One-step synthesis of Ta$_3$N$_5$ nanorod photoanode from Ta plate and NH$_4$Cl powder for photoelectrochemical water oxidation

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**Table S2.** Synthesis processes of Ta$_3$N$_5$ photoanodes
Experimental section

Preparation of \( \text{Ta}_3\text{N}_5/\text{Ta} \)

A metal tantalum sheet (The Nilaco company) with an area of \( 25 \times 7.5 \text{ mm}^2 \) and a thickness of 0.1 mm was taken as a Ta precursor. \( \text{NH}_4\text{Cl} \) was used to provide nitrogen source for nitridation reaction. Before experiment, the \( \text{NH}_4\text{Cl} \) powder was dehydrated by heating in a muffle furnace at 473 K for 2 h in air. The tantalum sheet was sequentially cleaned in acetone, ethanol, and ultrapure water under sonication and dried in nitrogen stream. In a typical procedure, the tantalum metal sheet and 15 mg of \( \text{NH}_4\text{Cl} \) powder were put into a quartz tube (\( \Phi 8 \text{ mm} \)). Then, the tube was sealed by flame after evacuating to an approximate pressure of 1.3 Pa. The length of the filled tube was around 80 mm equaling to an inner volume of 4 cm\(^3\). The samples were heated via a two-step temperature program with maintaining at 673–733 K for 2 h in the first step and 1023–1063 K for 2 h in the second one, and finally cooled down to room temperature naturally. The heating rate is 2.5 K min\(^{-1}\). The obtained \( \text{Ta}_3\text{N}_5/\text{Ta} \) thin films were washed with ultra-pure water before usage.

Surface modification with \( \text{Co(OH)}_x \) and \( \text{Ni(OH)}_x \) on \( \text{Ta}_3\text{N}_5 \) film

Before the PEC measurement, \( \text{Co(OH)}_x \) and \( \text{Ni(OH)}_x \) were deposited sequentially on the prepared \( \text{Ta}_3\text{N}_5/\text{Ta} \) film as oxygen evolution catalysts. For the \( \text{Co(OH)}_x \) deposition, the
Ta₃N₅/Ta samples were immersed in an aqueous solution containing 0.2 M CoSO₄ and 6.28 mM NH₃·H₂O for 30 min, and then washed with copious deionized water. The Ni(OH)ₓ layer was loaded over the above Co(OH)ₓ/Ta₃N₅/Ta through an electrodeposition route, in which 0.025 M NiSO₄ solution was used as an electrolyte in an undivided cell. An applied potential of 1.16 V vs Ag/AgCl was held until the charge passed through the outer circuit reached about 25 mC cm⁻².

**Materials characterization**

The morphologies of the samples were examined using a field-emission scanning electron microscope (SEM, JEOL JSM-7800F Prime) with an energy dispersive spectrometer (EDS) detector. The crystal structures of samples were investigated by X-ray diffraction (XRD, Bruker D8 Advance) with Cu Kα radiation.

**PEC measurements of Ta₃N₅/Ta photoelectrodes**

The PEC tests were conducted in a three-electrode system with a potentiostat (Gamry, Interface 1000T) under simulated AM 1.5G solar light irradiation (100 mW·cm⁻², SAN-EI ELECTRIC, Class AAA Solar simulator). The fabricated Ta₃N₅, a platinum wire, and a Ag/AgCl (saturated potassium chloride) were used as working, counter and reference electrodes, respectively. Unless otherwise noted, 0.5 M Na₂B₄O₇ aqueous solution with pH adjusted to 13 by adding NaOH was used as an electrolyte after saturation with Ar gas.
The measured potentials were converted to V vs RHE ($E_{RHE} = E_{Ag/AgCl} + 0.244 \text{ V} + 0.059 \text{ V} \times \text{pH}$). The photocurrent was measured by linear sweep voltammetry with a scan rate of 10 mV s$^{-1}$. The light was irradiated from the front side of electrodes for all cases. Incident photon-to-current efficiency (IPCE) was measured under monochromatic light irradiation, provided by a tungsten lamp equipped with a monochromator. The light intensity was obtained using a calibrated Si photodiode.

The amount of evolved oxygen was determined through operation in a three electrode system with a potentiostat (Interface 1000T, Gamry) at a potential of 1.0 V vs RHE in a closed configuration, in which the produced gases were analyzed by an online gas chromatograph (Agilent Technologies Inc., 490 Micro GC) using a thermal conductivity detector (TCD).

**Analysis of the products**

After the calcination of the quartz tube containing Ta metal plate and NH$_4$Cl powder, the products were characterized using a Fourier-transform infrared (FTIR) instrument before the quartz tube was opened. The FTIR spectra were obtained in a transmission mode with a VERTEX 70 spectrometer by averaging 64 scans at a resolution of 2 cm$^{-1}$. After that, the quartz tube was placed inside a soft plastic tube with Ar gas continuously flowing from one end and purging into 100 ml water at the other end. After the quartz tube was broken inside the plastic tube, the pH of the water was decreased owing to dissolution of HCl. The amount of HCl was calculated based on the change of the pH value. In a similar operation, the amount of hydrogen and nitrogen in the quartz tube were detected by connecting the
plastic tube to a gas chromatograph (GC). In this case, the HCl was trapped by a 1M NaOH solution before the sampling using a GC. The experimental data are summarized in Table S1.

**Summarization of the processes of synthesizing Ta$_3$N$_5$**

Table S2 summarizes several methods typically applied to synthesizing Ta$_3$N$_5$ photoanodes. In the early research, Ta$_3$N$_5$ electrodes were fabricated by physically stacking the particle precursor on a conductive substrate (such as FTO) using paste or electrophoretic deposition (EPD), etc.\(^1\) The high resistance between particle/particle and particle/substrate seriously inhibited the charge transport on Ta$_3$N$_5$. Abe and coworkers found that a post-necking treatment resulted in improvement of the photocurrent of Ta$_3$N$_5$ electrode due to the facilitation of electron transport between electrode particles (entry 1). After that, a more efficient particle transfer (PT) method (entry 2) was developed, by which a mono-particle layer of Ta$_3$N$_5$ was directly embedded in a metal substrate to improve the conductivity.\(^2\) Both entry 1 and 2 are *ex situ* method that is the preparation and deposition of Ta$_3$N$_5$ particles are separated. An *in situ* growth of Ta$_3$N$_5$ is generally supposed to further improve the conductivity. In this case, by employing a Ta-containing conductive substrate as the precursor of nitridation, the Ta$_3$N$_5$ particles are chemically bonded to the substrate in a molecular-level (entry 3 to 9).\(^3\) As shown in table 1, the photocurrent obtained from the *in situ* growth method is averagely higher than the *ex situ* one. At present, the top two currents produced over Ta$_3$N$_5$ photoanode were reported from entry 4 and 7.\(^4,7\) Except the conductivity, morphology is another key factor in determining the activity through affecting light absorbance, bulk charge transfer efficiency, and number of reactive surface
sites, etc. Of those works related to the morphology design, TaO$_x$ nanotube and nanorod precursors were prepared by a widely applied anodization (entry 5 and 6) or a recently-reported magnetron glancing angle deposition (entry 7) technique.$^{5,6,7}$ After high-temperature nitridation in NH$_3$ flow, the nanostructures of the 1D TaO$_x$ precursor were kept in the Ta$_3$N$_5$ product. From entry 1 to 7, it can be found that the use of TaO$_x$ precursor necessitates the use of NH$_3$ and the multi-step operation during preparation of Ta$_3$N$_5$. Li’s group reported a carbonate-assisted one-step synthesis of Ta$_3$N$_5$ films (entry 8).$^8$ This method enabled the direct synthesis of high-oxidation-state metal nitride films from metal precursors under ammonia flow, and the prepared Ta$_3$N$_5$ electrode exhibited promising water splitting performance. In case of using TaO$_x$ as precursor, the temperatures for synthesizing Ta$_3$N$_5$ are generally higher than 1100 K so as to break down the Ta-O bond. Compared with the previous reports, our work (entry 9) is featured with one-step, in situ, low-temperature (ca. 200 K lower than before) and none-NH$_3$ synthesis of nanostructured Ta$_3$N$_5$ photoanode.
**Figure S1.** EDS elemental mapping images of a cross-section of the Ta$_3$N$_5$/Ta sample. The scale bars are 500 nm. **a)** BSE image, **b)** N K series, **c)** O K series, **d)** Ta K series.
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Table S1. The amount of precursors and the constituents detected after the reaction of synthesizing Ta<sub>3</sub>N<sub>5</sub> from Ta and NH<sub>4</sub>Cl.

<table>
<thead>
<tr>
<th>Precursors</th>
<th>Amount of substance (μmol)</th>
<th>The reaction products</th>
<th>Amount of substance (μmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta metal plate</td>
<td>1700 ± 100</td>
<td>HCl</td>
<td>140 ± 20</td>
</tr>
<tr>
<td>NH&lt;sub&gt;4&lt;/sub&gt;Cl powder</td>
<td>280 ± 15</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>220 ± 20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>65 ± 10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ta&lt;sub&gt;3&lt;/sub&gt;N&lt;sub&gt;5&lt;/sub&gt;</td>
<td>1 ± 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Residual NH&lt;sub&gt;4&lt;/sub&gt;Cl&lt;sup&gt;a&lt;/sup&gt;</td>
<td>140 ± 20</td>
</tr>
</tbody>
</table>

<sup>a</sup>the amount was obtained by subtracting the amount of HCl from the NH<sub>4</sub>Cl precursor
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Table S2 Synthesis processes of Ta₃N₅ photoanodes

<table>
<thead>
<tr>
<th>Entry</th>
<th>Synthesis processes</th>
<th>Total steps</th>
<th>NH₃ flow (mL min⁻¹)</th>
<th>Temp. (k)</th>
<th>In/ex situ</th>
<th>J_{phot} (mA cm⁻²) at 1.23 V_RHE</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1ᵃ</td>
<td>Ta₂O₅ (\xrightarrow{NH_3}) Ta₃N₅ (\xrightarrow{EPD, necking}) Ta₃N₅/FTO</td>
<td>2</td>
<td>500</td>
<td>1123</td>
<td>ex situ</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>2ᵇ</td>
<td>Ta₂O₅ (\xrightarrow{PT}) Ta₃N₅ (\xrightarrow{sputter}) Ta₃N₅/Ta/Ti</td>
<td>2</td>
<td>100</td>
<td>1173</td>
<td>ex situ</td>
<td>3.5</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>Ta (\xrightarrow{sputter}) TaOₓ (\xrightarrow{NH_3}) Ta₂N₅/Ta</td>
<td>2</td>
<td>100</td>
<td>1113</td>
<td>in situ</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>Ta (\xrightarrow{Hydrothermal}) NaTaOₓ (\xrightarrow{NH_3}) Ta₃N₅/Ta</td>
<td>2</td>
<td>250</td>
<td>1223</td>
<td>in situ</td>
<td>12.1</td>
<td>4</td>
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<tr>
<td>5ᶜ</td>
<td>Ta (\xrightarrow{Anodization}) Ta₂O₃ nt/Ta (\xrightarrow{NH_3}) Ta₃N₅ nt/Ta</td>
<td>2</td>
<td>100</td>
<td>973</td>
<td>in situ</td>
<td>—</td>
<td>5</td>
</tr>
<tr>
<td>6ᵈ</td>
<td>Ta (\xrightarrow{sputter}) Ta₂O₅ nr/Ta (\xrightarrow{NH_3}) Ta₃N₅ nr/Ta</td>
<td>4</td>
<td>10</td>
<td>1273</td>
<td>in situ</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>7ᵈ</td>
<td>Ta (\xrightarrow{Vacuum heating}) CO₂ + NH₃ (\xrightarrow{Vacuum heating}) Ta₂O₅ nr/Ta (\xrightarrow{Vacuum heating}) Ta₃N₅ nr/Ta</td>
<td>2</td>
<td>250</td>
<td>1253</td>
<td>in situ</td>
<td>9.95</td>
<td>7</td>
</tr>
<tr>
<td>8</td>
<td>Ta (\xrightarrow{Annealing}) Ta₃N₅/Ta</td>
<td>1</td>
<td>250</td>
<td>1173</td>
<td>in situ</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>9ᵈ</td>
<td>Ta+NH₄Cl (\xrightarrow{Vacuum heating}) Ta₃N₅ nr/Ta</td>
<td>1</td>
<td>No</td>
<td>953</td>
<td>in situ</td>
<td>3.2</td>
<td>This work</td>
</tr>
</tbody>
</table>

(ᵃEPD: Electrophoretic deposition,ᵇPT: Particle transfer,ᶜnt: Nanotube,ᵈnr: Nanorod,ᶜUnder AM 1.5 solar simulator)
References