Supporting information

Visible light responsive rhodium and antimony-codoped SrTiO₃ powdered photocatalyst loaded with IrO₂ cocatalyst for solar water splitting

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Experimental details

Preparation of SrTiO₃ doped with Rh and Sb photocatalyst

SrTiO₃ powder codoped with Rh (0.5 mol%) and Sb (1.0 mol%) was prepared by a simple solid-state reaction. The starting materials of SrCO₃ (Kanto Chemical; 99.9%), TiO₂ (Soekawa Chemical; 99.9%), Rh₂O₃ (Wako Pure Chemical; 99.9%), and Sb₂O₃ (Nacalai Tesque; 98%) were mixed using an alumina mortar in a molar ratio of Sr:Ti:Rh:Sb = 1.03:0.985:0.005:0.01. The mixture was calcined at 1373 K for 10 h after precalcination at 1173 K for 1 h in air using an alumina crucible. Crystal phases of obtained powders were confirmed by X-ray diffraction (Rigaku;MiniFlex, Cu Ka). Diffuse reflection spectra were obtained by a UV-vis-NIR spectrometer (Jasco; UbsetV-570) and were converted from reflectance to absorbance by the Kubelka-Munk method.

Loading of cocatalyst

 IrO_2 , RuO_2 , and CoO_x cocatalysts were loaded by an impregnation method. $SrTiO_3$:Rh,Sb (0.5 g) and desired amounts of aqueous solutions of $(NH_4)_2IrCl_6$ and $Co(NO_3)_2$, and acetone solution of $Ru_3(CO)_{12}$ were added into a porcelain crucible and heated in air to remove the solvents. The resulting powder was calcined in air at 673 K for 2 h. IrO_2 cocatalyst was loaded also by photodeposition¹ and colloidal adsorption methods.² Ru cocatalyst was loaded by a

photodeposition method in which SrTiO₃:Rh,Sb dispersed in an aqueous methanol solution containing RuCl₃ was irradiated with visible light (λ >420 nm).

Photocatalytic reaction

Photocatalytic activities were evaluated by sacrificial H_2 and O_2 evolution, and water splitting using a gas-tight circulation system and an Ar flow system. An aqueous methanol solution (10 vol%) and an aqueous silver nitrate (0.2 mol L⁻¹) solution were employed for sacrificial H_2 and O_2 evolution, respectively. Water and a pH-controlled aqueous $H_2SO_{4 aq.}$ solution were used for water splitting. The photocatalyst powder (0.1-0.5 g) was dispersed by a magnetic stirrer in the reactant solution (120-600 mL) in a top-irradiation cell and an inner-irradiation cell. 300 W Xe lamp (Perkin-Elmer; CERMAX-PE300F) was used for an top-irradiation cell. The wavelength of the incident light was controlled with cutoff filters (HOYA; L42, Y44). When 400 W high pressure lamp was employed for an inner irradiation cell, an aqueous (2 mmol L⁻¹) filter of NaNO₂ was used to control the wavelength of the incident light (λ > 400 nm).³ A solar simulator with an AM-1.5 filter (YAMASHITA DENSO; YSS-80QA) was used for solar water splitting. The temperature of the reactant solution was kept at 293 K by circulating cooling water. Amounts of evolved H₂ and O₂ were determined using an online gas chromatograph (Shimadzu; GC-8A, MS-5A column, TCD, Ar carrier).

An apparent quantum yield and a solar energy conversion efficiency were defined by the following equations.

AQY(%) = (Number of reacted electrons / Number of incident photons) x 100Solar energy conversion(%) = (Output energy as H₂ / Energy of incident solar light(100 mW/cm²)) x 100

The photon flux of the monochromatic light was measured by a silicon photodiode (OPHIR; PD300-UV SH head and NOVA display).

References

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Table S1. Water splitting under visible light irradiation over SrTiO3:Rh(0.5%),Sb(1.0%)photocatalyst

En	Photocatalyst	Cocatalyst	Loading	Incident	Activity	
try		(wt%)	method	light	/ μ mol h ⁻¹	
					H_2	O ₂
1	SrTiO ₃ :Rh(0.5%),Sb(1.0%)	_	_	>440 nm	trace	0
2	SrTiO ₃ :Rh(0.5%),Sb(1.0%)	$CoO_x(1.0)$	Impregnation	> 440 nm	trace	trace
3	SrTiO ₃ :Rh(0.5%),Sb(1.0%)	RuO ₂ (1.0)	Impregnation	> 440 nm	0.12	0.07
4	SrTiO ₃ :Rh(0.5%),Sb(1.0%)	Ru(0.5)	Photodeposition	> 440 nm	0.50	0.28
5	SrTiO ₃ :Rh(0.5%),Sb(1.0%)	IrO ₂ (1.0)	Impregnation	> 440 nm	3.7	1.8
6	SrTiO ₃ :Rh(0.5%),Sb(1.0%)	IrO ₂ (3.0)	Impregnation	> 440 nm	4.4	1.9
7	SrTiO ₃ :Rh(0.5%),Sb(1.0%)	IrO ₂ (3.0)	Impregnation	> 300 nm	12	6.3
8	SrTiO ₃ : Rh(0.5%)	IrO ₂ (3.0)	Impregnation	> 440 nm	0.63	0
9	SrTiO ₃ :Rh(0.5%)	IrO ₂ (3.0)	Impregnation	> 300 nm	0.73	0
10	SrTiO ₃ :Sb(1.0%)	IrO ₂ (3.0)	Impregnation	> 300 nm	trace	0
11	SrTiO ₃	IrO ₂ (3.0)	Impregnation	> 300 nm	trace	0

Catalyst: 0.2 g, reactant solution: 120 mL of $H_2SO_{4 aq.}$ (pH 3.0), cell: top-irradiation cell with Pyrex window, light source: 300 W Xe lamp.



Figure S1 X-ray diffraction patterns of (a) non-doped $SrTiO_3$, (b) $SrTiO_3$:Rh(0.5%), (c) $SrTiO_3$:Rh(0.5%),Sb(1.0%), (d) $SrTiO_3$:Rh(0.5%),Sb(2.0%), and (e) the mixture of samples (b) and (d).



Figure S2 Raman spectra of (a) non-doped SrTiO₃ and (b) SrTiO₃:Rh(0.5%),Sb(1.0%). Excitation wavelengths of (A) and (B) were 532 nm and 785 nm, respectively.



Figure S3 Diffuse reflectance spectra of (a) non-doped $SrTiO_3$, (b) $SrTiO_3$:Rh(0.5%), (c) $SrTiO_3$:Rh(0.5%),Sb(1.0%), (d) $SrTiO_3$:Rh(0.5%),Sb(2.0%), (e) H₂-reduced $SrTiO_3$:Rh(0.5%), and (f) the mixture of samples (b) and (d).



Figure S4 Photographs of (a) $SrTiO_3:Rh(0.5\%)$, (b) $SrTiO_3:Rh(0.5\%),Sb(1.0\%)$, (c) $SrTiO_3:Rh(0.5\%),Sb(2.0\%)$, and (d) the mixture of samples (b) and (d).



Figure S5 Optimization of (a) pH of the reactant solution, (b) loading amounts of IrO_2 cocatalyst, and (c) calcination temperature in a solid-state reaction for water splitting using SrTiO₃:Rh(0.5%),Sb(1.0%). Catalyst: 0.2 g, solution: H₂SO₄ aq. 120 mL, cell; top-irradiation cell with Pyrex window, light source: 300-W Xe lamp with a cut off filter (λ >440 nm).



Figure S6 Photocatalytic water splitting over $IrO_2(3wt\%)/SrTiO_3:Rh(0.5\%),Sb(1.0\%)$ under visible light irradiation. Catalyst: 0.5 g, reactant solution: 600 mL of H₂SO₄ aq. (pH 3.0), light source: 400-W high-pressure Hg lamp, cell: inner irradiation cell made of Pyrex with an aqueous NaNO₂ filter (λ >400 nm) connected to an Ar flow system.



Figure S7 Photocatalytic solar water splitting over $IrO_2(3 wt\%)/SrTiO_3:Rh(0.5\%),Sb(1.0\%)$. Catalyst: 0.2 g, reactant solution: 120 mL of H₂SO₄ aq. (pH 3.0), light source: a solar simulator with an AM-1.5 filter (100 mW cm⁻²), cell: Ar flow system with 33 cm² of irradiated area.