Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information for:

Z-scheme water splitting under visible light irradiation over powdered metal-complex/semiconductor hybrid photocatalysts mediated with reduced graphene oxide

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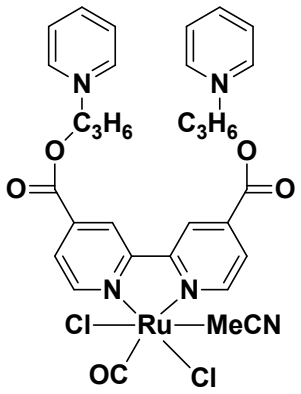
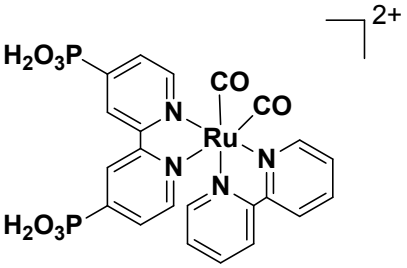


[Ru-pypcbpy]



[Ru-dpbpy]

Fig. S1 Structures of Ru-complexes.

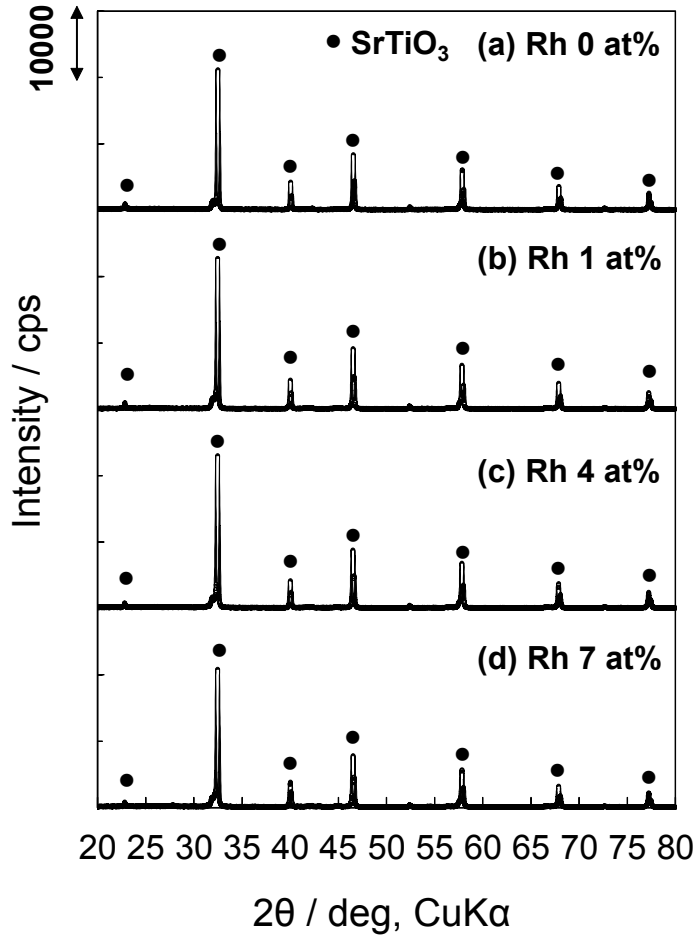


Fig. S2 XRD patterns of $SrTiO_3$:Rh (Rh: *x* at%) powders prepared by solid state reaction.

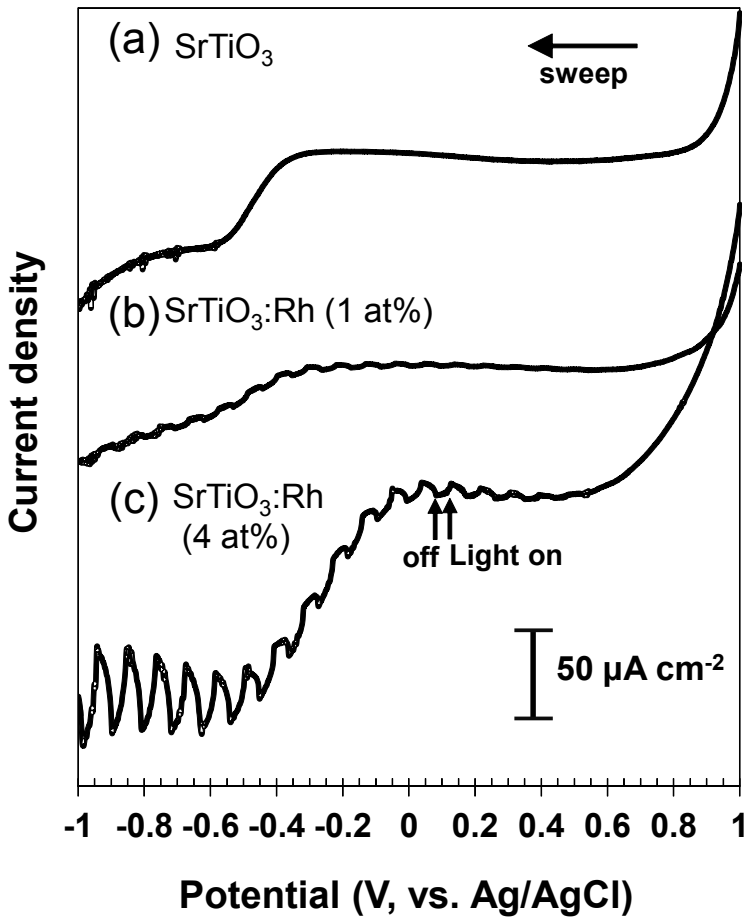


Fig. S3 Current-potential curves for $SrTiO_3$:Rh (x at%) at x = (a) 0, (b) 1, and (c) 4 at%. Electrolyte, 0.2 mol L^{-1} aqueous K_2SO_4 solution; sweep rate, 50 mV s^{-1}; light source, 300 W Xe lamp with an L42 cutoff filter (λ > 420 nm). The $SrTiO_3$:Rh photocatalyst electrodes were prepared by a squeegee method, where a paste composed of 20 mg of $SrTiO_3$:Rh photocatalyst powder, 20 μL of acetylacetone (Wako Pure Chemical Industries, 99%), and 40 μL of distilled water was coated onto a transparent fluorine-doped tin oxide (FTO) electrode and then calcined at 573 K for 2 h in air.

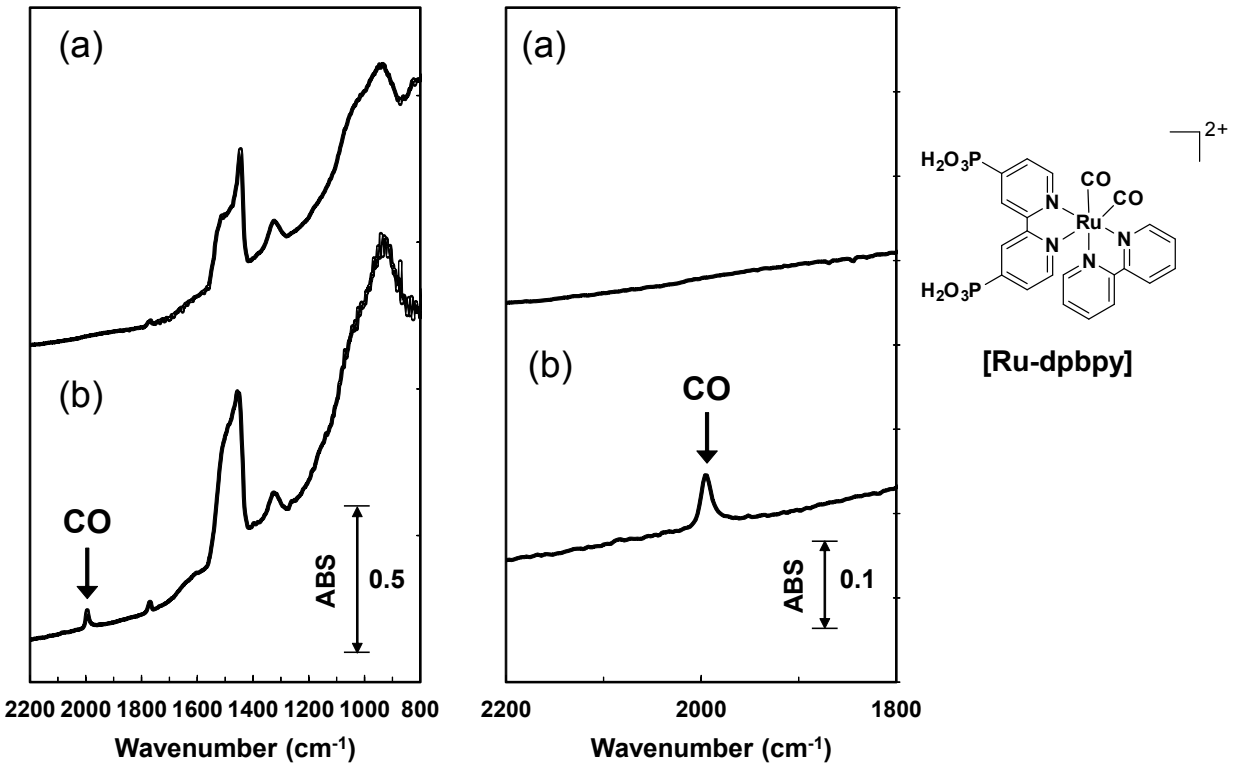


Fig. S4 DRIFTS spectra for (a) $SrTiO_3$:Rh (4 at%) and (b) [Ru-dpbpy]/$SrTiO_3$:Rh (4 at%).

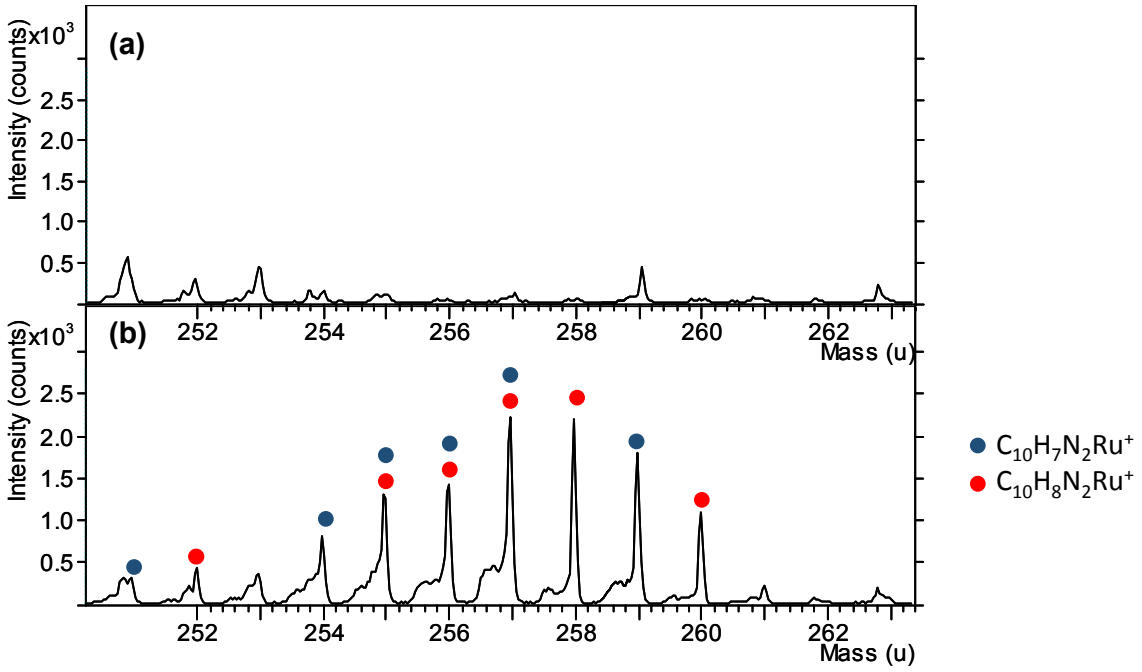


Fig. S5 TOF-SIMS positive spectra for (a) $SrTiO_3$: Rh (4 at%) and (b) [Ru-dpbpy]/$SrTiO_3$: Rh (4 at%).

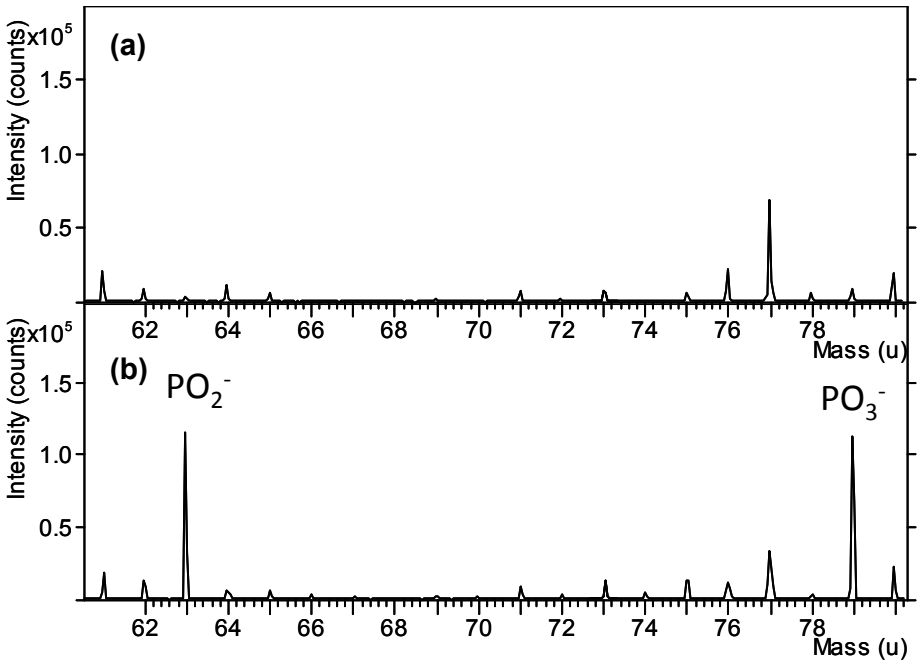


Fig. S6 TOF-SIMS negative spectra for (a) $SrTiO_3$: Rh (4 at%) and (b) [Ru-dpbpy]/$SrTiO_3$:Rh (4 at%).

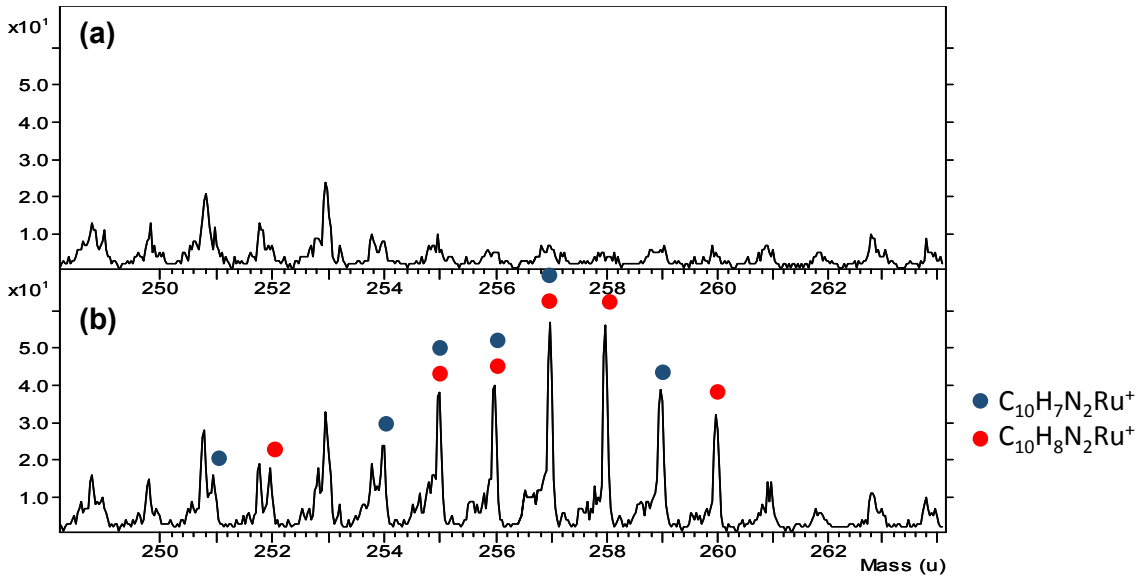


Fig. S7 TOF-SIMS positive spectra after photocatatalytic reaction (18 h) for the (a) ($SrTiO_3$:Rh)-(RGO/$BiVO_4$) and (b) ([Ru-dpbpy]/$SrTiO_3$:Rh)-(RGO/$BiVO_4$) systems. The Rh content of $SrTiO_3$:Rh is 4 at%. Reaction condition: catalysts (8 mg each) in 4 mL Ar-saturated water (pH 3.5 adjusted by H_2SO_4), at ambient temperature. Suspensions were irradiated using a 500 W Xe lamp with filters to produce light in the range of $390 < \lambda \leq 750$ nm.

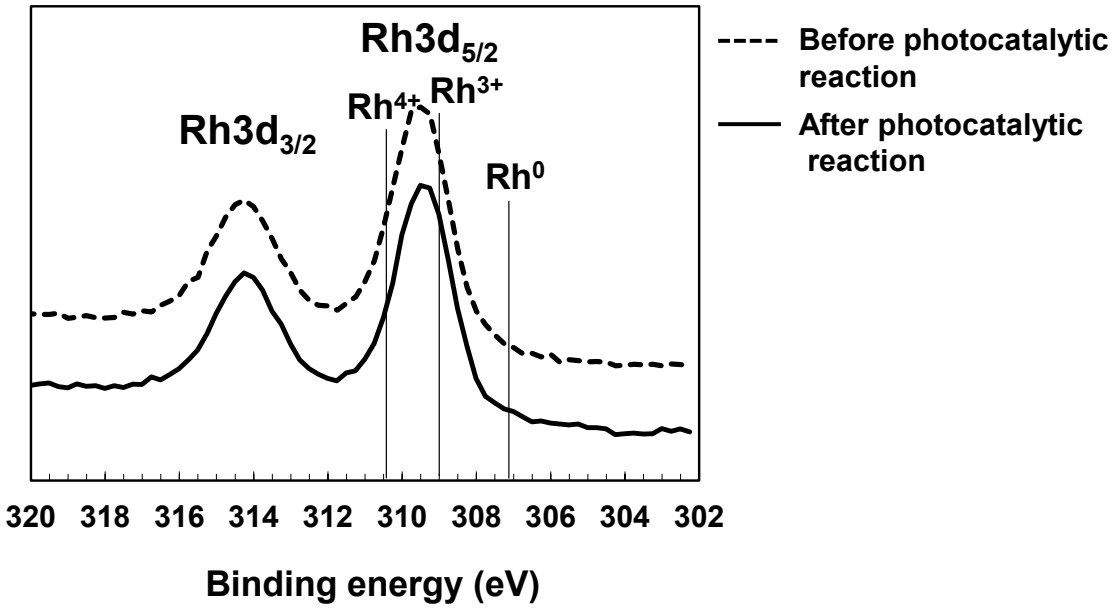


Fig. S8 Rh 3d XPS spectra for (a) before photocatalytic reaction and (b) after photocatalytic reaction for 18 h of ([Ru-dpbpy]/$SrTiO_3$:Rh)-(RGO/$BiVO_4$) system. The Rh content of $SrTiO_3$:Rh is 4 at%. Reaction condition: catalysts (8 mg each) in 4 ml Ar-saturated water (pH 3.5 adjusted by H_2SO_4), at ambient temperature. Suspensions were irradiated using a 500 W Xe lamp with filters to produce light in the range $390 < \lambda \leq 750$ nm filter.

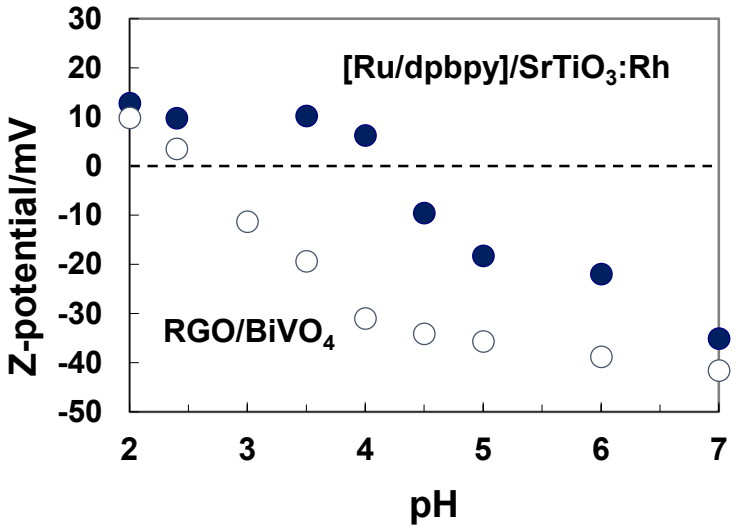


Fig. S9 Z-potential of [Ru-dpbpy]/$SrTiO_3$:Rh (4 at%, closed mark) and RGO/$BiVO_4$ (open mark) powder suspended in an aqueous solution.
Z-potential measurements were conducted using Zeta potential analyzer (MICROTEC ZEECOM ZC-2000).

Table S1 Photocatalytic activity under visible light irradiation of the ([Ru-dpbpy]/$SrTiO_3$:Rh <4 at%>)-(RGO/$BiVO_4$) system in a aqueous solution. [a]

entry	pH	Z-potential (mV)		amount of H_2 evolved/μmol
		[Ru-dpbpy]/$SrTiO_3$:Rh	(RGO/$BiVO_4$)	
1	2.4	+ 9.8	+ 3.5	0.24
2	3.5	+10.2	-19.3	3.14
3	4.0	+6.3	-31.0	3.00
4	7.0	-35.0	-41.5	1.59

[a] Reaction condition: catalysts (8 mg each) in 4 ml Ar-saturated aqueous solution (various pH) in a Pyrex glass test tube, at ambient temperature. pH adjusted with H_2SO_4 and NaOH. Solutions ware irradiated using a 500 W Xe lamp with filters to produce light in the range $390 < \lambda \leq 750$ nm filter 18 h. Hydrogen concentration was determined by gas chromatography.

Table S2 Photocatalytic H_2 evolution by water splitting under visible light irradiation over the (Ru-complex/$SrTiO_3$:Rh)-(RGO/$BiVO_4$) system.[a]

amount of doped Rh (at%)	[Ru-dpbpy][b] (0.18-0.19 wt%)	Amount of H_2 evolved (μmol)
0	×	0.00
0	○	0.00
0.5	×	0.01
0.5	○	0.79
1	×	0.02
1	○	1.83
4	×	0.42
4	○	3.06
7	×	0.75
7	○	2.82

[a] Reaction condition: catalysts (8 mg each) in 4 ml Ar-saturated water (pH3.5 adjusted by H_2SO_4), at ambient temperature. Suspensions were irradiated using a 500 W Xe lamp with filters to produce light in the range $390 < \lambda \leq 750$ nm filter 18 h.

[b] [Ru (4,4'-diphosphonate-2,2'-bipyridine)(2,2'-bipyridine)$(CO)_2$]$^{2+}$

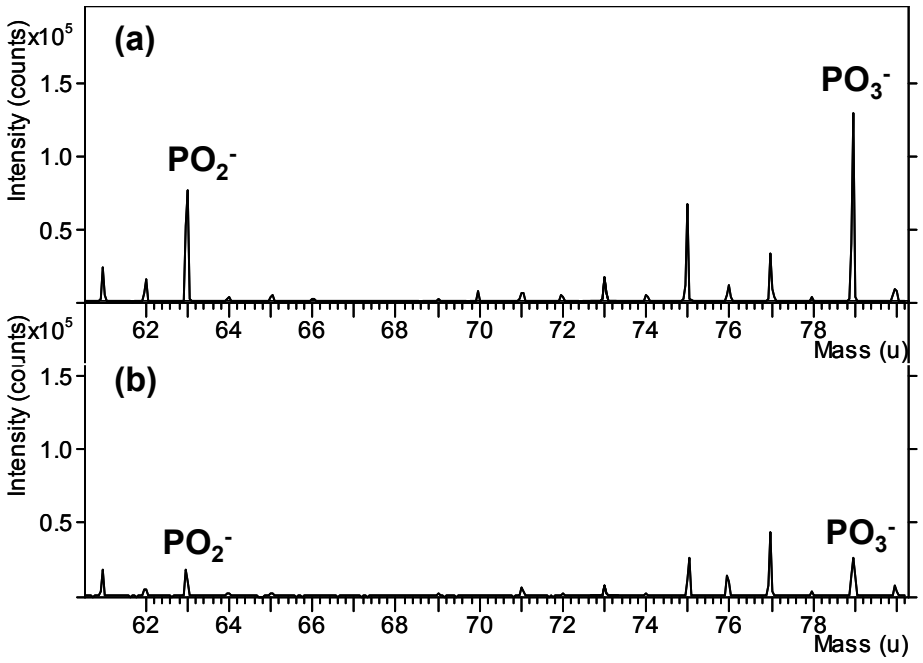


Fig. S10 TOF-SIMS negative spectra (a) before photoirradiation and (b) after photoirradiation (16 h) of the ([Ru-dpbpy]/$SrTiO_3$:Rh)–(RGO/$BiVO_4$) in a gas closed-circulation system. The Rh content of $SrTiO_3$:Rh is 4 at%. Reaction Conditions: catalysts (50 mg each) in water (pH 3.5 adjusted by H_2SO_4, 120 ml), λ > 420 nm (300 W Xe lamp), top-irradiation cell with a Pyrex glass window.

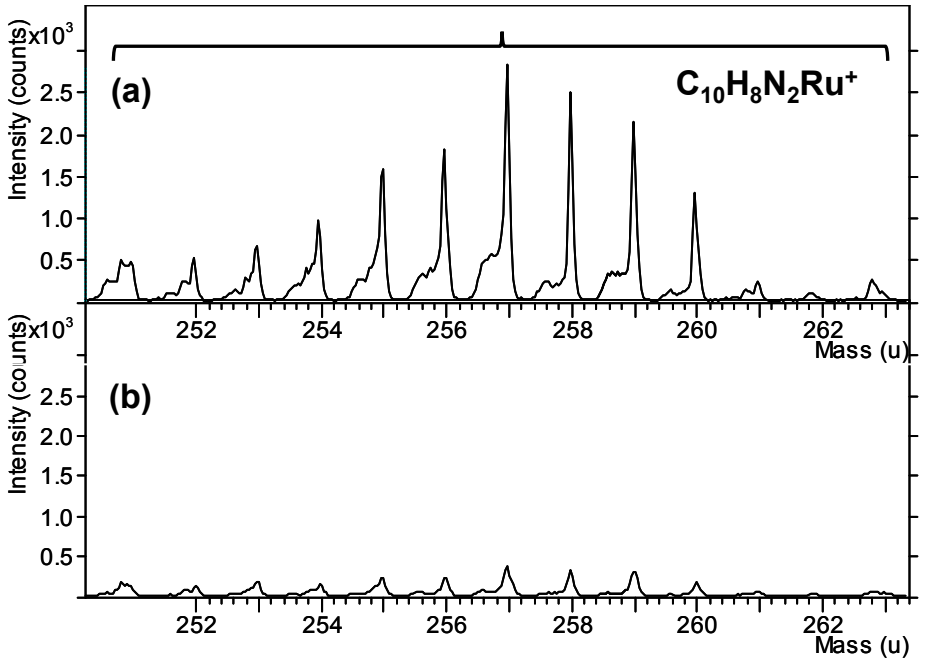


Fig. S11 TOF-SIMS positive spectra (a) before photoirradiation and (b) after photoirradiation (16 h) over the ([Ru-dpbpy]/$SrTiO_3$:Rh)–(RGO/$BiVO_4$) in a gas closed-circulation system. The Rh content of $SrTiO_3$:Rh is 4 at%. Reaction Conditions: catalysts (50 mg each) in water (pH 3.5 adjusted by H_2SO_4, 120 ml), λ > 420 nm (300 W Xe lamp), top-irradiation cell with a Pyrex glass

window.