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Novel Flux Coating Method for Fabrication of Layer of Visible-Light-Responsive Ta$_3$N$_5$ Crystals on Tantalum Substrate

Sayaka Suzuki,\textsuperscript{a} Hajime Wagata,\textsuperscript{a} Mugi Komatsu,\textsuperscript{a} Tsutomu Minegishi,\textsuperscript{b} Kazunari Domen,\textsuperscript{b} Shuji Oishi\textsuperscript{a} and Katsuya Teshima\textsuperscript{a,\textasteriskcentered c}\textsuperscript{*}

\textsuperscript{a}Department of Environmental Science and Technology, Faculty of Engineering, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan

\textsuperscript{b}Department of Chemical System Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

\textsuperscript{c}Center for Energy and Environmental Science, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan

E-mail: teshima@shinshu-u.ac.jp

*Corresponding Author: Katsuya Teshima
ABSTRACT

Layers of well-developed crystals of Ta$_3$N$_5$ were successfully fabricated on Ta substrates by a novel flux coating method in a flow of NH$_3$. The flux coating method is a simple one: the Ta substrates were coated with aqueous solutions of sodium compounds (= fluxes) and subsequently heated in a flow of NH$_3$, whereupon the surfaces of the Ta substrates were dissolved in the flux, resulting in Ta$_3$N$_5$ crystal layers. The Ta in the Ta$_3$N$_5$ was provided by the substrate. Therefore, crystal layers with good adhesion could be grown directly on the substrates. The shape of the individual crystals as well as the surface morphology of the layers formed was determined by the flux used. The crystals fabricated using NaCl-Na$_2$CO$_3$ as the flux were prismatic and had relatively smooth faces, covering the surface of the Ta substrate uniformly. The crystal growth field resulting from the use of this method yielded well-formed crystals, which presumably grew from a solution. Finally, it was confirmed that a thus-synthesized Ta$_3$N$_5$ crystal layer modified using Co-Pi as the cocatalyst generated a photoanodic current under visible-light irradiation.
Introduction

As hydrogen gains importance as a source of clean energy, transition metal (oxy)nitrides are increasingly receiving attention as visible-light-sensitive materials for the photocatalytic and photoelectrochemical splitting of water.\textsuperscript{1-4} Materials capable of absorbing visible light allow for the use of solar energy as an energy source. Hydrogen can be regarded as a source of genuine clean energy, if it is produced from water using sunlight and semiconductor photocatalysts and not fossil fuels. Among the various metal (oxy)nitrides used as catalysts for the synthesis of hydrogen, tantalum nitride (Ta\textsubscript{3}N\textsubscript{5}) has a band gap suitable for splitting water. Further, the narrowness of its band gap (2.1 eV) allows for the absorption of visible light with wavelengths of up to 600 nm.\textsuperscript{5,6} In the past five years, Ta\textsubscript{3}N\textsubscript{5} films have been used for the oxidation of water.\textsuperscript{7-13} Ta\textsubscript{3}N\textsubscript{5} powders and thin films (or photoanodes) are conventionally prepared by the nitridation of precursor powders and thin oxide films (mostly of Ta\textsubscript{2}O\textsubscript{5}) at relatively high temperatures in an NH\textsubscript{3} flow.\textsuperscript{5,6,11-15}

We had previously reported the fabrication of crystal layers of various oxides and fluorides using a flux coating method.\textsuperscript{16-20} Flux method is one of the crystal growth technique from high temperature solutions and allows for the fabrication of highly crystalline, idiomorphic crystals.\textsuperscript{21-24} In the case of conventional flux-based crystal
growth methods, the raw material (solute) and the flux (both in powder form) are placed in a suitable crucible. In contrast, in the proposed method, the raw materials are coated on the surface of the appropriate substrate in the form of a paste or an aqueous solution. When the substrate is heated, the flux components melt and dissolve the solute, resulting in the growth of crystals on the substrate surface. In some cases, the substrate can also be used as a source of raw materials. For instance, a layer of NaTaO$_3$ crystals could be fabricated using a piece of Ta foil both as the substrate and the Ta source.\textsuperscript{17} Moreover, we demonstrated that these NaTaO$_3$ crystals could be transformed into those of Ta$_3$N$_5$ by nitridation in an NH$_3$ flow.\textsuperscript{17} However, the cubic NaTaO$_3$ single crystals constituting the layer became cubic, polycrystalline Ta$_3$N$_5$, owing to changes in the crystal structure. The pores observed on the thus-fabricated particles were owing to the nitridation of Ta$_2$O$_5$ into Ta$_3$N$_5$.\textsuperscript{25}

On the basis of these results, we devised a novel flux coating method for synthesizing layers of nitride crystals. We employed this method for the direct fabrication of Ta$_3$N$_5$ crystal layers on Ta substrates. A part of the surface of the Ta substrate could be converted into well-formed crystals. To ensure the fabrication of well-formed Ta$_3$N$_5$ crystals, the correct flux must be used. The surface of the Ta substrate should be dissolved by the flux and undergo crystallization. In addition, the
flux should be reacted with Ta to form a precursor phase, because Ta$_3$N$_5$ cannot be produced by simply heating Ta; however, the precursor phase should be a temporary one. Moreover, the flux should be highly soluble in water, because an aqueous solution of the flux can be readily coated on hydrophilized substrates before they are heated. Further, any residual flux can be removed readily after heating. Given these facts, we first used sodium compounds as fluxes, because it is known that NaTaO$_3$ can be nitried into Ta$_3$N$_5$ even if the NaTaO$_3$ phase is formed by a reaction between the Ta surface and a Na compound (i.e., the flux).

**Experimental**

As mentioned above, in this study, layers of Ta$_3$N$_5$ crystals were fabricated by a novel flux coating method. Ta foil was used as both the substrate and the Ta source, and the nitrogen part of Ta$_3$N$_5$ came from the NH$_3$ gas used. Reagent-grade NaNO$_3$, NaCl, and Na$_2$CO$_3$ powders were used as the fluxes. First, the Na compounds (i.e., fluxes) were dissolved in distilled water to form solutions. The typical fabrication conditions are listed in Table 1. Next, 10 or 5 µL of the aqueous solutions was placed on the Ta substrates (10 × 15 × 0.1 mm), which had been dry-cleaned and hydrophilized by being irradiated under vacuum-ultraviolet light (λ = 172 nm) from a xenon excimer lamp.
(UER172-200, Ushio Inc.). The solution-coated substrates were dried in an electric oven at 100 °C for 30 min. Next, the substrates were put in an alumina boat, which was placed at the center of a horizontal alumina tube furnace (diameter = 24 mm). The substrates were then heated to 700–850 °C at a rate of 10 °C·min⁻¹ and held at this temperature for 0 or 1 h in an NH₃ flow to effect ammonolysis. The NH₃ flow rate was maintained at 100 mL·min⁻¹. Subsequently, the substrates were allowed to cool to 300 °C and then to room temperature inside the furnace in NH₃ and N₂ flows, respectively. The Ta₃N₅-coated substrates were then immersed in warm water to remove any residual flux. Next, any grown crystals exhibiting weak adhesion to the substrate surface were removed in water through weak sonication (US-104, 150 W, 38 kHz, SND Co., Ltd.).

The fabricated crystal layers were observed using scanning electron microscopy (SEM; JEOL, JCM-5700) and field-emission scanning electron microscopy (FESEM; JEOL, JSM-7600F). The crystal phases were studied using X-ray diffraction (XRD; Rigaku, MiniflexII). The ultraviolet-visible (UV-vis) absorption spectra of the crystal layers were obtained using a spectrophotometer (JASCO, V-670). The photoelectrochemical (PEC) properties of the Ta₃N₅ crystal layers were investigated using a three-electrode setup in an Ar atmosphere. Before the PEC measurements, the Ta₃N₅ crystal layers were modified using cobalt phosphate (Co-Pi) as a cocatalyst,
which was electrochemically coated onto the Ta$_3$N$_5$ crystal layers using a 0.5 mM solution of Co(NO$_3$)$_2$ in a potassium phosphate buffer. The fabricated Co-Pi/Ta$_3$N$_5$/Ta photoelectrode, an Ag/AgCl electrode, and a Pt wire were connected to a potentiostat and used as the working, reference, and counter electrodes, respectively. The electrolyte solution used was a 0.2 M aqueous Na$_2$SO$_4$ solution, whose pH value was adjusted to 13 using NaOH. The photoelectrode was irradiated using a 300 W Xe lamp equipped with a cut-off filter ($\lambda > 420$ nm).

**Results and Discussion**

**Fabrication of Ta$_3$N$_5$ crystal layers using various fluxes**

First, crystal layers were fabricated using various Na compounds as fluxes at a holding temperature of 850 °C and a holding time of 1 h. Fig. S1 shows digital photographs of the surfaces of the Ta substrates after the fabrication of the crystal layers and subsequent ultrasonication for 30 min. As can be seen from the digital photographs, layers of red crystals were formed for all fluxes; the exception was NaCl (Run No. 3). That the substrate surface color was dark red indicates that a large number of Ta$_3$N$_5$ crystals were formed. Considering that Ta$_3$N$_5$ cannot be synthesized by simply heating Ta in an NH$_3$ flow, it is likely that the Na compounds dissolved the surfaces of the Ta
substrates, resulting in the formation of precursor materials for Ta$_3$N$_5$. On the other hand, NaCl exhibited a low reactivity with respect to the Ta surface, since the color of the substrate surface in this case was similar to that of a Ta substrate heated in an NH$_3$ flow (Fig. S1c). In addition, when 5 µL of NaCl-Na$_2$CO$_3$ was used, the entire substrate surface turned light red (Run No. 5, Fig. S1e). Further, the crystal layer exhibited good adhesion to the substrate surface, because almost no crystals were removed during ultrasonication. However, the other crystal layers exhibited inhomogeneities in the surface color along the plane of the substrate surface. This indicates that the melts of the Na compounds used as the fluxes for these crystal layers did not cover the entire surface of the Ta substrate. In the cases when Na$_2$CO$_3$ and 10 µL of NaCl-Na$_2$CO$_3$ were used as the fluxes, numerous red crystals were formed; however, some of them were removed during ultrasonication, because they exhibited poor adhesion to the substrate, resulting in the observed inhomogeneities in the surface color.

Fig. 1 shows SEM images of the surfaces of the Ta$_3$N$_5$ crystal layers formed on the Ta substrates. When the crystal layer was fabricated using NaNO$_3$ as the flux, polyhedron crystals less than ~1 µm in size were observed; further, numerous pores were present on the surfaces of these crystals (Fig. S2a and 1a). The crystal layer fabricated using Na$_2$CO$_3$ as the flux consisted of well-formed prismatic crystals (marked
area in Fig. S1b, Fig. S2b and 1b). When NaCl was used as the flux, prismatic crystals less than 100 nm in width and 500 nm in length grew on the Ta surface (Fig. S2c and 1c). When 10 µL of an aqueous NaCl-Na$_2$CO$_3$ solution was used as the flux coating, aggregates of small particles were observed (Fig. S2d), while well-formed prismatic crystals were observed in high-magnification images (Fig. 1d). When the amount of the coating solution used was decreased to 5 µL, well-developed prismatic crystals with relatively smooth faces and angular corners grew on the entire substrate (Fig. 1e and 1f). These prismatic crystals were thought to be single crystals of Ta$_3$N$_5$. Finally, the thickness of the crystal layer was approximately 2.1 µm (Fig. S3).

Fig. 2 shows the XRD profiles for the crystal layers fabricated using the various Na compound as fluxes. All the crystal layers exhibited XRD patterns that contained diffraction lines attributable to Ta$_3$N$_5$ (○-marked lines), Ta$_2$N (▲-marked lines),$_{10,13}$ and Ta (owing to the substrate, ■-marked lines). When the crystal layers were fabricated using Na$_2$CO$_3$ and 10 µL of NaCl-Na$_2$CO$_3$ as the fluxes (Run No. 2, 4, respectively), low-intensity diffraction lines corresponding to NaTaO$_3$ were observed (●-marked lines) in addition those corresponding to Ta$_3$N$_5$, Ta$_2$N, and Ta (Fig. 2b and 2d). NaTaO$_3$ was formed by a reaction between Ta and Na$_2$CO$_3$ and did not undergo nitridation. When NaCl was used as the flux (Run No. 3), very weak diffraction lines corresponding
to Ta$_3$N$_5$ were observed at $2\theta$ of 15−38° (Fig. 2c). The small, prismatic crystals observed in the SEM image of the sample (Fig. 1c) were determined to be of Ta$_3$N$_5$. The crystal layer fabricated using NaCl-Na$_2$CO$_3$ as the flux (Run No. 4, 5) contained an unknown phase (★-marked lines) (Fig. 2d and 2e). The intensities of the corresponding diffraction lines were weaker than those of the lines for Ta$_3$N$_5$ (i.e., the target phase) in the case when 5 µL of NaCl-Na$_2$CO$_3$ was used as the flux. Thus, the amount of the unknown phase product would be small. On the basis of the digital photographs, SEM images, and XRD patterns of the various samples, we concluded that 5 µL of NaCl-Na$_2$CO$_3$ was the best flux for the direct fabrication of a layer of Ta$_3$N$_5$ crystals on a Ta substrate.

Next, we discuss the mechanisms of formation of Ta$_3$N$_5$ using the various fluxes. For all the fluxes, the Ta$_3$N$_5$ crystals were formed by the dissolution of the surface of the Ta substrate by the flux used and a subsequent reaction between the dissolved Ta and the flux. Considering that the Ta and N sources for Ta$_3$N$_5$ were the Ta substrate and NH$_3$ gas, respectively, the Na compounds (i.e., fluxes) coated on the surface of the Ta substrate might seem unnecessary. However, as mentioned previously, Ta$_3$N$_5$ cannot be produced by simply heating Ta metal in an NH$_3$ flow. Therefore, it is likely that the Ta$_3$N$_5$ crystals were formed via precursor materials that were produced by a reaction
between the Ta from the substrate surface and the flux used. Compounds related to the Ta-O, Na-Ta-O, and Ta-Cl systems, such as Ta₂O₅ and NaTaO₃, are probably the precursor materials formed. Ta₂O₅ is conventionally used as a precursor oxide for Ta₃N₅; however, it is difficult to synthesize Ta₂O₅ owing to the fact that the flux used (i.e., the oxygen source) is present in a small amount and given that the NH₃ gas used is usually of high purity. Therefore, it is probable that other tantalum oxides (TaOₓ (x < 5/2)) are the precursor materials for Ta₃N₅. In addition, we had previously reported that Ta₃N₅ can be produced by heating NaTaO₃ in an NH₃ flow. In the present study, NaTaO₃ or phases related to the Na-Ta-O system could be produced by reacting TaOₓ and Na₂CO₃ (as flux); this was proven by the results of the XRD analysis. Further, most of these compounds were transformed into Ta₃N₅. On the other hand, when NaCl was used as the flux, it could not oxidize Ta, as the former does not contain oxygen. The surface of the Ta substrate dissolved slightly in NaCl, and a small amount of a compound corresponding to the Ta-Cl system was formed as the precursor material, because TaCl₅ was also nitrided to Ta₃N₅. As a result, a few small Ta₃N₅ crystals were synthesized in the NH₃ flow.

Next, we compare the mechanisms by which Ta₃N₅ crystal layers were formed when NaNO₃ (Run No. 1) and Na₂CO₃ (Run No. 2, 4, 5) were used as the fluxes. When
NaNO₃ was used as the flux, the Ta₃N₅ crystals were formed by a process different from those when the other fluxes were used; this was owing to the fact that the melting point of NaNO₃ (308 °C) is relatively low. The process for the formation of Ta₃N₅ crystals using NaNO₃ as the flux is illustrated in Fig. S4a. NaNO₃ melted at approximately 300 °C during the temperature elevating process and reacted with Ta surface of the substrate. This resulted in the growth of polyhedral NaTaO₃ crystals, as has been mentioned previously.²⁸ At this temperature, NH₃ gas does not react with the Ta, because the decomposition temperature of NH₃ is 600 °C or higher.²⁹ Further, the reaction between NaNO₃ and the Ta surface is not affected by NH₃. NaNO₃ decomposes at approximately 360 °C to produce NaNO₂ and O₂; further heating mainly produces Na₂O. NaNO₃ is consumed by the formation of NaTaO₃ crystals via NaNO₂ and Na₂O. Almost all of the NaNO₃ is consumed at approximately 600 °C, which is the decomposition temperature of NH₃. Next, the NaTaO₃ is transformed into Ta₃N₅ by nitridation both before and during the holding process (holding temperature of 850 °C). The crystal-layer fabrication method employed in this study is a single-step process, that is, it only involves one heating stage, in which heating is performed in an NH₃ flow; however, the actual process for the formation of the Ta₃N₅ crystal layer is a two-step one, involving the fabrication of NaTaO₃ and its subsequent nitridation to Ta₃N₅. This
process is almost the same as one reported previously;\textsuperscript{17} the difference is that, in the present case, NaTaO\(_3\) is produced in an NH\(_3\) flow and not in an atmosphere rich in oxygen. The nitridation process resulted in numerous pores on the surfaces of the synthesized crystals, owing to the change in the crystal structure resulting from the change in the crystal phase. In addition, a dark red (\textit{i.e.}, thick) layer of Ta\(_3\)N\(_5\) crystals was formed, because a thick layer of NaTaO\(_3\) crystals was grown owning to the use of a low heating rate (10 °C·min\(^{-1}\)). This was in contrast to the previous study, in which the NaTaO\(_3\) crystal layer was formed using a heating rate as high as 100 °C·min\(^{-1}\). As described above, the Ta\(_3\)N\(_5\) crystal layer was formed in two steps, owing to the low melting point of NaNO\(_3\). To obtain a layer consisting of Ta\(_3\)N\(_5\) single crystals, both the formation of the precursor-oxide phases and their nitridation should occur simultaneously in the solution (\textit{i.e.}, the liquid phase).

In contrast, Na\(_2\)CO\(_3\) has a melting point of 851 °C; therefore, the precursor NaTaO\(_3\) does not form readily before the decomposition of the NH\(_3\) gas (\textit{i.e.}, at temperatures lower than 600 °C). During the fabrication of the Ta\(_3\)N\(_5\) crystal layer using Na\(_2\)CO\(_3\) as the flux, Na\(_2\)CO\(_3\) melted at approximately 850 °C during the holding process. Thus, both the formation of the precursor phases and their nitridation occurred almost simultaneously, as is the case when Ta\(_3\)N\(_5\) crystals are grown from a solution.
The process for the formation of Ta₃N₅ crystals using Na₂CO₃ as the flux is illustrated in Fig. S4b. Well-developed Ta₃N₅ crystals surrounded by flat surfaces could be grown successfully, as shown in Fig. 1b.

However, the thus-formed crystal layer exhibited poor uniformity and coverage, as shown in Fig. S1b, because the holding temperature was the same as the melting point of Na₂CO₃. Therefore, the melt reacted with the surface of the Ta substrate before it could spread uniformly and wet the surface. This problem can be solved by using a higher holding temperature. However, in this case, the Ta substrate would get directly nitrided into other tantalum nitrides such as Ta₅N₆ and Ta₂N.¹⁰ Therefore, the holding temperature was kept at 850 °C, and the flux used was one having a melting (or dissolution) temperature that lay between the decomposition temperature of NH₃ (i.e., greater than 600 °C) and the holding temperature (850 °C). When NaCl and Na₂CO₃ are mixed in a molar ratio of 4:1, the liquidus temperature is approximately 730 °C.³⁰ That is to say, the melting point of Na₂CO₃ decreases from 851 °C to 730 °C. Consequently, when NaCl-Na₂CO₃ was used as the flux, it increased the uniformity and degree of coverage of the formed Ta₃N₅ crystal layer, as shown in Fig. S1d and S1e. It is assumed that this was because the flux spread uniformly on the surface of the Ta substrate, subsequently reacting with the surface and NH₃. In view of the crystal layers formed
using Na₂CO₃ and NaCl individually as fluxes, the Ta surface was dissolved mainly by Na₂CO₃, with NaCl aiding the spreading of Na₂CO₃. When 10 µL of NaCl-Na₂CO₃ (Run No. 4) and Na₂CO₃ alone (Run No. 2) were used as the fluxes, the amount of Na₂CO₃ coated on the surface of the Ta substrate was greater than that when 5 µL of NaCl-Na₂CO₃ was used as the flux. The crystal layers fabricated using these fluxes exhibited XRD patterns that contained weak diffraction lines corresponding to NaTaO₃. This was either because a large amount of NaTaO₃ was formed or because the nitridation process was blocked by Na₂CO₃, which was redundant.

Table S1 shows the crystallite sizes obtained from the XRD patterns of the crystal layers. The crystals fabricated using NaCl and NaCl-Na₂CO₃ as the fluxes had larger crystallite sizes than those of the crystals fabricated using NaNO₃ and Na₂CO₃. We believe that the evaporation of the flux was the driving force for the growth of the Ta₃N₅ crystals. NaCl evaporates readily compared to the other fluxes. Therefore, highly crystalline Ta₃N₅ was fabricated when the NaCl was employed as the flux.

Process for formation of Ta₃N₅ crystal layer using NaCl-Na₂CO₃ as flux
Next, crystal layers were fabricated at various holding temperatures using NaCl-Na₂CO₃ as the flux (molar ratio = 4:1, amount of flux used = 5 µL). The holding time was fixed to 0 h (i.e., the samples were heated to the highest temperature and then cooled immediately), keeping in mind the formation process of the Ta₃N₅ crystal layers.

For convenience, we have used the terms "holding temperature" and “holding time” even when the holding time was zero. Fig. S5 shows digital photographs of the crystal layers fabricated at various temperatures. The crystal layers fabricated at temperatures lower than 800 °C were almost white. On the other hand, a red crystal layer was obtained at 850 °C (Fig. S5d). SEM images showed that the crystal layer prepared at 700 °C had a lower surface roughness than those of the other layers (Fig. 3a). In the former case, the flux could not dissolve the surface of the Ta substrate to a sufficient degree, owing to the low temperature and the short heating time. At 750 °C, small prismatic and cuboid crystals were observed. The surface roughness increased, because the heating temperature exceeded the liquidus temperature of the NaCl-Na₂CO₃, resulting in the rapid dissolution of the surface of the Ta substrate. In the case of the crystal layer fabricated at 800 °C, the number of prismatic crystals formed was higher. At 850 °C, almost all the crystals formed were prismatic. Further, they were larger than those formed at temperatures lower than 800 °C. The prismatic and cuboid crystals are
presumed to be of Ta$_3$N$_5$ and NaTaO$_3$, respectively. When nitrogen is incorporated during the fabrication process, prismatic Ta$_3$N$_5$ crystals are generated. In contrast, using a poor nitrogen source resulted in cuboid NaTaO$_3$. Fig. 4 shows the XRD profiles for the crystal layers fabricated at 700–850 °C for 0 h. At 700 °C, no diffraction line corresponding to Ta$_3$N$_5$ was observed (Fig. 4a). On increasing the heating temperature, the intensity of the diffraction lines corresponding to NaTaO$_3$ and Ta$_3$N$_5$ decreased and increased, respectively. At 850 °C for 0 h, Ta$_3$N$_5$ became the main phase (Fig. 4d).

Finally, the crystal layer fabricated at a holding temperature of 850 °C and a holding time of 1 h did not exhibit a diffraction line corresponding to NaTaO$_3$, as shown in Fig. 2e.

Next, on the basis of the SEM and XRD results, we discuss the formation of crystal layers when NaCl-Na$_2$CO$_3$ is used as the flux. In the case of the layer fabricated at 700 °C, assuming that the decomposition temperature of NH$_3$ gas is approximately 600 °C, the flux-coated Ta substrate is heated for only approximately 11 min in an atmosphere of decomposed NH$_3$, given that the heating rate is 10 °C·min$^{-1}$. The NaCl-Na$_2$CO$_3$ flux dissolves the surface of the Ta substrate slightly and reacts with it. As a result, cuboid NaTaO$_3$ crystals grow without there being a reaction with NH$_3$. By increasing the holding temperature and holding time, nitrogen can be incorporated into
the crystals in a large enough concentration during crystallization. Therefore, Ta₃N₅ and NaTaO₃ are formed in greater and lower amounts, respectively. We believe that the prismatic Ta₃N₅ crystallized owing to flux evaporation.

**PEC properties of the Ta₃N₅ crystal layers**

Fig. S6 shows the absorption spectrum for the Ta₃N₅ crystal layer fabricated using NaCl-Na₂CO₃ as the flux at 850 °C for 1 h (see Supporting Information for experimental details). The optical absorption edge of the Ta₃N₅ crystals was approximately 600 nm, and their band gap was determined to be approximately 2.1 eV. Fig. 5 shows the current–potential curve for a Ta₃N₅ crystal layer modified with Co-Pi as a cocatalyst. The Ta₃N₅ crystal layer was formed using NaCl-Na₂CO₃ as the flux at 850 °C for 1 h. An anodic photocurrent associated with the oxidation of water was generated. The onset potential was measured to be approximately 0.4 V<sub>RHE</sub>, while the photocurrent density was 1.5 mA·cm<sup>-2</sup> at 1.23 V<sub>RHE</sub>. That the performance of this modified layer was relatively quite poor might be attributed to its low thickness, impurities, and the state of the substrate/crystal layer interface. However, these results indicated that Ta₃N₅ crystal layers fabricated using the proposed flux coating method
can potentially be used as n-type semiconductor electrodes under visible-light irradiation.

**Conclusion**

Layers of Ta$_3$N$_5$ crystals were fabricated by a novel flux coating method in an NH$_3$ flow. The thus-synthesized crystal layers exhibited good adhesion to the substrate, because the Ta component of Ta$_3$N$_5$ was provided by the Ta substrate, and the Ta$_3$N$_5$ crystals grew directly on the substrate. The shape of the individual crystals constituting the crystal layer was determined by the flux used. The crystal layer fabricated using NaCl-Na$_2$CO$_3$ as the flux consisted of well-formed, prismatic crystals surrounded by flat surfaces, while that formed using NaNO$_3$ as the flux consisted of cuboid crystals whose surfaces were covered with numerous pores. Thus, to synthesize a layer of well-formed Ta$_3$N$_5$ crystals, compounds having the appropriate melting point and a high ability to dissolve Ta should be used as the flux. That is to say, the flux should exhibit high solubility and reactivity with respect to Ta. However, the flux and its components should not remain in the crystal layer because the sodium compounds used as the flux are “extra” components as far as the Ta$_3$N$_5$ phase is concerned. In addition, a Ta$_3$N$_5$ crystal layer modified with Co-Pi as a cocatalyst acted as a photoelectrode under
visible-light irradiation; this was confirmed by PEC measurements. Finally, we believe that the proposed method of fabricating crystal layers using a flux coating in an NH$_3$ flow could be used to fabricate crystal layers of several other nitrides as well.
References


Figure captions

Table 1  Conditions for the synthesis of Ta<sub>3</sub>N<sub>5</sub> crystal layers.

Fig. 1  Surface SEM images of the crystal layers fabricated using (a) NaNO<sub>3</sub> (Run No. 1), (b) Na<sub>2</sub>CO<sub>3</sub> (Run No. 2), (c) NaCl (Run No. 3), and (d–f) NaCl-Na<sub>2</sub>CO<sub>3</sub> as the fluxes. (d) 10 µL (Run No. 4) and (e, f) 5 µL (Run No. 5) of an aqueous NaCl-Na<sub>2</sub>CO<sub>3</sub> solution were used as the fluxes.

Fig. 2  XRD profiles of the crystal layers fabricated using (a) NaNO<sub>3</sub> (Run No. 1), (b) Na<sub>2</sub>CO<sub>3</sub> (Run No. 2), (c) NaCl (Run No. 3), and (d, e) NaCl-Na<sub>2</sub>CO<sub>3</sub> as the fluxes; ICDD PDFs of (f) NaTaO<sub>3</sub> and (g) Ta<sub>3</sub>N<sub>5</sub>. (d) 10 µL (Run No. 4) and (e) 5 µL (Run No. 5) of an aqueous NaCl-Na<sub>2</sub>CO<sub>3</sub> solution were used as the fluxes.

Fig. 3  SEM images of the crystal layers fabricated using NaCl-Na<sub>2</sub>CO<sub>3</sub> 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. 4  XRD profiles of the crystal layers fabricated using NaCl-Na<sub>2</sub>CO<sub>3</sub> 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).

ICDD PDFs of (e) NaTaO$_3$ and (f) Ta$_3$N$_5$.

Fig. 5  Current-potential curves for Co-Pi/Ta$_3$N$_5$/Ta. The Ta$_3$N$_5$ crystal layer was fabricated using NaCl-Na$_2$CO$_3$ as the flux at 850 °C for 1 h (Run No. 5). The electrolyte was a 0.2 M aqueous Na$_2$SO$_4$ solution with a pH of 13, which was adjusted by adding NaOH. The photoelectrode was irradiated with a 300 W Xe lamp equipped with a cut-off filter (λ > 420 nm). The electrode potential was swept in the positive direction at a rate of 10 mV·s$^{-1}$.

Table S1  Crystallite sizes of the crystal layers fabricated using the various fluxes.

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.

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.
Table 1  Conditions for the synthesis of Ta₃N₅ crystal layers.

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<th>run no.</th>
<th>flux (molar ratio)</th>
<th>NaNO₃ / g</th>
<th>Na₂CO₃ / g</th>
<th>NaCl / g</th>
<th>water /mL</th>
<th>Na conc. / M</th>
<th>holding temp. / °C</th>
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Fig. 1  Surface SEM images of the crystal layers fabricated using (a) NaNO₃ (Run No. 1), (b) Na₂CO₃ (Run No. 2), (c) NaCl (Run No. 3), and (d–f) NaCl-Na₂CO₃ as the fluxes. (d) 10 µL (Run No. 4) and (e, f) 5 µL (Run No. 5) of an aqueous NaCl-Na₂CO₃ solution were used as the fluxes.
Fig. 2  XRD profiles 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; ICDD PDFs of (f) NaTaO$_3$ and (g) Ta$_3$N$_5$. (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. 3  SEM images of the crystal layers fabricated using NaCl-Na₂CO₃ 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. 4  XRD profiles of the crystal layers fabricated using NaCl-Na₂CO₃ 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). ICDD PDFs of (e) NaTaO₃ and (f) Ta₃N₅.
Fig. 5  Current-potential curves for Co-Pi/Ta₃N₅/Ta. The Ta₃N₅ crystal layer was fabricated using NaCl-Na₂CO₃ as the flux at 850 °C for 1 h (Run No. 5). The electrolyte was a 0.2 M aqueous Na₂SO₄ solution with a pH of 13, which was adjusted by adding NaOH. The photoelectrode was irradiated with a 300 W Xe lamp equipped with a cut-off filter (λ > 420 nm). The electrode potential was swept in the positive direction at a rate of 10 mV·s⁻¹.
A graphical abstract

\[ \text{Ta}_3\text{N}_5 \] crystal layers were fabricated on Ta substrates by a novel flux coating method in an \( \text{NH}_3 \) flow.