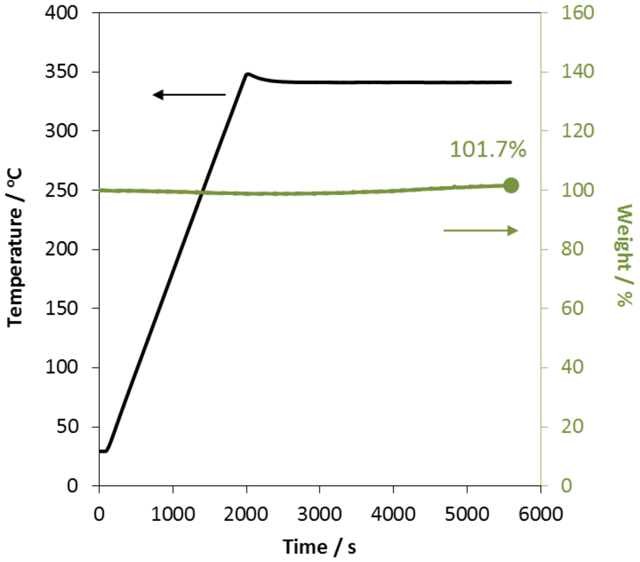

Fig. S12 TG analysis of XC-72 at the same heating conditions as the impregnation.

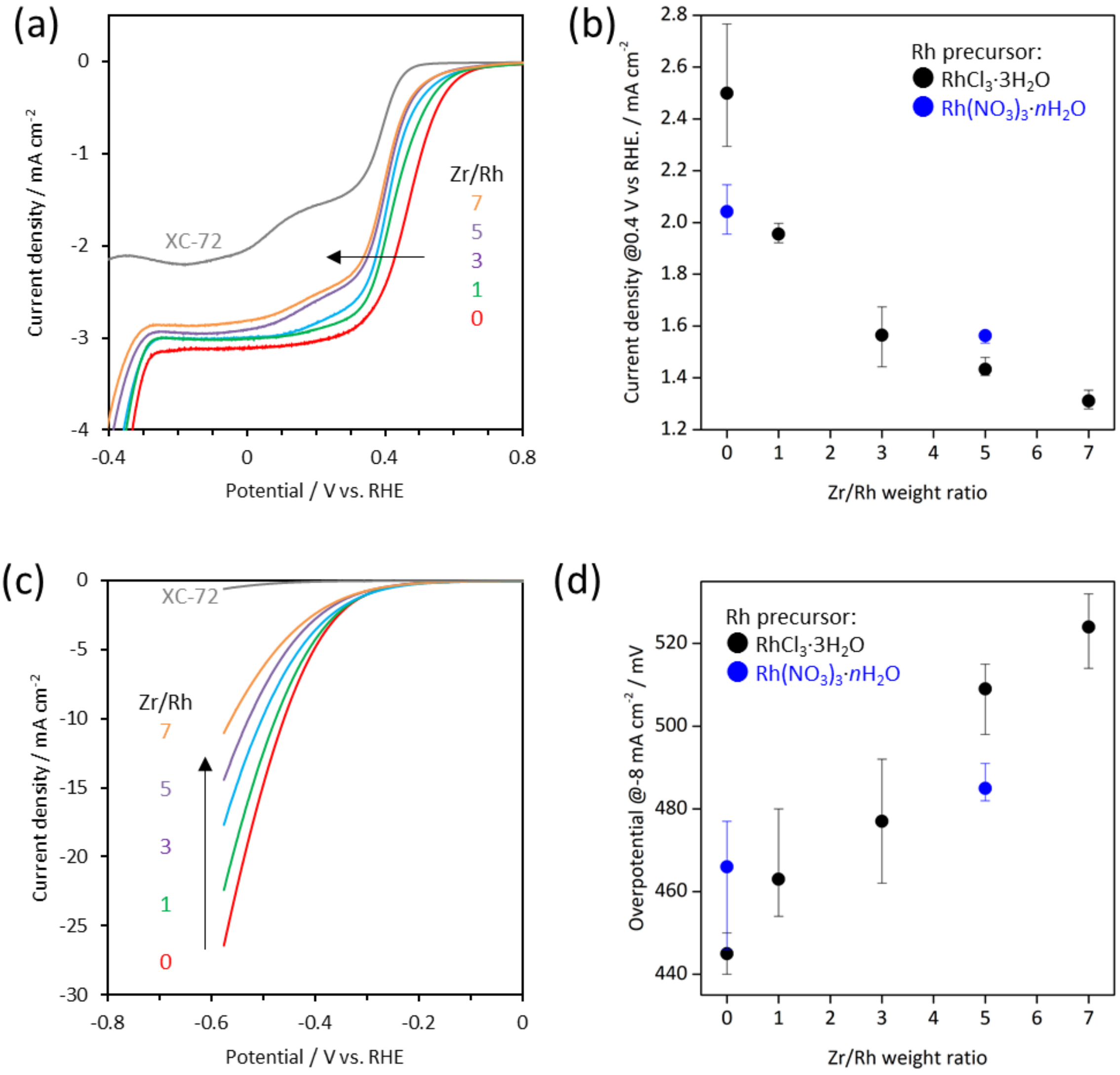

Fig. S13 ORR and HER performance of $RhZrO_x$ cocatalysts on XC-72 with various weight ratios of Zr/Rh. (a) *I-V* curves of $RhZrO_x$ (Zr/Rh: 0–7 w/w%) loaded XC-72 in O_2-saturated 1 M Na_2SO_4. (b) Current density at 0.4 V vs. RHE for each sample. (c) *I-V* curves of $RhZrO_x$ (Zr/Rh: 0–7 w/w%) loaded XC-72 in Ar-saturated 1 M Na_2SO_4. (d) Overpotential of HER at –8 mA·cm^{-2} for each sample. The $RhZrO_x$ prepared from $RhCl_3·3H_2O$ (black dots) and $Rh(NO_3)_3·xH_2O$ (blue dots) are shown as comparison. All scans were conducted at 3600 rpm rotation.

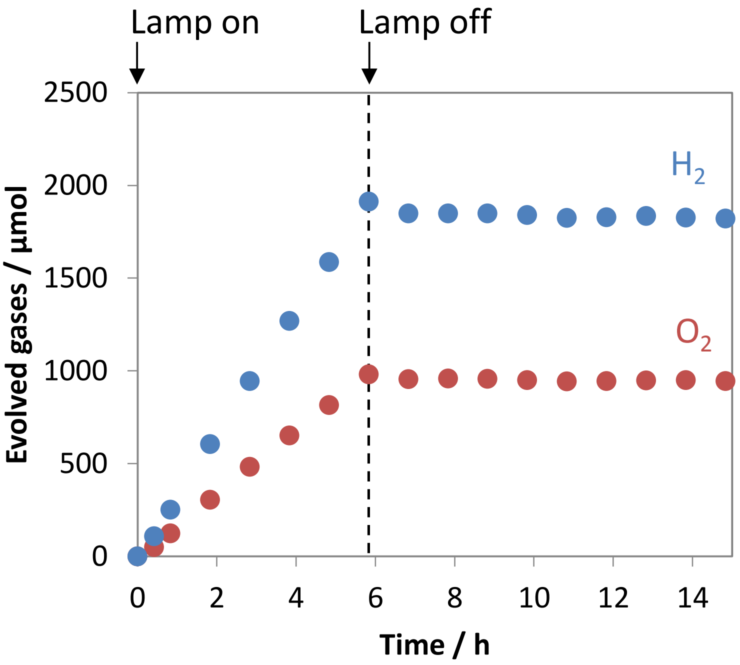

Fig. S14 Time courses of gases evolution over $RhZrO_x/SrTiO_3$:Al (Rh = 0.1 wt% and Zr = 0.5 wt% vs. $SrTiO_3$:Al) during and after light irradiation. Reaction conditions: catalyst, 100 mg; solution, 100 mL of H_2O; light source, 300 W Xe lamp.

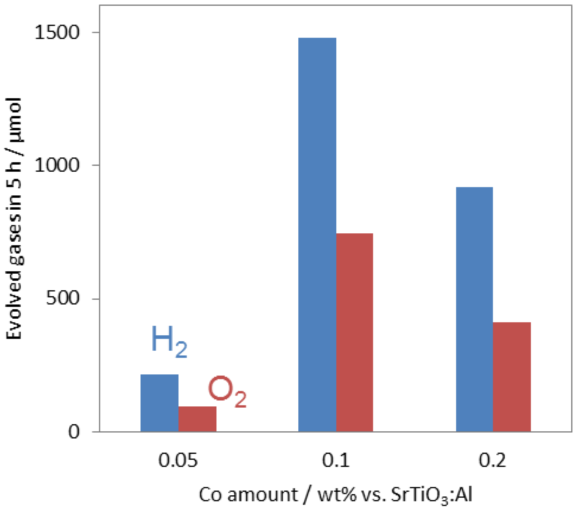

Fig. 15 Photocatalytic activities of (CoO_x+$RhZrO_x$)/$SrTiO_3$:Al with 0.05, 0.1 and 0.2 wt% CoO_x vs $SrTiO_3$:Al. Reaction conditions: catalyst, 10 mg; solution, 20 mL of H_2O; light source, 300 W Xe lamp (λ = 300–450 nm).

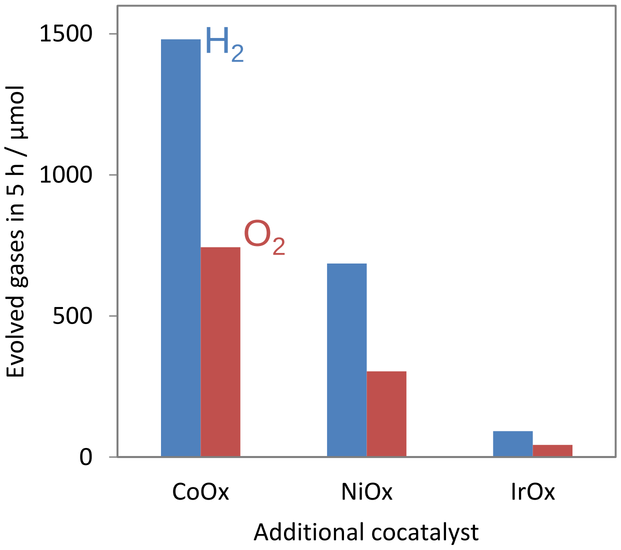

Fig. S16 Photocatalytic activities of $RhZrO_x$/$SrTiO_3$:Al with oxygen evolution cocatalysts (0.1 wt% vs $SrTiO_3$:Al). Reaction conditions: catalyst, 10 mg; solution, 20 mL of H_2O; light source, 300 W Xe lamp (λ = 300–450 nm)

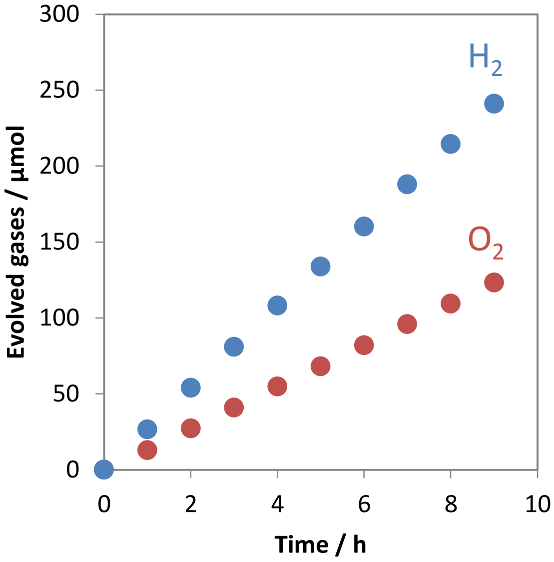

Fig. S17 Time courses of gases evolution of (CoO_x+$RhZrO_x$)/$SrTiO_3$:Al (Co = 0.1 wt%, Rh = 0.1 wt% and Zr = 0.5 wt% vs. $SrTiO_3$:Al) under simulated sunlight.

Table S3 Comparison of AQY of $SrTiO_3$ based photocatalysts

Photocatalyst	Light wavelength (nm)	AQY (%)	Reference
$Rh_{0.5}Cr_{1.5}O_3$/ $SrTiO_3$	350	4.3	H. Kato *et al.* *Catal. Sci. Technol.* 2013, **3**, 1733.
Ni@NiO/$Sr_{1.25}Mg_{0.3}TiO_x$	300–400	9.1	K. Han *et al.* *ChemSusChem* 2017, **10**, 4510.
$Rh_{0.3}Cr_{1.7}O_3$/ $SrTiO_3$:Na	360	16	Y. Sakata *et al.* *Appl. Catal. A Gen.* 2016, **521**, 227.
$Rh_{2-y}C_yO_3$/$SrTiO_3$:Al	360	30	Y. Ham *et al.* *J. Mater. Chem. A* 2016, **4**, 3027.
CoO_x+$RhZrO_x$/$SrTiO_3$:Al	365	33	This work
$RhCrO_x$/$SrTiO_3$:Al	365	56	Y. Goto *et al.* *Joule* 2018, **2**, 509.
MoO_y/$RhCrO_x$/$SrTiO_3$:Al	365	69	T. H. Chiang *et al.* *ACS Catal.* 2018, **4**, 2782.
CoOOH+Rh@Cr_2O_3/$SrTiO_3$:Al	365	91.6	T. Takata *et al*. *Nature* 2020, **581**, 411.