SrTiO$_3$ Photoanode Prepared by Particle Transfer Method for Oxygen Evolution from Water with High Quantum Efficiency

Y. Ham,$^a$ T. Minegishi,$^{a,b}$ T. Hisatomi$^a$ and K. Domen$^a$

$^a$ Department of Chemical System Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

$^b$ JST, PRESTO, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Corresponding Author

Kazunari Domen, domen@chemsys.t.u-tokyo.ac.jp
Table S1  Work function of metals used as the contact layer [6].

<table>
<thead>
<tr>
<th>Metal</th>
<th>Work function / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta</td>
<td>4.25</td>
</tr>
<tr>
<td>Ti</td>
<td>4.33</td>
</tr>
<tr>
<td>Mo</td>
<td>4.6</td>
</tr>
<tr>
<td>Au</td>
<td>5.1</td>
</tr>
<tr>
<td>Ni</td>
<td>5.15</td>
</tr>
</tbody>
</table>

Figure S1  (a) Secondary electron (SE) image and (b) backscattering electron (BSE) image of STO/Ta(PT). The brightness in the BSE image is proportional to the density.
Figure S2  Band diagrams of (a) before and (b) after contact formation between Au and SrTiO₃. The Schottky barrier height is equal to the difference between the work functions of SrTiO₃ ($\phi_{STO}$) and Au ($\phi_{Au}$) [S1]. CBM and VBM are the conduction band minimum and valence band maximum, respectively.
Figure S3  Current-time (I-t) curve for STO/Ta(PT) photoanode at 1.23 V<sub>RHE</sub>. A 0.1 M Na₂SO₄ + NaOH aqueous solution with pH = 13 and a 300 W xenon lamp equipped with a cold mirror (λ > 300 nm) were used as the electrolyte and light source. The vibrations of photocurrent are because of adsorption and desorption of oxygen babbles.
Figure S4  Spectrum of the 300 W xenon lamp (LX300, Perkin Elmer).

Figure S5  *I*-E curves for photoanodes prepared from Al:STO particles by PT method under the light and the dark. A 0.1 M Na₂SO₄ + NaOH aqueous solution with pH = 13 and a 300 W xenon lamp equipped with a cold mirror (λ > 300 nm) were used as the electrolyte and light source. The applied potential was swept at -10 mVs⁻¹.
Figure S6  *I-E* curves for photoanodes prepared from a single-crystal wafer of Nb-doped STO under the light and the dark. A 0.1 M Na$_2$SO$_4$ + NaOH aqueous solution with pH = 13 and a 300 W xenon lamp equipped with a cold mirror (λ > 300 nm) were used as the electrolyte and light source. The applied potential was swept at -10 mVs$^{-1}$. 
Figure S7  Schematic of the particle transfer method. A suspension of SrTiO$_3$ powder was prepared by dispersing SrTiO$_3$ powder in isopropanol by sonication and stirring. The photocatalytic particles were deposited on a glass plate using the prepared suspension through a drop casting followed by drying. The contact and conductor layers were deposited either by vacuum evaporation method or radio-frequency magnetron sputtering method. The material and deposition condition of contact layer are essential to form ohmic contact. To obtain sufficient conductivity and mechanical strength, a thicker conductor layer was formed using radio-frequency magnetron sputtering on top of the contact layer. The layers were bonded to another glass plate by adhesives and then peeled off from the original glass plate. The excess particles on the electrode which are not contact with contact layer directly were removed by ultra-sonication in water.
S1. Preparation of SrTiO₃ particles [S2]

Pristine SrTiO₃

SrTiO₃ (Wako Pure Chemicals Industries, Ltd, 99.9%) was used without any treatment.

Undoped SrTiO₃ synthesized via the flux method

SrTiO₃ (Wako Pure Chemicals Industries, Ltd, 99.9%), Al₂O₃ (Sigma-Aldrich Co, LLC., nanopowder), and SrCl₂ (Kanto Chemicals Co., Inc., 98.0%, anhydrous) were used as raw materials. SrTiO₃ and SrCl₂ were mixed in an agate mortar and then calcined in an yttria crucible at 1100 °C for 10 h. The resulting SrTiO₃ was separated from the solidified mass by repeated washing with deionized water until no white AgCl precipitate formed in the rinse solutions upon adding AgNO₃.

Al-doped SrTiO₃ synthesized via solid-state reaction

SrTiO₃ (Wako Pure Chemicals Industries, Ltd, 99.9%) and Al₂O₃ (Sigma-Aldrich Co, LLC., nanopowder) were thoroughly mixed in an agate mortar. The mixture was heated in an alumina crucible at 1100 °C for 10 h.
# S2. Characterization results for prepared SrTiO₃ particles [S2]

<table>
<thead>
<tr>
<th>Composition (ICP-OES)</th>
<th>Hydrogen evolution rate in photocatalytic overall water splitting / mmol h⁻¹</th>
<th>§</th>
</tr>
</thead>
<tbody>
<tr>
<td>2[Al] / ([Sr]+[Ti])</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al:STO</td>
<td>1.0 at.%</td>
<td>575</td>
</tr>
<tr>
<td>Pristine SrTiO₃</td>
<td>N.D.</td>
<td>1.3</td>
</tr>
<tr>
<td>Al-doped SrTiO₃ synthesized via solid-state reactions</td>
<td>0.1 at.%</td>
<td>150</td>
</tr>
<tr>
<td>Undoped SrTiO₃ synthesized via the flux method</td>
<td>N.D</td>
<td>4.2</td>
</tr>
</tbody>
</table>

§ A mixed oxide of rhodium and chromium was loaded as a cocatalyst by the impregnation method prior to the examination of photocatalytic overall water splitting.

References
