Supporting Information

CoOₓ modified SnNb₂O₆ Photoelectrode for Highly Efficient Oxygen Evolution from Water
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Experimental Characterization
Crystal phases of the obtained powders were confirmed using X-ray diffraction (Rigaku; SmartLab, Cu Kα). The X-ray diffraction (XRD) patterns were collected from 5° to 70° (2θ) using a step size 0.02°. The source power and current of Cu Kα radiation were 40 kV and 30 mA, respectively. Diffuse reflection spectra (DRS) were obtained using a UV-VIS-NIR spectrometer (JASCO; V-670) and were converted from reflectance to absorbance by the Kubelka-Munk method. Photocatalyst powders and photoelectrodes were observed using a scanning electron microscope (Hitachi High-Technologies; SU8020). Focused ion beam (SEIKO Instruments; SMI2050) was used to cut photoelectrodes for the cross-section observation.

Calculations

$E_{Ag/AgCl}$ was converted to $E_{RHE}$ according the following equation.

$$E_{RHE}[V] = (E_{Ag/AgCl} + 0.199 + 0.059 \times pH)[V] \quad (eq. S1)$$

IPCE was determined by the following equation.

$$IPCE[\%] = \frac{J[\text{mA/cm}^2] \times 1240[\text{V} \times \text{nm}]}{P_{mono}[\text{mW/cm}^2] \times \lambda[\text{nm}]} \times 100 \quad (eq. S2)$$

Here, $P_{mono}$, and $\lambda$ represent intensity and wavelength of incident monochromatic light, respectively.
Fig. S1 H-type cell for photoelectrochemical measurement equipped with an on-line gas chromatography.
**Fig. S2** An X-ray diffraction pattern of SnNb$_2$O$_6$ photocatalyst powder. The inset shows an SEM image of SnNb$_2$O$_6$ photocatalyst powder.
Fig. S3 XPS spectra of Sn3d$_{5/2}$ of (a, a’) non-loaded and (b, b’) CoO$_x$-loaded SnNb$_2$O$_6$ photoelectrodes (a, b) before and (a’, b’) after photoelectrochemical measurements.
Table S1 XPS areas of Sn$^{2+}$ and Sn$^{4+}$ ions and calculated proportions of Sn$^{2+}$ ions at the surface of non-loaded and CoO$_x$-loaded SnNb$_2$O$_6$ photoelectrodes.

<table>
<thead>
<tr>
<th>sample</th>
<th>measurement</th>
<th>XPS area</th>
<th>proportion of Sn$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>non-loaded SnNb$_2$O$_6$</td>
<td>before</td>
<td>53000</td>
<td>33000</td>
</tr>
<tr>
<td>non-loaded SnNb$_2$O$_6$</td>
<td>after</td>
<td>55500</td>
<td>14000</td>
</tr>
<tr>
<td>CoO$_x$-loaded SnNb$_2$O$_6$</td>
<td>before</td>
<td>50000</td>
<td>32000</td>
</tr>
<tr>
<td>CoO$_x$-loaded SnNb$_2$O$_6$</td>
<td>after</td>
<td>17500</td>
<td>5000</td>
</tr>
</tbody>
</table>

[Proportion of Sn$^{2+}$]=\[\text{XPS area of Sn}^{2+}\]/(\text{[XPS area of Sn}^{2+}\) + \text{[XPS area of Sn}^{4+}\])
Fig. S4 Schematic of chemical states of Sn species at the surface of non-loaded and CoO\textsubscript{x}-loaded SnNb\textsubscript{2}O\textsubscript{6} photoelectrodes before and after photoelectrochemical measurements.
**Fig. S5** SEM images of (a) non-loaded, (b) CoO₉(0.5 wt%)-loaded, and (c) CoO₉(1.0 wt%)-loaded SnNb₂O₆ photocatalysts. The calcination temperature in air for loading of CoOₓ cocatalyst was 473 K.
**Fig. S6** Effect of calcination temperature in air for loading of a CoOₓ cocatalyst on the photoelectrochemical performance of a CoOₓ(0.5wt%)/SnNb₂O₆ photoanode. Electrolyte, 0.125 mol L⁻¹ K₂B₄O₇ aqueous solution (pH 9.4); light source, solar simulator (AM 1.5G, 100 mW cm⁻²).
**Fig. S7** Time courses of photocurrent of a CoO₅x(0.5wt%)/SnNb₂O₆ photoelectrode at 0.0–1.2 V_{RHE}. Electrolyte, 0.125 mol L⁻¹ K₂B₄O₇ aqueous solution (pH 9.4); light source, solar simulator (AM 1.5G, 100 mW cm⁻²).