

## Supporting information

### **Highly crystalline $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ of a photocatalyst valence-band-controlled with Bi(III) for solar water splitting**

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## Experimental

### Characterization

The crystal structure of the synthesized  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  was identified by powder X-ray diffraction (Rigaku; MiniFlex600). The surface areas (S.A.) were determined by a BET measurement (Coulter; SA3100). Morphologies of the  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  particles were observed with scanning electron microscope (JEOL; JSM-7400F). Diffuse reflectance spectra (DRS) were measured using UV-vis-NIR spectrometer with an integrating sphere (Jasco; UbeatV-570) and were converted from reflectance to absorbance mode by the Kubelka-Munk method. The elemental composition of obtained  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  was measured with an X-ray fluorescence spectrometer (Rigaku; NEX DE). Chemical states of cocatalysts and photocatalysts were investigated with X-ray photoelectron spectroscopy (XPS) (JEOL; JPS-9010MC).

### Photocatalytic reaction

Photocatalytic water splitting was carried out in a gas-closed-circulation system. Photocatalyst powder (0.3 g) was dispersed in distilled water (120 mL) in a top-irradiation cell with a Pyrex window. A 300 W Xe-arc lamp (PerkinElmer; Cermax-PE300BF) and a solar simulator (Asahi spectra; HAL-320) were employed as a light source. Amounts of evolved  $\text{H}_2$  and  $\text{O}_2$  gasses were determined with a gas chromatograph (Shimadzu; GC-8A, MS-5A, Ar carrier gas, TCD detector).

Apparent quantum yields (AQY) were measured using a 300 W Xe-arc lamp (PerkinElmer; Cermax-PE300BF) with band-pass filters. The photon flux of the monochromatic light was measured using a silicon photodiode head (OPHIR; PD300-UV head and NOVA display). An AQY and a solar to hydrogen energy conversion efficiency (STH) were estimated using the following equations (1) and (2).

$$\begin{aligned} [\text{AQY} \ %] &= [\text{the number of reacted electrons or holes}]/[\text{the number of incident photons}] \times 100 \\ &= [(\text{the number of evolved } \text{H}_2 \text{ molecules}) \times 2]/[\text{the number of incident photons}] \times 100 \end{aligned} \quad (1)$$

$$\begin{aligned} [\text{STH} \ %] &= [(\Delta G^0(\text{H}_2\text{O})/\text{kJ mol}^{-1}) \times [\text{rate of } \text{H}_2 \text{ evolution}/\mu\text{mol h}^{-1}]] \\ &\quad /([\text{irradiation time/s}] \times [\text{solar energy (AM-1.5 G)/mW cm}^{-2}] \times [\text{irradiation area/cm}^2]) \times 100 \\ &= (237 \times [\text{rate of } \text{H}_2 \text{ evolution}/\mu\text{mol h}^{-1}])/(3600 \times 100 \times 25) \times 100 \end{aligned} \quad (2)$$

### Loading cocatalyst

$\text{RhCr}_2\text{O}_x$  and  $\text{CoOOH}$  cocatalysts were simultaneously loaded *in situ* by a photodeposition (PD) method using aqueous solutions of  $\text{Rh}(\text{NO}_3)_3$  (Kanto Chemical; > 80.0% as anhydrous),  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Kanto Chemical; 98.0~103.0%) and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Wako Pure Chemical; 99.5%), according to previous reports.<sup>1-4</sup> An added amount of a cocatalyst was calculated as a molar ratio (mol%) of a cocatalyst to  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ .

**Table S1** Lattice constants and M-O-M (M = Ti, Ta) bond angles of AgTaO<sub>3</sub>, Na<sub>0.5</sub>Bi<sub>0.5</sub>TaO<sub>3</sub> and Na<sub>0.5</sub>La<sub>0.5</sub>TaO<sub>3</sub> with trigonal crystal systems.

Material	Lattice constants				M-O-M bond angle / °
	a,b / Å	c / Å	$\alpha, \beta$ / °	$\gamma$ / °	
<sup>a</sup> AgTaO <sub>3</sub>	5.5281	13.7159	90	120	164
<sup>b</sup> Na <sub>0.5</sub> Bi <sub>0.5</sub> TaO <sub>3</sub>	5.4779	13.485	90	120	165
<sup>c</sup> Na <sub>0.5</sub> La <sub>0.5</sub> TaO <sub>3</sub>	5.4839	13.4183	90	120	168

<sup>a</sup>ICSD 40830, <sup>b</sup>ICSD 193813, <sup>c</sup>ICSD 245626.

**Table S2** Elemental composition determined by an XRF of Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub> synthesized by SSR and FM at various temperature

Synthesis condition		Molar ratio of Bi/Ti
Method	Temperature/K	
SSR	1173	0.45
SSR	1273	0.46
SSR	1373	0.46
FM	1173	0.42
FM	1273	0.43
FM	1373	0.42
FM	1473	0.46

**Table S3** Photocatalytic overall water splitting over  $\text{Na}_{0.5}\text{La}_{0.5-x}\text{Bi}_x\text{TiO}_3$  synthesized by a flux method at 1273 K for 5 h under UV irradiation

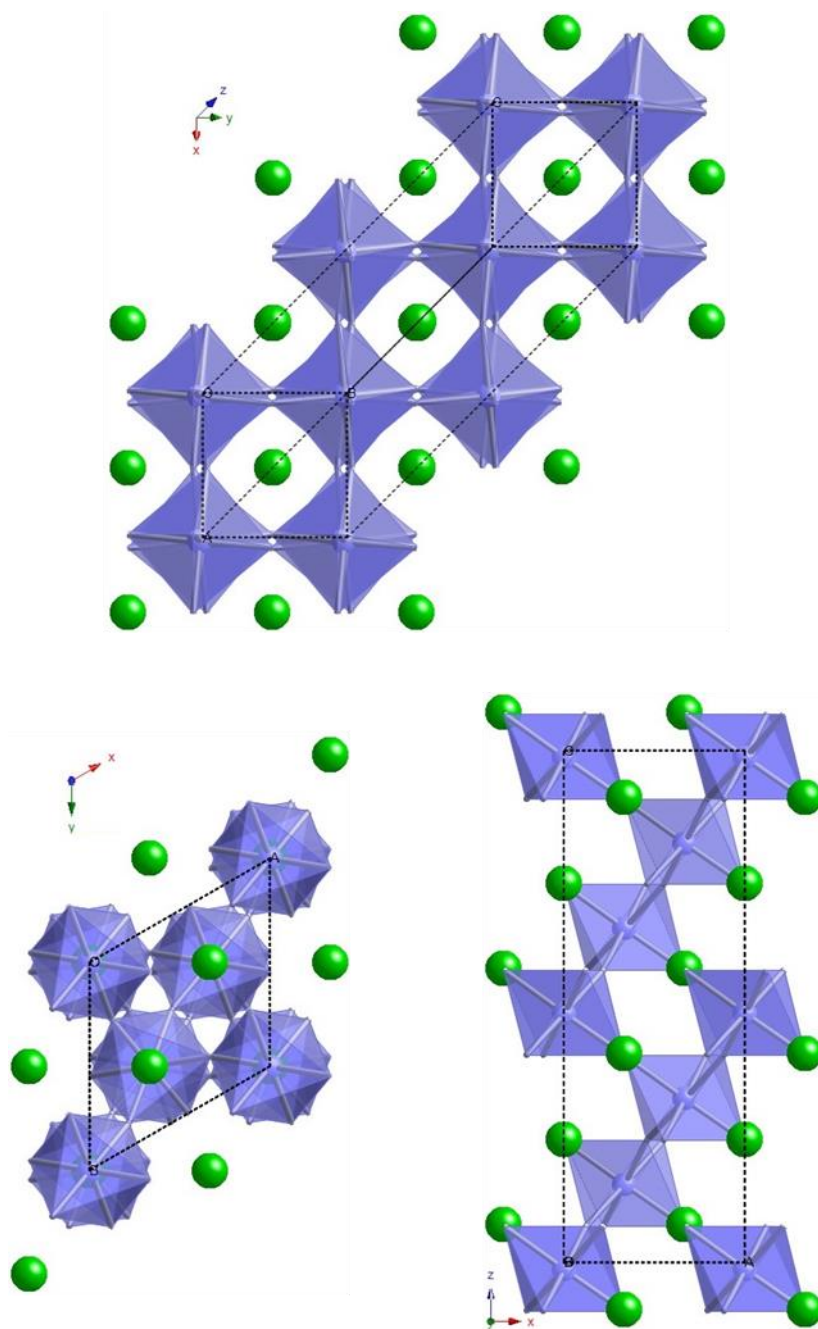
Photocatalyst	Cocatalyst(mol%)	Activity/ $\mu\text{mol h}^{-1}$	
		H <sub>2</sub>	O <sub>2</sub>
$\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$	–	Trace	0
$\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$	$\text{RhCr}_2\text{O}_x(0.05)$	122	59
$\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$	$\text{RhCr}_2\text{O}_x(0.75)$	126	60
$\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$	$\text{RhCr}_2\text{O}_x(0.1)$	131	63
$\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$	$\text{RhCr}_2\text{O}_x(0.1) + \text{CoOOH}(0.01)$	150	71
$\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$	$\text{RhCr}_2\text{O}_x(0.1) + \text{CoOOH}(0.02)$	160	77
$\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$	$\text{RhCr}_2\text{O}_x(0.1) + \text{CoOOH}(0.025)$	153	73
$\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$	$\text{RhCr}_2\text{O}_x(0.1) + \text{CoOOH}(0.05)$	142	67
$\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$	$\text{RhCr}_2\text{O}_x(0.1) + \text{CoOOH}(0.1)$	140	67
$\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$	$\text{RhCr}_2\text{O}_x(0.2)$	102	50
$\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$	$\text{RhCr}_2\text{O}_x(0.3)$	113*	53*
$\text{Na}_{0.5}\text{La}_{0.25}\text{Bi}_{0.25}\text{TiO}_3$	$\text{RhCr}_2\text{O}_x(0.1) + \text{CoOOH}(0.02)$	20	9.7
$\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$	$\text{RhCr}_2\text{O}_x(0.1) + \text{CoOOH}(0.02)$	14	6.8

Photocatalyst: 0.3 g, cocatalyst: PD (*in situ*),

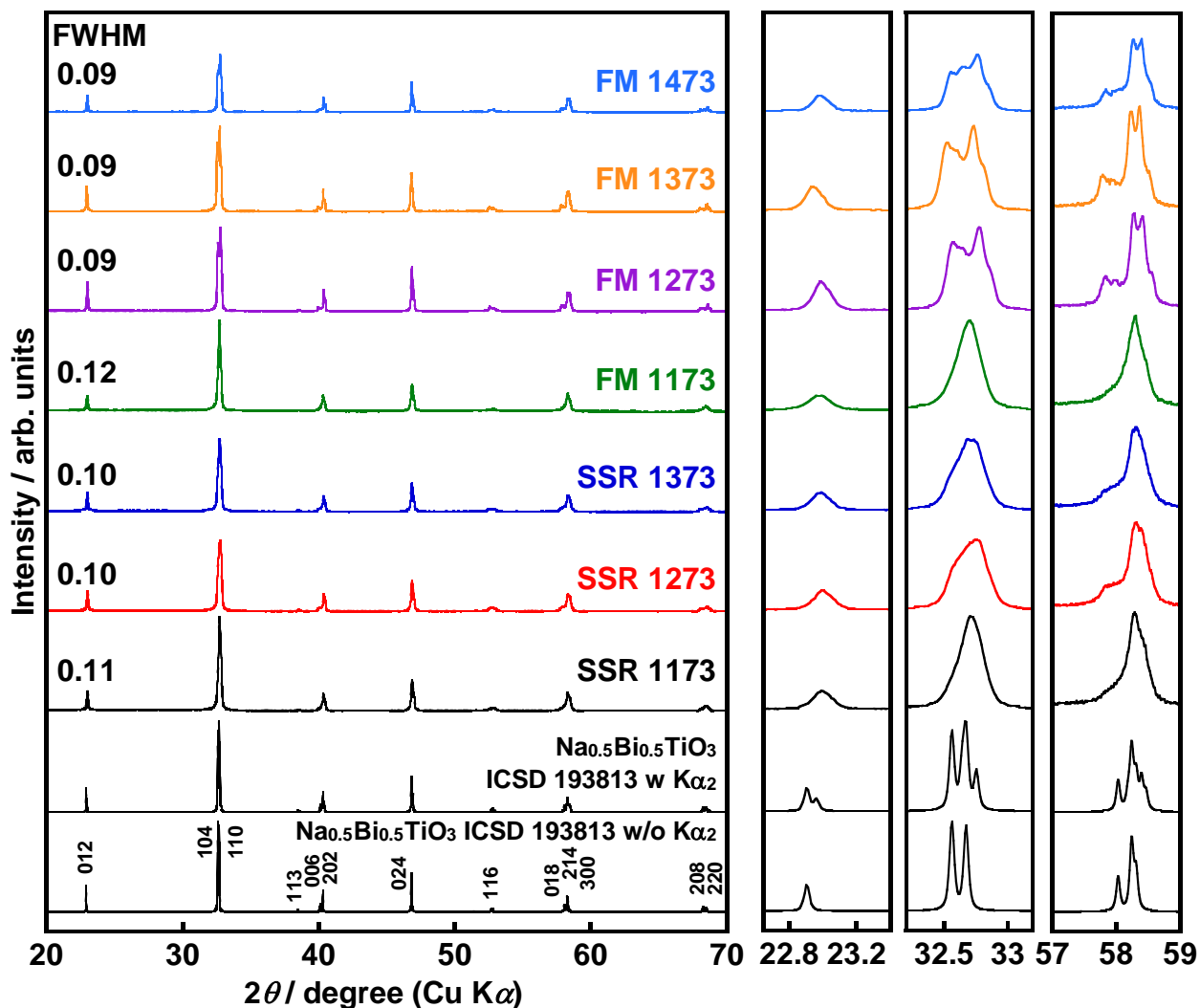
reactant solution: distilled water (120 mL), cell: top-irradiation cell with a Pyrex window, light source: 300 W Xe-arc lamp ( $\lambda > 300$  nm). \*The activities were not stable.

**Table S4** Photon flux of incident light and rates of gas evolutions on AQY measurements for photocatalytic water splitting over  $\text{RhCr}_2\text{O}_x(0.1\text{mol}\%)/\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3/\text{CoOOH}(0.02\text{mol}\%)$

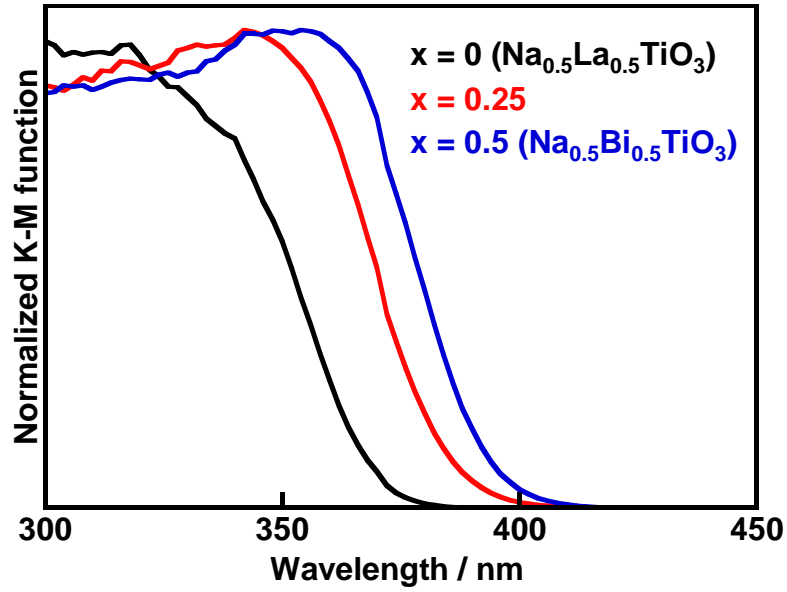
Incident light / nm	Photon flux / mW	Photon number / h	Activity / $\mu\text{mol h}^{-1}$		AQY %
			H <sub>2</sub>	O <sub>2</sub>	
440	28.9	$4.65 \times 10^{32}$	0	0	0
420	76.5	$5.82 \times 10^{32}$	0.2	0.1	0.041
400	86.6	$6.28 \times 10^{32}$	4.2	1.9	0.77
380	29.7	$2.05 \times 10^{32}$	5.4	2.5	3.0
370	71.3	$4.78 \times 10^{32}$	14	6.9	3.5
360	64.8	$4.23 \times 10^{32}$	14	6.6	4.0
350	74.6	$4.73 \times 10^{32}$	21	10	5.1
340	50.3	$3.10 \times 10^{32}$	12	5.8	4.7
320	5.88	$3.41 \times 10^{31}$	1.2	0.5	3.5



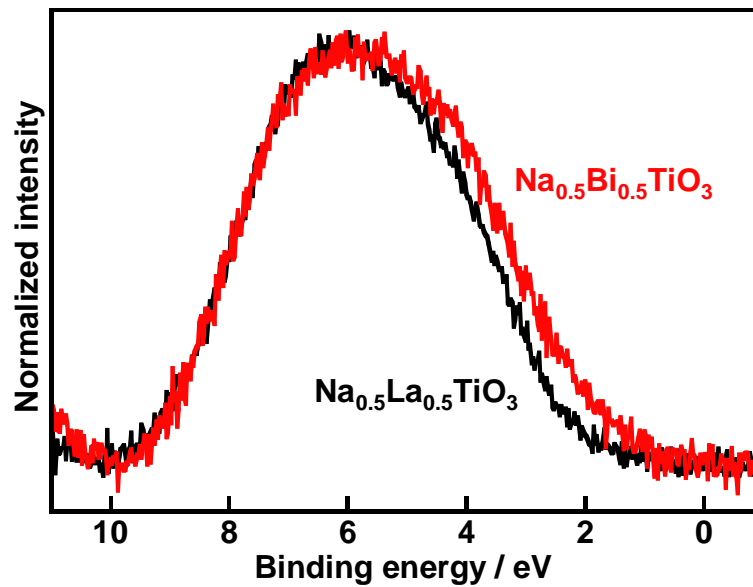
**Fig. S1** Crystal structure of trigonal  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  (ICSD 193813).



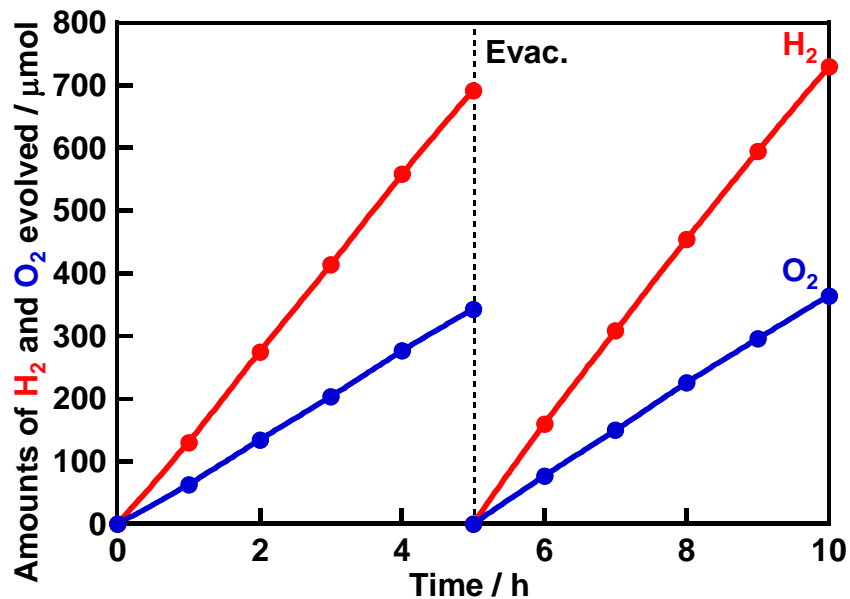
**Fig. S2** XRD patterns of ICSD Collection Code 193813 (trigonal Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub>) with/without peaks due to K $\alpha$ <sub>2</sub> and Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub> synthesized by a solid state reaction and a flux method at various calcination temperatures. Peaks due to K $\alpha$ <sub>2</sub> in the measured XRD patterns were not removed. The intensity of patterns in right side figure were enlarged 5 times. Plane indices for Na<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub> were referred to PDF No. 1-74-9525.



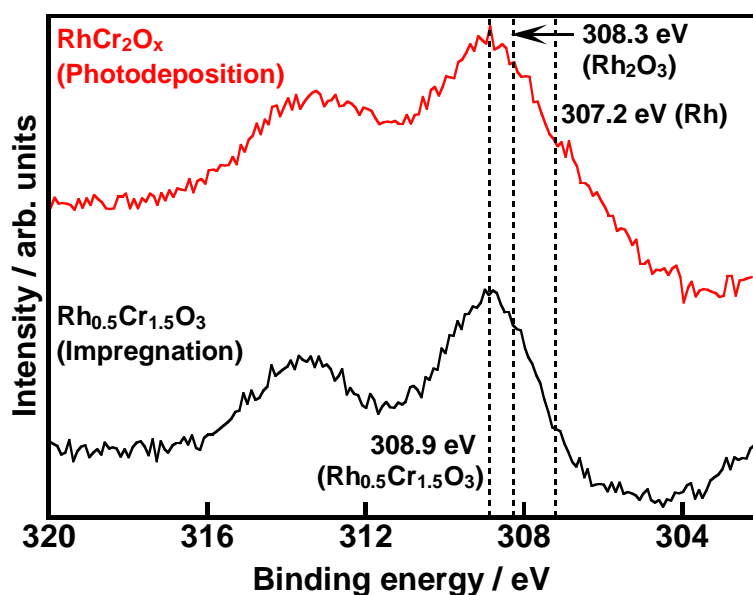
**Fig. S3** Diffuse reflectance spectra of  $\text{Na}_{0.5}\text{La}_{0.5-x}\text{Bi}_x\text{TiO}_3$  ( $x = 0, 0.25, 0.5$ ) synthesized by a flux method at 1273 K for 5 h.



**Fig. S4** XPS spectra at valence band regions of  $\text{Na}_{0.5}\text{M}_{0.5}\text{TiO}_3$  ( $\text{M} = \text{La}, \text{Bi}$ ) synthesized by a flux method at 1273 K for 5 h. Binding energies were corrected with  $\text{Ti}2p_{3/2}$  peaks (458.7 eV). Backgrounds of the spectra were subtracted by the Shirley method.



**Fig. S5** Photocatalytic overall water splitting over  $\text{RhCr}_2\text{O}_x(0.1\text{mol}\%)/\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3/\text{CoOOH}(0.02\text{mol}\%)$  under UV irradiation.  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  was synthesized by FM at 1273 K. Photocatalyst: 0.3 g, cocatalyst: PD (*in situ*), reactant solution: distilled water (120 mL), cell: top-irradiation cell with a Pyrex window, light source: 300 W Xe-arc lamp ( $\lambda > 300$  nm).



**Fig. S6** Rh 3d X-ray photoelectron spectra of  $\text{RhCr}_2\text{O}_x(0.1\text{mol}\%)/\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3/\text{CoOOH}(0.02\text{mol}\%)$  loaded by PD (*in situ*, after the reaction seen in Fig. S5) and  $\text{Rh}_{0.5}\text{Cr}_{1.5}\text{O}_3(0.2\text{mol}\%)/\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  loaded by an impregnation method at 625 K for 1 h.  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  was synthesized by FM at 1273 K. Binding energies of all peaks were corrected with C 1s (284.2 eV). All assigned binding energies for Rh,  $\text{Rh}_2\text{O}_3$  and  $\text{Rh}_{0.5}\text{Cr}_{1.5}\text{O}_3$  were referred to a previous report.<sup>5,6</sup>



## References

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