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; UbbetV-570) and were converted from reflectance to absorbance by the Kubelka-Munk method.

Loading of cocatalyst

IrO₂, RuO₂, and CoOₓ cocatalysts were loaded by an impregnation method. SrTiO₃:Rh,Sb (0.5 g) and desired amounts of aqueous solutions of (NH₄)₂IrCl₆ and Co(NO₃)₂, and acetone solution of Ru₃(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. IrO₂ cocatalyst was loaded also by photodeposition¹ and colloidal adsorption methods.² Ru cocatalyst was loaded by a
photodeposition method in which SrTiO$_3$:Rh,Sb dispersed in an aqueous methanol solution containing RuCl$_3$ was irradiated with visible light (\( \lambda > 420 \) 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 an pH-controlled aqueous H$_2$SO$_4$ 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 NaNO$_2$ was used to control the wavelength of the incident light (\( \lambda > 400 \) nm). 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 H$_2$ and O$_2$ 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.

\[
\text{AQY(\%)} = \left( \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \right) \times 100
\]

\[
\text{Solar energy conversion(\%)} = \left( \frac{\text{Output energy as H}_2}{\text{Energy of incident solar light(100 mW/cm}^2)} \right) \times 100
\]

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

**References**

**Table S1.** Water splitting under visible light irradiation over SrTiO$_3$:Rh(0.5%),Sb(1.0%) photocatalyst

<table>
<thead>
<tr>
<th>Entry</th>
<th>Photocatalyst</th>
<th>Cocatalyst (wt%)</th>
<th>Loading method</th>
<th>Incident light</th>
<th>Activity / µmol h$^{-1}$</th>
<th>H$_2$</th>
<th>O$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SrTiO$_3$:Rh(0.5%),Sb(1.0%)</td>
<td>–</td>
<td>–</td>
<td>&gt; 440 nm</td>
<td>trace</td>
<td>0</td>
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<tr>
<td>2</td>
<td>SrTiO$_3$:Rh(0.5%),Sb(1.0%)</td>
<td>CoO$_2$(1.0)</td>
<td>Impregnation</td>
<td>&gt; 440 nm</td>
<td>trace</td>
<td>trace</td>
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<tr>
<td>3</td>
<td>SrTiO$_3$:Rh(0.5%),Sb(1.0%)</td>
<td>RuO$_2$(1.0)</td>
<td>Impregnation</td>
<td>&gt; 440 nm</td>
<td>0.12</td>
<td>0.07</td>
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<tr>
<td>4</td>
<td>SrTiO$_3$:Rh(0.5%),Sb(1.0%)</td>
<td>Ru(0.5)</td>
<td>Photodeposition</td>
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<tr>
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<td>IrO$_2$(1.0)</td>
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<td>&gt; 440 nm</td>
<td>3.7</td>
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<td>6</td>
<td>SrTiO$_3$:Rh(0.5%),Sb(1.0%)</td>
<td>IrO$_2$(3.0)</td>
<td>Impregnation</td>
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<td>7</td>
<td>SrTiO$_3$:Rh(0.5%),Sb(1.0%)</td>
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<td>Impregnation</td>
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<td>9</td>
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<td>IrO$_2$(3.0)</td>
<td>Impregnation</td>
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<td>0</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>SrTiO$_3$</td>
<td>IrO$_2$(3.0)</td>
<td>Impregnation</td>
<td>&gt; 300 nm</td>
<td>trace</td>
<td>0</td>
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</table>

Catalyst: 0.2 g, reactant solution: 120 mL of H$_2$SO$_4$ 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 SrTiO₃, (b) SrTiO₃:Rh(0.5%), (c) SrTiO₃:Rh(0.5%),Sb(1.0%), (d) SrTiO₃:Rh(0.5%),Sb(2.0%), and (e) the mixture of samples (b) and (d).
Figure S2 Raman spectra of (a) non-doped SrTiO$_3$ and (b) SrTiO$_3$: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) H$_2$-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 SrTiO$_3$:Rh(0.5%),Sb(1.0%). Catalyst: 0.2 g, solution: H$_2$SO$_4$ aq. 120 mL, cell; top-irradiation cell with Pyrex window, light source: 300-W Xe lamp with a cut off filter ($\lambda$>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 H$_2$SO$_4$ aq. (pH 3.0), light source: 400-W high-pressure Hg lamp, cell: inner irradiation cell made of Pyrex with an aqueous NaNO$_2$ filter ($\lambda$>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 H$_2$SO$_4$ 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 cm$^2$ of irradiated area.