Effects of interfacial layers on the photoelectrochemical properties of tantalum nitride photoanodes for solar water splitting†

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This work describes the effects of interlayers on the structural, crystalline and photoelectrochemical properties of Ta₃N₅ photoanodes. Nb₅N₅ interlayers with different thicknesses are formed between Ta₃N₅ films and Ta back substrates using a thin film transfer method. Zone-axis images and electron diffraction patterns of cross-sections of the resulting Ta₃N₅/Nb₅N₅/Ta/Ti electrodes acquired by transmission electron microscopy evidence the formation of a 200 nm thick oriented Ta₃N₅ grain layer in the vicinity of the interlayer. This oriented Ta₃N₅ layer promotes electron transport throughout the Ta₃N₅ film. As a result, a Ta₃N₅ photoanode incorporating a Nb₅N₅ interlayer exhibits a higher photocurrent during the oxygen evolution reaction. These results obtained using the Ta₃N₅/interlayer/substrate configuration elucidate the key role played by the buffer layer in achieving efficient water splitting with Ta₃N₅ photoelectrodes.

Introduction

Photoelectrochemical (PEC) water splitting is a process used to store solar light energy via the formation of hydrogen. Ta₃N₅, an n-type semiconductor, has been widely applied as a photoanode for the PEC oxygen evolution reaction (OER). With a bandgap of 2.1 eV, Ta₃N₅ absorbs visible light up to 600 nm (ref. 4) and can potentially yield a maximum photocurrent of 12.5 mA cm⁻² under irradiation by sunlight (AM 1.5G).

Photoanodes are typically prepared as either thin films, nanostructures (such as nanorods and nanotubes) or particulate layers. In addition, doping, surface modification and other strategies have been applied to achieve high photocurrents and negative onset potentials during PEC water oxidation. Theoretical studies have indicated that Ta₃N₅ is an anisotropic semiconductor material in which holes are heavier than electrons, resulting in low mobility of the minority charge carriers (i.e., the holes), while the porosity of the Ta₃N₅ layer in a Ta₃N₅ photoanode is believed to limit the bulk transport of the majority charge carriers (electrons). Controlling both the structure and crystallinity of Ta₃N₅ films is a critical aspect of improving the PEC performance of this material because these parameters significantly affect the charge separation efficiency as well as the light absorption of the Ta₃N₅.

Studies on the growth of GaN films suggest that a GaN or AlN buffer layer will generate high crystalline quality in the upper GaN film and a similar effect is anticipated in the case of Ta₃N₅ film growth. In order to fabricate semiconductor/conductor configurations for use as photoelectrodes, Ta₃N₅ films are generally grown on conductive substrates, such as metallic Ta foils or Pt, by nitridation under a flow of NH₃ gas and at high temperatures (800–1000 °C). To date, Ta₃N₅ photoanodes with state-of-the-art PEC performance have been fabricated on Ta foil substrates. However, an impurity interlayer consisting of TaN phases is inevitably formed between the Ta₃N₅ film (or nanorods and nanotubes) and the underlying Ta foil during the nitridation process. The effects of this interlayer on electron transport in the Ta₃N₅ film and at the Ta₃N₅/TaN interface are expected to alter the PEC performance of Ta₃N₅ photoanodes.

In the present work, the effects of interlayers on the growth of Ta₃N₅ films and on the PEC performance of Ta₃N₅ photoanodes were assessed by introducing a niobium nitride (NbN₅) layer at the interface between the Ta₃N₅ film and the conductive substrate by a thin film transfer technique. Inert Si wafers were used as synthesis platforms for the formation of the NbN₅ and Ta₃N₅ bilayer films. After the film transfer process, the NbN₅ surface layer acted as a back contact to conduct photogenerated electrons...
from the Ta$_3$N$_5$ film to the back conductive layer, and the introduction of a NbN$_x$ interlayer was found to enhance the photocurrent of the Ta$_3$N$_5$ photoanodes. The growth mechanism of the Ta$_3$N$_5$ films in the presence of the NbN$_x$ layer and the effects of the interlayer on the structural, crystalline and PEC properties of the Ta$_3$N$_5$ films are discussed based on the results of this study.

**Experimental section**

**Sample preparation**

A NbN$_x$ layer was introduced as an interlayer between Ta$_3$N$_5$ and a conductive substrate using a film transfer process, as depicted in Fig. 1. The sections of a single-crystal Si (100) substrate (1 × 1 cm, Nilaco) were cleaned by sequential ultrasonic irradiation and the resulting multi-layered films were sequentially deposited on the Si substrates by radio frequency (RF) magnetron sputtering (ULVAC, MNS-2000-RFG3) and the resulting multi-layered films were oxidized in a muffle furnace at 700 °C for 2 h with a temperature ramp rate of 15 °C min$^{-1}$. The Nb$_2$O$_5$/Ta$_2$O$_5$/Si samples fabricated in this manner were subsequently moved to a tube furnace and nitrided in a flow of NH$_3$ gas (100 sccm) at 900 °C for 2 h with a temperature ramp rate of 20 °C min$^{-1}$, forming a nitride bilayer on the Si substrates. To transfer these nitride films onto a conductive substrate, metallic Ta (150 nm) and Ti (approximately 5 μm) layers were sequentially deposited on the NbN$_x$/Ta$_3$N$_5$/Si sample by RF magnetron sputtering, serving as the contact and conductive layers, respectively. Because the physical contact between the Ta$_3$N$_5$ film and the Si substrate was weakened by the strain imparted upon adding the metallic Ta/Ti layers, the Ti/Ta/NbN$_x$/Ta$_3$N$_5$ films were readily peeled away from the underlying Si substrate using carbon tape supported with glass slides. For comparison purposes, a Ta$_3$N$_5$/Ta/Ti film without a NbN$_x$ interlayer was synthesized in the same manner. The electrode areas exposed to the electrolyte solution were approximately 0.2 cm$^2$. Each of the Ta$_3$N$_5$ films used in this work was 630 nm thick, while the thickness of the NbN$_x$ layer varied from 50 to 200 nm.

**Characterization**

Scanning electron microscopy (SEM, S-4700, Hitachi), transmission electron microscopy and scanning transmission electron microscopy (TEM, STEM, JEM-2800, JEOL) with energy dispersive X-ray fluorescence spectroscopy (EDX, EX-24055GT, JEOL) were used to characterize the morphologies and structures of the thin films. Samples for cross-sectional SEM and STEM assessments were prepared by ion milling and focused ion beam (FIB) milling, respectively. X-ray diffraction (XRD) patterns were recorded using an X-ray diffractometer (Rigaku Ultima III) with Cu Kα radiation (λ = 0.15405 nm, 40 mA and 40 mA). The average crystallite size in the Ta$_3$N$_5$ films (n = 3, ±σ) was calculated using the Scherrer equation. X-ray fluorescence spectroscopy (XPS, JEOL, JPS-90SX) was performed using Mg Kα radiation (8 kV and 10 mA), employing the C 1s peak at 284.8 eV as an internal standard to calibrate the binding energies.

**Electrochemical measurement**

Prior to the PEC measurements, each Ta$_3$N$_5$ photoelectrode was deposited with a thin layer of Co(OH)$_2$, using an impregnation method. This was accomplished by adding an aqueous NaOH solution (50 mM, 2.5 mL) to an aqueous Co(NO$_3$)$_2$ solution (6.3 mM, 10 mL) and immersing the Ta$_3$N$_5$ electrodes in the mixture for 1 h. The PEC properties of the Ta$_3$N$_5$ photoanodes were measured using a three-electrode cell with a Ag/AgCl reference electrode (in saturated aqueous KCl) and Pt wire as the counter electrode. The Ag/AgCl reference potential was converted to the reversible hydrogen electrode (RHE) potential according to the Nernst relationship

\[
E (V \text{ vs. RHE}) = E (V \text{ vs. Ag/AgCl}) + 0.059 \times \text{pH} + 0.197 \tag{1}
\]

where 0.197 represents the standard potential of the KCl-saturated Ag/AgCl electrode at 25 °C. An aqueous solution of potassium phosphate (KPi, 0.5 M, pH 13) was used as the electrolyte. During these trials, the Ta$_3$N$_5$ photoelectrodes were illuminated by using a chopped AM 1.5G solar simulator (San-EI Electric, XES-4052-CE). Linear-sweep voltammetry (LSV) was employed, scanning from 1.5 to 0 V vs. RHE to evaluate the photocurrent density and onset potential. The photocurrent decay of each Ta$_3$N$_5$ photoelectrode was examined in the chronoamperometric mode at 1.0 V vs. RHE. Evolved gaseous H$_2$ and O$_2$ were simultaneously collected in an air-tight cell and quantified using a micro gas chromatograph (Agilent, 3000A, Micro GC) to calculate the faradaic efficiency.

The incident photon-to-current conversion efficiency (IPCE) was measured under monochromatic irradiation from a Xe lamp (MAX-302, Asahi Spectra) in a 0.5 M KPi electrolyte. The wavelength-dependent IPCEs were calculated using the equation

\[
\text{IPCE} = 1240 \times \left( I_{\text{light}} - I_{\text{dark}} \right)(\lambda \times P_{\text{input}}) \times 100\% \tag{2}
\]

where λ (nm) is the wavelength of the monochromatic irradiation, $I_{\text{light}}$ (mA cm$^{-2}$) is the chronoamperometric photocurrent density, $I_{\text{dark}}$ (mA cm$^{-2}$) is the dark current density and $P_{\text{input}}$ is the input power.
(mW cm\(^{-2}\)) is the incident photon density as determined by using a Si photodiode detector.

To compare the relative electrochemically active surface areas and roughness factors of different Ta\(_3\)N\(_5\) photoelectrodes, the scan-rate dependencies of cyclic voltammograms were estimated according to a previously reported method.\(^{26}\) All of the electrodes were tested at different scan rates, varying from 5 to 300 mV s\(^{-1}\), with a capacitive current estimated at \(-0.1\) V vs. Ag/AgCl. Mott–Schottky measurements were performed in a 0.5 M KPi electrolyte at a frequency of 1000 Hz with an AC amplitude of 10 mV, using an impedance analyzer (METEK, VersaSTAT3-200). The flat band potential and donor dopant density values of the Ta\(_3\)N\(_5\) photoanodes were determined according to the Mott–Schottky relationship

$$\frac{1}{C^2} = \frac{2}{ee\epsilon_0 N_D r^2} \left( E - E_{fb} - \frac{kT}{e} \right),$$

where \(C_{sc}\) (F cm\(^{-2}\)) is the space-charge capacity per surface area, \(\epsilon_0\) (C V\(^{-1}\) cm\(^{-1}\)) is the permittivity of free space, \(\epsilon\) is the dielectric constant of Ta\(_3\)N\(_5\), \(N_D\) (cm\(^{-3}\)) is the donor density, \(r\) is the roughness factor of the Ta\(_3\)N\(_5\) electrode, \(k\) (1.38 \times 10\(^{-23}\) J K\(^{-1}\)) is the Boltzmann constant, \(E\) (V vs. RHE) is the applied potential, and \(E_{fb}\) (V vs. RHE) represents the flat band potential of the Ta\(_3\)N\(_5\) electrode. The flat band potential could be derived from the x-axis intercept, while the donor density could be obtained from the slope of a Mott–Schottky plot. Electrochemical impedance spectra (EIS) were measured from 100 kHz to 0.1 Hz using an impedance analyzer under simulated AM 1.5G light in a 0.5 M KPi electrolyte. To alleviate the photocorrosion of Ta\(_3\)N\(_5\) photoelectrodes, all the samples were tested in the presence of sacrificial reagent 0.5 M SO\(_3\)^{2−} at 1.0 V vs. RHE. The obtained Nyquist plots were fitted from 100 kHz to 1 Hz with an equivalent circuit model to rule out the fluctuations at frequency lower than 1 Hz.

**Results and discussion**

**Structure and crystallinity**

A top-view SEM image of a Ta\(_3\)N\(_5\)/NbN\(_x\)/Ta/Ti sample after the thin film transfer is shown in Fig. 2(a). The surface of the Ta\(_3\)N\(_5\) film exhibits roughness originating from the porous contact at the Ta\(_3\)N\(_5\)/Si interface in the parent NbN\(_x\)/Ta\(_3\)N\(_5\)/Si sample. The possible exposure of the NbN\(_x\) interlayer to the film surface is ruled out by the XPS data obtained from the Ta\(_3\)N\(_5\)/NbN\(_x\)/Ta/Ti film, as shown in Fig. S1.† In addition, the absence of Ta species on the surface of the parent NbN\(_x\)/Ta\(_3\)N\(_5\)/Si sample suggests that the Ta\(_3\)N\(_5\) film was not in direct contact with the underlying metallic substrate. The layered structure of the Ta\(_3\)N\(_5\)/NbN\(_x\)/Ta/Ti sample is clearly observed in the cross-sectional SEM image presented in Fig. 2(b). Here, the NbN\(_x\) layer is evident as a region of darker contrast, with a thickness of approximately 100 nm. In the magnified view, a porous structure is observed throughout the Ta\(_3\)N\(_5\)/NbN\(_x\) film, due to the oxidation of the metallic film and the substitution of O\(^{2−}\) ions by N\(^{3−}\) ions during the nitridation process, just as occurs during the nitridation of Ta\(_2\)O\(_5\) powder to Ta\(_3\)N\(_5\). Despite its porous structure, the NbN\(_x\) layer is in intimate contact with the Ta\(_3\)N\(_5\) film and the Ta contact layer. The EDX mapping images (Fig. 3) demonstrate that the distribution of Nb was confined to the interlayer region, so there was no appreciable doping of Nb into the Ta\(_3\)N\(_5\) film.

**Fig. 2** (a) Top-view and (b) cross-sectional SEM images of a Ta\(_3\)N\(_5\)/NbN\(_x\)/Ta/Ti film. The scale bars are (a) 5 µm, (b) 500 nm, and 100 nm for the zoomed image.

**Fig. 3** (a) Cross-sectional STEM image of a Ta\(_3\)N\(_5\)/NbN\(_x\)/Ta/Ti film and (b)–(e) EDX elemental mappings of the image in (a). All scale bars are 500 nm.

**Fig. 4** XRD patterns of (a) Ta\(_3\)N\(_5\)/Si, (b)–(d) NbN\(_x\)/Ta\(_3\)N\(_5\)/Si with NbN\(_x\) thicknesses of (b) 50, (c) 100, and (d) 200 nm, and (e) NbN\(_x\) (100 nm)/Si samples. XRD patterns of NbN\(_x\) (PDF# 74-0606) and Ta\(_3\)N\(_5\) (PDF# 79-1533) are presented at the bottom and the top, respectively, as references.
Fig. 4 presents the XRD patterns of NbN_x/Ta_3N_5/Si samples with different NbN_x thicknesses prior to the thin film transfer, as a means of confirming the nitridation products. A Ta_3N_5 phase was evidently formed regardless of whether a NbN_x layer was present or not. In addition, impurity phases such as TaN_x or SiN_x were absent. The diffraction pattern of the NbN_x layer deposited on a Si substrate (Fig. 4(e)) suggests that NbN_x was the main phase formed in the NbN_x/Ta_3N_5/Si sample, although the crystallinity of this specimen was low, and the diffraction peaks of the (101) and (211) planes of the Nb_4N_5 overlap with those generated by the (110) and (113) planes of the Ta_3N_5 at 24.4° and 36.0°, respectively. A peak attributable to NbN_x (x ≤ 1) was also detected at 34.0° when the thickness of the NbN_x layer was at its maximum (200 nm). Nevertheless, the XRD peaks obtained from the NbN_x/Ta_3N_5/Si primarily provide information regarding the Ta_3N_5 phase because the Ta_3N_5 peaks are much stronger than those generated by the Nb_4N_5 and other NbN_x phases. It should also be noted that NbN_x was not observed, as expected because Nb^{5+} is prone to reduction to Nb^{4+} or lower-valence nitride species.²⁷

The crystallite sizes of the Ta_3N_5 films were calculated from the (110) diffraction peak at 24.4°. The data in Table 1 demonstrate that each of the Ta_3N_5 films had almost identical average crystallite sizes, in the range of 40–45 nm. Thus, the effect of the NbN_x layer on the crystallite size in the Ta_3N_5 film was not significant. Notably, the intensity ratio (K_m) obtained from the peaks at 24.4° and 36.0°, which correspond to the (110) and (113) planes of Ta_3N_5, decreased from 2.4 to 0.5–0.8 when NbN_x layers were present on the Ta_3N_5 films.

The crystalline growth of each Ta_3N_5 film was examined in detail by acquiring cross-sectional TEM images of Ta_3N_5/NbN_x films (Fig. 5). These bright field (BF) zone-axis TEM images provide a clear view of the multi-layered structure of the Ta_3N_5/NbN_x/Ta samples, and the bright spots scattered within the darker contrast can provide information regarding the sizes and boundaries of individual grains. In Fig. 5(a) and (b), a high density of bright spots is observed throughout the 100 nm-thick NbN_x interlayer, suggesting that the grain size of the NbN_x phase was much less than the layer thickness of 100 nm (likely below 10 nm). This result agrees with the low-crystalline NbN_x phase indicated by the XRD patterns in Fig. 4. Notably, the Ta_3N_5 region close to the Ta_3N_5/NbN_x interface generated fewer bright spots when over 200 nm in thickness, as shown in Fig. 5(c), indicating the presence of fewer boundaries among the Ta_3N_5 grains near the interface with the NbN_x layer, while the rest of the Ta_3N_5 film exhibited a number of bright spots.

Selected area electron diffraction (SAED) patterns taken from the regions at 100 nm to the film surface and 100 nm to the Ta_3N_5/NbN_x interface are displayed in the insets of Fig. 5(b) and (c), respectively. The Ta_3N_5 near the interface with the NbN_x generated a more ordered diffraction pattern compared to the Ta_3N_5 close to the surface, which was characterized by random diffractions. This finding indicates that the arrangement of the Ta_3N_5 grains was well oriented in the vicinity of the NbN_x interlayer. It should be noted that crystallite orientation was not observed at the interface between the Ta_3N_5 film and the Ta/Ti substrate of the Ta_3N_5/Ta/Ti film without a NbN_x interlayer, as seen in Fig. S2.†

As suggested by the SAED pattern, the formation of a highly oriented 200 nm Ta_3N_5 layer is not continuous throughout the entirety of the 630 nm Ta_3N_5 film. The growth mode of the Ta_3N_5 film in the presence of the NbN_x interlayer appears to be consistent with that observed for Ta_3N_5 films directly grown on Ta foil substrates by thermal nitridation, as reported by Pinaud et al.⁴⁸ The electrochemically active surface areas (ECSAs) of the Ta_3N_5 films fabricated by Pinaud’s group were found to exhibit minimal change up to a film thickness of 260 nm due to the growth of a compact Ta_3N_5 film. However, the ECSA increased by one or two orders of magnitude when the film thickness was increased from 260 to 630 nm, owing to the growth of disordered layers over top of the compact Ta_3N_5 films. The formation of an oriented Ta_3N_5 layer was also observed in the present Ta_3N_5 films grown on Ta foil substrates (Fig. S3†). Therefore, it is believed that both Ta_3N_5 films grown on Ta substrates and films nitrided in contact with a NbN_x interlayer have similar growth mechanisms, presumably involving Ta_3N_5 and NbN_x with the same crystal structures⁴⁸,²⁹ acting as interlayers, respectively.

Table 1: Average crystallite sizes in Ta_3N_5 films with different NbN_x layer thicknesses, as estimated from XRD peaks at 24.4°, as well as the ratios of the (110) and (113) diffraction intensities of the peaks at 24.4° and 36.0°.

<table>
<thead>
<tr>
<th>NbN_x thickness (nm)</th>
<th>Crystallite size (nm)</th>
<th>Peak intensity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>42.6 ± 1.8</td>
<td>2.4 ± 0.2</td>
</tr>
<tr>
<td>50</td>
<td>44.3 ± 1.8</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td>100</td>
<td>41.8 ± 4.4</td>
<td>0.7 ± 0.2</td>
</tr>
<tr>
<td>200</td>
<td>42.0 ± 2.7</td>
<td>0.8 ± 0.1</td>
</tr>
</tbody>
</table>

Fig. 5: (a) Zone-axis TEM images of the cross-section of a Ta_3N_5 film on a Ta/Ti substrate with a NbN_x interlayer. The region (200 nm thick) within the white dashed lines represents the oriented Ta_3N_5 layer. SAED patterns of Ta_3N_5 crystallinites near (b) the surface of the Ta_3N_5 film, and (c) the interface of the Ta_3N_5/NbN_x. The insets are diffraction patterns from the selected regions highlighted by the circles. All scale bars are 200 nm.
Photoelectrochemical properties

Current–potential curves obtained from the Ta$_3$N$_5$ film photoelectrodes deposited with a layer of Co(OH)$_2$ as an OER catalyst are shown in Fig. 6(a). In the absence of the NbN$_x$ interlayer, the Ta$_3$N$_5$ photoelectrode exhibited an anodic photocurrent of approximately 2.0 mA cm$^{-2}$ at 1.23 V vs. RHE. The photocurrent densities increased significantly for the Ta$_3$N$_5$ films with NbN$_x$ interlayers 50–100 nm in thickness. However, the higher resistance of the NbN$_x$ (Nb$_4$N$_5$) interlayer compared to that of the metallic Ta substrate lowered the electron mobility. As a result, the photocurrent decreased as the thickness of the NbN$_x$ interlayer increased from 100 to 200 nm. Moreover, the onset potential of the photoanodic current generated by the Ta$_3$N$_5$/NbN$_x$ (100 nm)/Ta/Ti electrode shifted cathodically by 0.1 V from 0.9 V vs. RHE relative to the Ta$_3$N$_5$/Ta/Ti electrode. The NbN$_x$ (Nb$_4$N$_5$ or NbN) phase acts as a conductive contact for the transport of the majority charge carriers (electrons) collected from the Ta$_3$N$_5$ film.

To confirm that the enhancement of the photocurrent of Ta$_3$N$_5$/NbN$_x$ photoanodes is associated with the PEC water oxidation performance, gaseous H$_2$ and O$_2$ evolved at the counter electrode and the photoanode at 1.0 V vs. RHE were analyzed using a micro gas chromatograph (Fig. 6(b)). It was confirmed that the amounts of H$_2$ and O$_2$ were virtually equal to the values calculated based on the total charge passed through the system. In addition, the ratio of H$_2$ to O$_2$ was close to 2 : 1. These results indicate that the faradaic efficiency during the OER process was unity when employing the Ta$_3$N$_5$/NbN$_x$ photoanode. However, the gas evolution rates decreased in accordance with changes in the photocurrent over time, as can be seen in Fig. 6(c). The decreased photocurrent and O$_2$ evolution rate likely resulted from dissolution of the Co-based catalysts from the surface of the Ta$_3$N$_5$ film into the electrolyte solution. The loss of the Co-based catalyst led to direct exposure of the Ta$_3$N$_5$ film to the electrolyte solution, and consequently to gradual degradation of the photoanode because bare Ta$_3$N$_5$ photoanodes are prone to photocorrosion. A uniform coverage of the Ta$_3$N$_5$ electrode with protective and catalytic layers is likely to stabilize the photocurrent. In addition, the Co-based catalyst can be replaced by other oxygen-evolution catalysts (e.g. NiO$_2$), which are electrochemically stable against the dissolution under alkaline conditions.

The IPCE spectra shown in Fig. 7 are consistent with the increases in photocurrent densities brought about by the NbN$_x$ interlayers (see Fig. 6(a)). The onset of a photoresponse at 600 nm corresponds to the direct band gap of Ta$_3$N$_5$ at 2.1 eV. It should be noted that a shoulder is observed at 500 nm in each of the IPCE plots. This is also ascribed to the direct transition of Ta$_3$N$_5$ between the N 2p and Ta 5d states, as was suggested by earlier optical and theoretical studies of Ta$_3$N$_5$ films. The IPCEs of Ta$_3$N$_5$/NbN$_x$ photoelectrodes at 400–550 nm were evidently increased compared to the bare Ta$_3$N$_5$ photoelectrode. Because less than 5% of light can traverse through the Ta$_3$N$_5$ film to the NbN$_x$ interlayer below 550 nm (see Fig. S4†), it is unlikely that the photoresponse of the Ta$_3$N$_5$/NbN$_x$ electrode was affected by the light absorption characteristics of the NbN$_x$ interlayer and the Ta$_3$N$_5$/NbN$_x$ interface. Therefore, it is thought that the enhancements in the IPCE and the photocurrent density of the Ta$_3$N$_5$/NbN$_x$ photoelectrodes are primarily due to the changes in the structural features of the Ta$_3$N$_5$ film induced by the NbN$_x$ interlayer.

![Fig. 6](image_url)  
**Fig. 6** (a) Current–potential curves obtained from Ta$_3$N$_5$/Ta/Ti and Ta$_3$N$_5$/NbN$_x$/Ta/Ti photoelectrodes with different NbN$_x$ interlayer thicknesses. (b) Hydrogen and oxygen gas evolution with respect to the total charge passed, as calculated from the (c) current–time curve obtained from the Co(OH)$_2$/Ta$_3$N$_5$/NbN$_x$ (100 nm)/Ta/Ti photoelectrode held at 1.0 V vs. RHE. The PEC activities and gas evolution were assessed in a 0.5 M potassium phosphate solution (pH 13) under simulated AM 1.5G light.

![Fig. 7](image_url)  
**Fig. 7** IPCE spectra of Ta$_3$N$_5$/Ta/Ti and Ta$_3$N$_5$/NbN$_x$/Ta/Ti photoelectrodes with different NbN$_x$ interlayer thicknesses.
Charge separation and transport

In the PEC water oxidation process, light harvesting, charge separation and transport, and hole injection are the three key processes that define the PEC activity and IPCE. The light harvesting of the Ta3N5 films would not be expected to have been altered by the NbNx interlayers because the film thickness and crystallite size were unchanged. It is also believed that the hole injection process was not affected by the presence of the interlayer because of the similarities in the roughness factors, flat band potentials, and donor densities. ECSA values were estimated from the double-layer charging in the cyclic voltammograms (CVs) as a means of examining the surface roughness of the Ta3N5 electrodes (Fig. S5†), and the roughness factor was found to be barely changed by the presence of the NbNx interlayer. Mott–Schottky plots (Fig. S6†) were used to estimate the flat band potentials and the carrier densities, with values of −0.06 and −0.08 V vs. RHE, respectively. Hence, charge separation and transport are evidently the major factors contributing to the enhancement of the photocurrent by the NbNx interlayer. Electrochemical impedance spectra (EIS) of Ta3N5 and Ta3N5/NbNx electrodes are shown in Fig. 8. The Nyquist plots with a feature of single capacitance were fitted using the Randles equivalent circuit model, similar to the case for hematite photoanodes in the presence of [Fe(CN)6]3−/4− redox couples.33 This equivalent circuit consists of the series resistance (Rs) of the NbNx and Ta/Ti layers, the capacitance of the bulk Ta3N5 film (CPE), and the charge transfer resistance from the valence band of Ta3N5 to the solution (RCT), which may be associated with resistances representing bulk recombination and charge transfer at the electrolyte/semiconductor interface. The values of the charge transfer resistance (RCT, Table S1†) of all the Ta3N5/NbNx photoelectrodes were smaller than that of the unmodified Ta3N5 photoelectrode although the surface reaction was the same, oxidation of sulfite ions on the Ta3N5 surface. This result suggests an increase in the population of holes that survive recombination with electrons and successfully reach the semiconductor/liquid junction as a result of promotion of charge separation and transport processes by the NbNx interlayers. The Rs increased with the thickness of the NbNx layer because of its lower conductivity. However, the contribution of Rct to the total resistance is negligible.

Two charge generation and transport scenarios can be considered, depending on whether photons are absorbed near the Ta3N5 film surface (case i) or the Ta3N5/NbNx interface (case ii), as depicted in Fig. 9. Long-distance electron transport and short-distance hole transport occur in the former case (i) while long-distance hole transport and short-distance electron transport take place in the latter case (ii). The analysis of the integrated photocurrent calculated on the basis of the standard AM 1.5G (ASTM G173-03) spectrum and the IPCE spectra (Fig. S7†) indicates that the short-wavelength light absorbed near the Ta3N5/NbNx electrode surface showed a larger contribution to the enhancement in photocurrent than the long-wavelength light absorbed near the Ta3N5/NbNx interface. The formation of an oriented Ta3N5 layer (200 nm thick) by the NbNx interlayer probably promotes the electron mobility in the Ta3N5 film near the Ta3N5/NbNx interface. Therefore, photogenerated charges near the surface may contribute to the PEC water oxidation more effectively in the presence of a NbNx interlayer, given that the migration distance required for holes to reach the surface is shorter in a disordered Ta3N5 layer. Nevertheless, it should be pointed out that the photons absorbed near the Ta3N5/NbNx interface are not necessarily utilized efficiently even in the presence of a NbNx interlayer because holes generated deeper in the Ta3N5 film have a higher probability of recombining with electrons before reaching the surface, since the hole mobility is lower than the electron mobility.36 As a consequence, the photocurrent observed in the present study was still lower than the maximum theoretical value for Ta3N5, so it is most likely necessary to tune the thicknesses of the oriented and disordered Ta3N5 layers.

A photoanode configuration consisting of a lower oriented Ta3N5 layer and an upper disordered Ta3N5 layer represents a combination of a short migration distance for photoexcited holes and efficient electron transport toward the back conductor layer. The introduction of the NbNx interlayer effectively realizes this ideal photoanode configuration and thus enhances the PEC performance. This result suggests that the structural and PEC properties of Ta3N5 photoanodes can be improved by designing appropriate interlayers, regardless of the nitridation of the Ta3N5 film and the particular back conductor material employed. The
film transfer method developed in this study presents a means of studying such aspects owing to the controllability of the thickness and the stacking order of multilayers.

Conclusions

NbN layers principally consisting of Nb4N5 were introduced as interlayers between Ta3N5 films and the back substrate, using the film transfer method. The Nb4N5 interlayer did not change the phase purities and the crystallite sizes of the Ta3N5 films significantly, although the preference in the crystalline orientation of the Ta3N5 film was enhanced by the Nb4N5 phase. The photocurrents obtained from Ta3N5 photoelectrodes during the PEC water oxidation reaction increased significantly in the presence of the NbN layers. The results of zone-axis imaging and electron diffraction from cross-sectional TEM revealed that ordered growth of the Ta3N5 film occurred and a 200 nm layer of highly grain-oriented Ta3N5 was formed near the Ta3N5/NbN interface. The formation of an oriented Ta3N5 layer did not affect the ECSA, flat band potential or carrier density of a 630 nm Ta3N5 film. The increased photocurrent associated with the presence of a NbN interlayer is primarily attributed to the increased long distance electron mobility in the Ta3N5 film. The film growth on the NbN layers observed in this work demonstrates the key roles of a buffer layer in the design and synthesis of efficient Ta3N5 photoelectrodes.

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References