Electronic Supplementary Information (ESI)

**Novel Flux Coating Method for Fabrication of Layer of Visible-Light-Responsive Ta₃N₅ Crystals on Tantalum Substrate**

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Materials and reagents
To fabricate the Ta$_3$N$_5$ crystal layers, Ta foil (99.95 %, Nilaco Corporation), NaNO$_3$ (99.0 %, Wako Pure Industries, Ltd.), NaCl (99.5 %, Wako Pure Industries, Ltd.), and Na$_2$CO$_3$ (99.8 %, Wako Pure Industries, Ltd.) were used. The solution-coated substrates were heated using NH$_3$ (99.9995 %, Sumitomo Seika Chemicals Co., Ltd.) and N$_2$ (99.9995 %, Taiyo Nippon Sanso Corporation) gases. For the modification using a cocatalyst, Co(NO$_3$)$_2$·6H$_2$O (99.5 %, Wako Pure Industries, Ltd.), K$_2$HPO$_4$ (99.0 %, Kanto Chemicals), KH$_2$PO$_4$ (99.5 %, Kanto Chemicals), Na$_2$SO$_4$ (99.0 %, Wako Pure Industries, Ltd.), and NaOH (97.0 %, Wako Pure Industries, Ltd.) were used. All the chemicals were used as-purchased without further purification.

Fabrication of samples for UV-vis spectral measurements
We could not measure the Kubelka-Munk spectrum for the Ta$_3$N$_5$ crystal layers on the Ta substrate with accuracy, because of absorption by the Ta substrate. Therefore, we fabricated the Ta$_3$N$_5$ crystal layers on a silica-glass substrate, and subsequently measured their light absorption properties in the transmission mode.
First, a layer of Ta was deposited on the silica-glass substrate (20 × 20 × 0.5 mm) by sputtering (Kenix Co., Ltd., RF sputter system, KXS-410B) using a Ta target (99.99 %, High Purity Chemicals). The deposited Ta layer had a thickness of approximately 60 nm. The subsequent procedures for the fabrication of the Ta$_3$N$_5$ crystal layers were basically the same as those of the fabrication of the layers on the Ta substrates. The Ta layer was dry-cleaned and hydrophilized by being irradiated under vacuum-ultraviolet light (λ = 172 nm). Next, 13.3 µL of the NaCl-Na$_2$CO$_3$ aqueous solution was placed on the Ta layer. Because 5 µL of the solution was used for the Ta substrates, which had dimensions of 10 × 15 mm, the amount of solution used was increased to 13.3 µL for the silica-glass substrates, which were larger in size (dimensions of 20 × 20 mm). The solution-coated substrates were dried in an electric oven at 100 °C for 30 min. Subsequently, the substrates were heated to 850 °C at a rate of 10 °C·min$^{-1}$ and held at this temperature for 1 h in an NH$_3$ flow (100 mL·min$^{-1}$).
Fig. S1  Digital photographs of the crystal layers fabricated using (a) NaNO$_3$ (Run No. 1), (b) Na$_2$CO$_3$ (Run No. 2), (c) NaCl (Run No. 3), and (d, e) NaCl-Na$_2$CO$_3$ as the fluxes. (d) 10 µL (Run No. 4) and (e) 5 µL (Run No. 5) of an aqueous NaCl-Na$_2$CO$_3$ solution were used as the fluxes.
Table S1  Crystallite sizes of the crystal layers fabricated using the various fluxes.

<table>
<thead>
<tr>
<th>run no.</th>
<th>flux (molar ratio)</th>
<th>amount of coating / µL</th>
<th>crystallite size / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaNO₃</td>
<td>10</td>
<td>18.3</td>
</tr>
<tr>
<td>2</td>
<td>Na₂CO₃</td>
<td>10</td>
<td>18.0</td>
</tr>
<tr>
<td>3</td>
<td>NaCl</td>
<td>10</td>
<td>36.6</td>
</tr>
<tr>
<td>4</td>
<td>NaCl-Na₂CO₃ (4 : 1)</td>
<td>10</td>
<td>31.1</td>
</tr>
<tr>
<td>5</td>
<td>NaCl-Na₂CO₃ (4 : 1)</td>
<td>5</td>
<td>36.1</td>
</tr>
</tbody>
</table>
Fig. S2  Low-magnification surface SEM images of the crystal layers fabricated using (a) NaNO$_3$ (Run No. 1), (b) Na$_2$CO$_3$ (Run No. 2), (c) NaCl (Run No. 3), and (d, e) NaCl-Na$_2$CO$_3$ as the fluxes. (d) 10 µL (Run No. 4) and (e) 5 µL (Run No. 5) of an aqueous NaCl-Na$_2$CO$_3$ solution were used as the fluxes.
Fig. S3  Cross-sectional SEM image of the crystal layer fabricated using NaCl-Na$_2$CO$_3$ as the flux at 850 °C for 1 h (Run No. 5).
Fig. S4  Illustration of the formation mechanism of Ta$_3$N$_5$ crystal layers using (a) NaNO$_3$, (b) Na$_2$CO$_3$, and (c) NaCl-Na$_2$CO$_3$ as the fluxes.
Fig. S5  Digital photographs of the crystal layers fabricated using NaCl-Na$_2$CO$_3$ as the flux at different holding temperatures and a holding time of 0 h: (a) 700 °C (Run No. 6), (b) 750 °C (Run No. 7), (c) 800 °C (Run No. 8), and (d) 850 °C (Run No. 9).
Fig. S6  UV-vis absorption spectrum of the crystal layers fabricated on the silica-glass substrate using NaCl-Na$_2$CO$_3$ as the flux at 850 °C for 1 h.