3D interconnected nanoporous Ta₃N₅ films for photoelectrochemical water splitting: thickness-controlled synthesis and insights into stability

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ABSTRACT Solar-driven photoelectrochemical (PEC) water splitting is a promising technology for sustainable hydrogen production, which relies on the development of efficient and stable photoanodes for water oxidation reaction. The thickness and microstructure of semiconductor films are generally crucial to their PEC properties. Herein, three-dimensional (3D) interconnected nanoporous Ta₃N₅ film photoanodes with controlled thickness were successfully fabricated *via* galvanostatic anodization and NH₃ nitridation. The porous Ta₃N₅ nanoarchitectures (NAs) of 900 nm in thickness showed the highest PEC performance due to the optimal light-harvesting and charge separation. Compared with the hole-induced photocorrosion, the electrochemical oxidation at high anodic potentials resulted in severer performance degradation of Ta₃N₅. Although the surface oxide layer on deteriorated Ta₃N₅ photoanodes could be removed by NH₃ re-treatment, the PEC performance was only partially recovered. As an alternative, anchoring a dual-layer Co(OH)₂/CoOOH co-catalyst shell on the porous Ta₃N₅ NAs demonstrated substantially enhanced PEC performance and stability. Overall, this work provides reference to controllably fabricate 3D nanoporous Ta₃N₅-based photoanodes for efficient and stable PEC water splitting *via* optimizing the light absorption, hole extraction, charge separation and utilization.

Keywords: Ta₃N₅, 3D interconnected porous nanoarchitectures, thickness-controlled synthesis, photoelectrochemical water splitting, photostability

INTRODUCTION

Semiconductor photoelectrochemical (PEC) water split-

ting has been regarded as a promising way to directly convert solar energy into storable clean fuels, which is greatly significant for alleviating the world-wide environmental and energy problems [1,2]. To meet the minimum solar-to-hydrogen (STH) conversion efficiency of 10% for commercial applications, various kinds of the state-of-the-art PEC tandem cells have been designed [2], and a key and challenging task is to develop the efficient and stable photoanodes for oxygen evolution reaction (OER) under sunlight irradiation [3–5]. Tantalum nitride (Ta₃N₅) is a promising n-type semiconductor photoanode for solar-driven PEC overall water splitting due to its relatively narrow band gap of 2.1 eV, suitable band edges straddling the water redox potentials and a theoretical maximum STH efficiency of up to 15.9% [3,6]. However, the practical application of Ta₃N₅ photoanodes is hindered by their unsatisfactory photostability and low photoconversion efficiency due to poor electrical mobility (<4.4 cm² V⁻¹ s⁻¹) and fast carrier recombination (<10 ps) [7–10].

In recent years, many attempts have been devoted to improving the PEC performance of Ta₃N₅ photoanodes, including nanostructure design, metal ion doping, surface modification, interface engineering and heterojunction construction [3–5,10–15]. It should be noted that the thickness of semiconductor film also has significant influence on its PEC performance [16–20]. More specifically, a thicker photoelectrode film usually results in poorer charge-transfer ability and more possibility of charge recombination, while the ultra-thin film shows low light-harvesting efficiency due to light reflection and

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scattering. Thus, the PEC performance can be inherently optimized by thickness regulation to reach the balance between charge separation and light absorption efficiency. For example, Feng *et al.* [17] found that the optimal thickness of Ta₃N₅ nanotubular films for PEC water splitting was 240 nm, and the thicker films (750 nm and 6 μ m) showed much lower PEC performance due to the longer electron migration path and increased charge recombination rate. Wang *et al.* [18] proposed a controlled film-transfer method to fabricate the interlayer-free Ta₃N₅/Ta/Ti photoanode whose PEC activity decreased with the Ta₃N₅ thickness increasing from 570 to 1620 nm. Unfortunately, much thinner Ta₃N₅ films could not be obtained by this strategy. Pinaud and co-workers [19] prepared Ta₃N₅ films with varied thicknesses *via* the direct thermal oxidation and nitridation of Ta foils, whereas such Ta₃N₅ photoanodes usually exhibited lower PEC performance than the nanostructural film counterparts [11]. Besides, owing to the bulk stresses induced by the thermal treatment and density difference among Ta, Ta₂O₅ and Ta₃N₅ [19,21], the excessively thick and compact Ta₃N₅ films will exhibit poor structural adherence to the substrates, which greatly inhibits the interfacial electron transport to counter electrode for hydrogen evolution reaction (HER). To solve this issue, constructing porous microstructure has emerged as an effective route [22]. Meanwhile, it can reduce photon scattering, facilitate surface reactions and serve as good support for co-catalyst loading. Therefore, the controllable synthesis of Ta₃N₅ film photoanodes with desired thickness and porous microtexture is urgently needed for optimal light-harvesting and charge transfer/separation efficiency, but it is still challenging.

From the point of view of thermodynamics, Ta₃N₅ is susceptible to self-oxidation by photogenerated holes [8], and also the surface of Ta₃N₅ thin film tends to be partially hydrolyzed in water [9]. The above always lead to terrible performance degradation under long-term light irradiation. To overcome this issue, surface modification by OER co-catalysts was proposed and extensively investigated as an indispensable way to fabricate high-performance photoanodes [3–5,10–14]. The incorporation of water oxidation catalysts can efficiently extract photogenerated holes from Ta₃N₅, thus reducing the hole concentration on Ta₃N₅ and also suppressing the bulk recombination of charge carriers.

In this work, three-dimensional (3D) interconnected nanoporous Ta₃N₅ photoanodes with controlled film thickness were successfully fabricated by galvanostatic anodization and thermal NH₃ nitridation. The unique

porous film was constructed by numerous 1D worm-like nanorods, which is extremely beneficial for the film adherence, light absorption, charge transfer/separation and co-catalyst loading. Importantly, it was found that the electrochemical oxidation at high applied potentials resulted in a severer performance degradation of Ta₃N₅ relative to the hole-induced photocorrosion. By thermal NH₃ nitridation, the PEC responses of the used Ta₃N₅ photoanodes could be only partially recovered, whereas the *in-situ* deposited Co(OH)_x/CoOOH dual-layer co-catalyst shell on 3D Ta₃N₅ nanoarchitectures (NAs) substantially enhanced the PEC performance and stability due to the promoted hole extraction and collection, increased active sites, improved charge separation and surface reaction dynamics. This work provides a promising approach to develop high-performance photoanodes for solar-to-fuel conversion *via* microstructure tailoring and surface modification.

EXPERIMENTAL SECTION

Sample preparation

In a typical process, Ta foils (99.95%, 0.2 mm, Nilaco) were mechanically polished and then ultrasonically cleaned in acetone, ethanol and deionized (DI) water in sequence for 30 min. The clean Ta electrodes were anodized at a constant current density of 2 mA cm⁻² with a Pt sheet as the counter electrode in the electrolyte composed of 1 vol% HF (46%–48%, Wako), 95 vol% H₂SO₄ (95%, Wako) and DI water. The anodization process was monitored by a Solartron SI 1287 electrochemical interface. After that, the anodized Ta electrodes were rinsed with DI water and dried with a N₂ gun. Finally, Ta₃N₅ film photoanodes were obtained after annealing at 900°C for 2 h under NH₃ flow (20 cm³ min⁻¹) in a self-designed quartz reactor.

The thickness of anodized Ta layer (d_{Ta} , nm) can be precisely tailored *via* controlling the anodization time (t , s) according to the linear relationship between d_{Ta} and t ($d_{Ta} = 0.45 \times t$, Fig. S1). The as-obtained Ta₃N₅ samples were denoted as T-27, T-54, T-108, T-162, T-216, T-270, corresponding to the anodizing time of 1, 2, 4, 6, 8 and 10 min, respectively.

Co(OH)_x was deposited on the porous Ta₃N₅ photoanode (T-162) by a facile impregnation method. A colloidal Co(OH)_x solution was firstly prepared by mixing 0.1 mol L⁻¹ Co(Ac)₂ (> 95%, Wako) and 0.2 mol L⁻¹ NaOH (97%, Wako) solutions with a volume ratio of 1:1 under magnetic stirring. The T-162 electrode was then immersed into the Co(OH)_x colloid and maintained for

1 h. After that, the electrode (denoted as CT-162) was rinsed with DI water and dried naturally in air. Repeating the above steps could obtain a thicker co-catalyst layer, but the photoanode exhibited lower PEC performance (Fig. S2).

Characterization

X-ray diffraction (XRD) patterns were collected on a Rigaku D/MAX 2550 VB/PC diffractometer. UV-vis diffuse reflectance spectra (UV-vis DRS) were measured by Perkin-Elmer Lambda 950 UV-Vis-NIR spectrophotometer. The morphology and microstructures were characterized by scanning electron microscopy (SEM, Hitachi S-3400N), field emission scanning electron microscopy (FE-SEM, ZEISS GeminiSEM 500 and Philips XL30 FEG) and transmission electron microscopy (TEM, JEOL JEM-2100F). The energy dispersive X-ray spectroscopy (EDS) analysis was performed using an EDAX Genesis XM2 detector equipped on the TEM. X-ray photoelectron spectroscopy (XPS) analysis was conducted on a Kratos Axis Ultra DLD spectrometer.

PEC measurements

The PEC tests were performed in the three-electrode configuration using an Ag/AgCl electrode, Pt plate and Ta₃N₅ photoanodes as the reference electrode, counter electrode and working electrodes, respectively. Before the measurements, the electrolyte (1.0 mol L⁻¹ NaOH, pH 13.6) was purged with Ar gas and the working electrodes were immersed in the electrolyte for ca. 10 min until the open-circuit potential (E_{oc}) reached a steady state. A 300 W Xenon lamp (MAX-303, Asahi Spectra) equipped with a UV cutoff filter was used as the visible-light source ($\lambda > 400$ nm). The measured potentials vs. Ag/AgCl electrode ($E_{Ag/AgCl}$) were converted to the reversible hydrogen electrode scale (E_{RHE}) according to the Nernst equation: $E_{RHE} = E_{Ag/AgCl} + 0.059\text{pH} + 0.197$. Electrochemical impedance spectra (EIS) were measured at 1.23 V vs. RHE with a frequency range of 10⁵–0.1 Hz and an amplitude of 10 mV. The wavelength-dependent incident photon-to-current conversion efficiency (IPCE, %) was calculated according to the equation:

$$\text{IPCE}(\%) = \left[(1240 / \lambda) \times (J_{\text{light}} - J_{\text{dark}}) / P_{\text{light}} \right] \times 100,$$

where λ is the wavelength of incident light (nm), P_{light} is the light intensity at the specific wavelength (mW cm⁻²), J_{light} and J_{dark} are the current densities (mA cm⁻²) under light irradiation and in dark, respectively. The MAX-303 Xe lamp equipped with bandpass filters was used as the monochromatic light source. The above PEC measure-

ments were performed on the Solartron SI 1287/1260 electrochemical workstation. The cyclic voltammetry (CV) and Mott-Schottky (frequency: 500–1000 Hz; amplitude: 10 mV) curves were measured in dark on a CHI 760E electrochemical workstation using 1.0 mol L⁻¹ NaOH (98%, Admas-beta) as electrolyte. The applied bias photon-to-current efficiency (ABPE, %) was calculated using the following equation:

$$\text{ABPE}(\%) = J_{\text{ph}} (1.23 - E_{\text{app}}) \times (100 / P_{\text{solar}}),$$

where J_{ph} is the measured photocurrent density (mA cm⁻²), E_{app} is the applied potential (V vs. RHE), P_{solar} is the intensity of the simulated solar light (100 mA cm⁻²), supplied by a CEL-S500 sunlight simulator equipped with AM 1.5G filter (Beijing China Education Au-light Co. Ltd.).

RESULTS AND DISCUSSION

Phase composition and energy band structure

Fig. 1a shows the XRD patterns of the as-prepared photoanodes. The intense and sharp diffraction peaks at ca. 38.4° and 69.4° (2θ) can be indexed to cubic Ta phase (JCPDS card No. 04–0788) and the characteristic peaks of orthorhombic Ta₃N₅ phase (JCPDS card No. 79–1533) are also observed with much lower intensity, suggesting the formation of Ta₃N₅ layer adhered to Ta substrate. The relative intensity of Ta₃N₅ peaks gradually increases with the anodization time prolonged, meaning the thickening of Ta₃N₅ films. Note that T-27 shows the stronger diffraction signals of hexagonal Ta₂N (JCPDS Card No. 26–0985) than those of Ta₃N₅, which can be mainly attributed to the formation of thicker suboxide layer under Ta₂O₅ film in such a short anodization time. Interestingly, Ta₂N peaks tend to be weaker and broader with the increase of anodization time, manifesting the thinning of underlying Ta₂N layer and the thickening of Ta₃N₅ film (as illustrated in Fig. S3a). The Ta₂N interlayer is crucial to the adherence of Ta₃N₅ films to the back substrates and its higher conductivity than Ta₃N₅ can substantially facilitate electron transfer between the Ta₃N₅ film and Ta substrate, thus enhancing the PEC water-splitting performance [5,11,13,14]. As shown in Fig. S3b, the color change of the photoanode can reflect its composition evolution. The grey film corresponds to amorphous Ta₂O₅ (Fig. S4), and then it converts into crystalline Ta₃N₅ in red after NH₃ nitridation. Noticeably, no obvious orange or red color can be seen on T-27 and T-54 (Fig. S3c), probably associated with the rather thin Ta₃N₅ films and the color interference from the underlying

Ta₂N/Ta substrates. As displayed in Fig. 1b, the UV-vis DRS of Ta₃N₅ photoanodes show a characteristic visible-light absorption band in the range of 400–600 nm, consistent with the previous studies [11,15,17,20,23]. Notably, the absorption edges steepen gradually with the increase of film thickness, indicating an enhanced light-harvesting ability. In general, the stronger light absorption efficiency means more photogenerated electrons and holes, which is favorable for the PEC water-splitting reactions. According to the empirical equation: $E_g = 1240/\lambda$, the energy band gap (E_g) of the Ta₃N₅ films is estimated to be 2.0–2.1 eV (ca. 2.04 eV for T-162, Fig. 1c). Fig. 1d shows the Mott-Schottky plots of T-162 to determine the flat band potential (E_{fb}) of Ta₃N₅ based on the equation [23–25]:

$$1/C^2 = 2(E_{app} - E_{fb} - k_B T/e) / \varepsilon \varepsilon_0 A^2 e N_D,$$

where C , k_B , T , e , ε_0 , ε , A , and N_D are the capacitance at electrode/solution interface, Boltzmann's constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), absolute temperature (298 K), elementary electron charge ($1.6 \times 10^{-19} \text{ C}$), vacuum permittivity ($8.85 \times 10^{-14} \text{ F cm}^{-1}$), relative dielectric constant of Ta₃N₅ (ca. 8), electrode area and donor concentration, respectively. The positive slope of Mott-Schottky plots suggests the n-type semiconductor nature of Ta₃N₅ [25],

and particularly the E_{fb} of Ta₃N₅ is estimated at 0.02 V vs. RHE. Considering that the conduction band edge potential (E_{CB}) of Ta₃N₅ is more negative by 0.3 V than its E_{fb} [6], the E_{CB} and valance band edge potential (E_{VB}) of Ta₃N₅ can be determined to be −0.28 and 1.76 V vs. RHE, respectively. Apparently, such a band alignment is suitable for overall water splitting under sunlight or visible light irradiation, as illustrated in Fig. 1e.

PEC performance for water splitting

As shown in Fig. 2a, the stable E_{oc} in dark is indicative of the interfacial electronic equilibrium between the photoanode and electrolyte. Once exposed to light irradiation, the E_{oc} sharply shift negatively with the generation of a pronounced photovoltage (ΔE_{oc}), due to the accumulation of photogenerated electrons within the Ta₃N₅ films. Also, it is a characteristic of n-type semiconductor, which can be demonstrated by the positive photocurrent at the anodic potentials [23,24,26,27]. In general, the charge collection capacity of the light-excited photoanodes can be used to infer their PEC performance because a larger ΔE_{oc} means a stronger driving force for surface OER. Hence, T-27 and T-54 will exhibit a lower PEC activity due to their smaller ΔE_{oc} , mainly attributable to the inefficient light absorption and limited available

Figure 1 (a) XRD patterns, (b) UV-vis DRS and (c) energy band gaps of the as-prepared Ta₃N₅ photoanodes. (d) Mott-Schottky plots and (e) band alignment of T-162 photoanode.

Figure 2 (a) E_{oc} , (b, c) LSV, (d) zero-current potential and current density at 1.23 V vs. RHE. (e) EIS of the Ta₃N₅ photoanodes under visible-light irradiation ($\lambda > 400$ nm). (f) The fitted resistance and capacitance values from EIS data based on the equivalent circuit model: R_s represents the solution resistance; the capacitance C and resistance R_{ct} reveal the charge-transfer behavior across the electrode-electrolyte interface.

photogenerated charge carriers. When the anodization time is longer than 4 min, the samples have no evident difference in ΔE_{oc} , suggesting that they have enough film thickness for effective charge generation and electron collection. Fig. 2b shows the linear sweep voltammetry (LSV) curves of the as-prepared Ta₃N₅ photoanodes under the chopped visible-light irradiation ($\lambda > 400$ nm). Evidently, these photoanodes exhibit relatively small photocurrent densities below $50 \mu\text{A cm}^{-2}$ around the E_{oc} , and the anodic photocurrent responses are significantly elevated with the increase of applied potential higher than 0.9 V vs. RHE, which indicates that the fast recombination of photogenerated electron-hole pairs is greatly suppressed by the external bias. Importantly, the thickness of Ta₃N₅ films has a significant effect on their PEC performances, and T-162 possesses the optimal film thickness for PEC water splitting with the highest water-oxidation photocurrent density of 0.81 mA cm^{-2} at 1.23 V vs. RHE. Compared with T-162, T-216 and T-270 with thicker films have the stronger light absorption but exhibit lower PEC performances, which can be explained in two aspects: more photogenerated holes may be quenched by electrons during their migration to surface in a thicker film; the driving force of external bias is less effective in a

thicker semiconductor film due to the increased electronic resistance. Consequently, the highest PEC performance of T-162 should be attributed to the synergy of advantageous light harvesting and charge separation. In addition, T-162 also has the lowest zero-current potential lower than 0.4 V vs. RHE (Fig. 2c), once again revealing its best PEC performance. The photocurrents and zero-current potentials of all the Ta₃N₅ photoanodes are summarized in Fig. 2d, highlighting the thickness-dependent PEC performance. Fig. 2e shows the EIS Nyquist plots of the photoanodes to further evaluate the charge transfer behaviors across the electrode-electrolyte interface. Obviously, T-162 has the fastest charge transport due to its smallest arc radius, as proved by the fitted data (listed in Fig. 2f). The larger R_{ct} of T-27 and T-54 should be mainly ascribed to their weaker light-harvesting ability (i.e., less photoinduced charge carriers). Considering that the value of C is associated with the porosity of film electrodes [28,29], it can be inferred that the thicker Ta₃N₅ photoanodes (such as T-162 and T-216) will possess higher specific surface area that is beneficial to the PEC reactions. The above results suggest that the PEC performances of Ta₃N₅ photoanodes are strongly dependent on the film thickness and particularly T-162 has the

optimal film thickness with advantageous light absorption, charge separation and utilization.

Morphology and film thickness

As shown in Fig. 3a, T-162 photoanode has a flat surface, on which many opened hollow spheres (average diameter < 300 nm) are attached (Fig. 3b and Fig. S5a). Similar surface morphology is also observed on T-216 (Fig. S5b), while the spherical particles disappear on T-108 and T-54 with thinner film thickness (Fig. S5c and d). To some extent, the presence of hollow spheres is related to the specific growth mechanism of the oxide films in $\text{HF-H}_2\text{SO}_4\text{-H}_2\text{O}$ electrolyte and also it implies the formation of porous microstructure within the films. The high-magnification FE-SEM image in Fig. 3c presents the abundant nanopores (average size < 10 nm) densely distributed at the surface of the T-162 film. Whereas, the bottom of the film exhibits a compact structure consisting of numerous closely connected nanoparticles with an average size smaller than 50 nm (Fig. 3d). Cross-sectional FE-SEM images (Fig. 3e and f) clearly present a typical 3D interconnected porous nanoarchitecture that is constructed by lots of 1D curly nanorods. Combined with XRD results, it can be concluded that the Ta-based

photoanode has a sandwich structure: nanoporous Ta_3N_5 film/thin Ta_2N interlayer/Ta substrate. The large and intact nanoporous film shown in Fig. 3g can suggest its good structural stability, and the worm-like building blocks of the 3D interconnected Ta_3N_5 NAs have an average width of 26.4 nm (Fig. 3h and i). It is worth mentioning that such a unique porous texture can promote the release of high bulk stress during synthesis, thus improving the structural integrity of the Ta_3N_5 film and its adherence to the substrate. More importantly, the nanoporous Ta_3N_5 film closely adhered to the underlying Ta_2N can create many well-developed channels for charge transport from Ta_3N_5 to Ta substrate. It is conceivable that such a 1D nanostructure-built 3D interconnected porous film tightly grown on the conductive substrate has attractive advantages including high specific surface area, good light harvesting (reduced photon scattering), abundant adsorption/reactive sites, fast mass transport/diffusion, efficient hole injection into electrolyte for OER (small radical size of 1D nanostructures) and electron migration to the counter electrode for HER, which is in general extremely beneficial to the PEC water-splitting reaction [22,30–32]. As shown in Fig. S6, the Ta_3N_5 film thicknesses ($d_{\text{Ta}_3\text{N}_5}$) of T-27, T-54, T-108, T-162 and T-216

Figure 3 SEM (a, b) and FE-SEM images of T-162: top (c), bottom (d) and cross-sectional view (e, f). (g) Typical TEM image of T-162 film. (h) Typical TEM images of 1D worm-like nanostructures and (i) the corresponding diameter distribution.

electrodes were measured to be about 145, 315, 610, 900 and 1200 nm, respectively. Note that the thickness of Ta_3N_5 film in Fig. 3e seems to be larger than that in Fig. S6a, due to the cracks formed during the sample preparation for SEM measurements. Based on the above results, the proportional relationship between d_{Ta} and $d_{\text{Ta}_3\text{N}_5}$ can be estimated as: $d_{\text{Ta}_3\text{N}_5} = 5.576 \times d_{\text{Ta}}$ (Fig. 3i), and thereby the relationship between $d_{\text{Ta}_3\text{N}_5}$ and t is determined to be $d_{\text{Ta}_3\text{N}_5} = 2.51 \times t$. Therefore, such a galvanostatic anodization and NH_3 nitridation strategy may open up a new avenue to controllably fabricate Ta_3N_5 photoanodes with advantageous film thickness and microstructure just through controlling the anodization time.

Formation mechanism

According to the literature [13,14,17,25,29,33,34], 1D Ta_2O_5 nanotube arrays are usually obtained by electrochemical anodization of Ta electrodes in $\text{HF}/\text{H}_2\text{SO}_4$ -based electrolytes. Herein, the formation mechanism of such a 3D interconnected nanoporous film was investigated. Generally speaking, the growth of the self-organized Ta_2O_5 nanostructures in the $\text{HF}-\text{H}_2\text{SO}_4-\text{H}_2\text{O}$ electrolyte is strongly dependent on the equilibrium situation between oxide formation and dissolution [34,35], which can be clarified through monitoring the voltage over time. Fig. 4a shows the plots of voltage against anodization time ($V-t$) during galvanostatic anodization. According to the curve characteristics, the growth process of nanoporous Ta_2O_5 films can be divided into three stages. In stage I, the voltage increases quickly to ~ 4.0 V, corresponding to the formation of a compact initial oxide layer on the Ta substrate with increased surface electric resistance [14,33,34]. The presence of dense nanoscopic

pores can be ascribed to the specific anodic polarization process in HF -based electrolyte. In stage II, the voltage decreases gradually with the increase of anodization time until ~ 80 s, due to the permeation of electrolyte into the pores of initial layer and the dissolution of oxide layer. In stage III, the successive anodization of underlying Ta substrate and the chemical dissolution of Ta_2O_5 proceed simultaneously, leading to the formation of self-ordered 1D Ta_2O_5 nanostructures. Further prolonging the anodization time, the Ta_2O_5 film thickens and meanwhile the increased electric resistance in the circuit results in an elevated voltage under the galvanostatic mode. In this stage, the $V-t$ curves of the samples exhibit a nearly same slope, suggesting that a steady growth process of 1D Ta_2O_5 nanostructures has been established under diffusion control [33]. Ultimately, 3D interconnected porous Ta_2O_5 NAs were formed between the initial compact layer and suboxide TaO_x layer on the Ta substrate. Herein, the generation of TaO_x interlayer between the Ta_2O_5 film and Ta substrate is probably associated with the hindering effect of Ta_2O_5 film on the further oxidation of underlying Ta, which can hardly be avoided in the electrochemical anodization synthesis [5,11,13,29]. It is noteworthy that the weak electrical field at the initial stages (<5 V) can be mainly responsible for the growth of 1D worm-like nanostructures because the orderly arranged 1D Ta_2O_5 nanotube arrays on Ta substrates are obtained at 14 V in the same electrolyte (Fig. S7). The above proposed formation mechanism of 3D interconnected nanoporous Ta_2O_5 films on Ta substrates is schematically illustrated in Fig. 4b. It is anticipated that such a constant-current anodization strategy can be extended to fabricate other metal oxide photoelectrodes

Figure 4 (a) $V-t$ plots for the galvanostatic anodization of Ta electrodes. (b) Schematic illustration of the growth mechanism for 3D interconnected porous NAs.

with controllable film thickness, advantageous porous microstructure and structural coherence for highly efficient PEC reactions.

Stability investigation

Fig. 5a shows the transient photocurrent responses of T-162 under the chopped visible-light irradiation ($\lambda > 400$ nm) at E_{oc} , which reveals a slight performance degradation after the second run due to the hole-induced surface self-oxidation of Ta_3N_5 [8,10]. Whereas, a fast photocurrent decay is observed at 1.23 V vs. RHE (Fig. 5b), which can be ascribed to the electrochemical oxidation of Ta_3N_5 at the higher anodic potential than E_{oc} . As shown in Fig. 5c, the second-run LSV curve of T-162 exhibits a distinct photocurrent degradation especially at the applied potentials higher than 0.9 V vs. RHE. Furthermore, the other photoanodes with different film thicknesses also show similar performance degradation (Fig. 5d, e and Fig. S8), but interestingly their performance degradation happens at lower potentials (<0.75 V vs. RHE) than that of T-162, which indicates that the faster charge transport can restrain the hole accumulation and thereby alleviate the surface oxidation process. The photocurrent degradation percentage of all the photoanodes at 1.23 V vs. RHE are summarized in Fig. 5f.

Apparently, the performance degradation of Ta_3N_5 has no relevance to the film thickness but inherently depends on its own physicochemical property. Based on the above results, it can be concluded that the hole-induced photocorrosion and bias-induced electrochemical oxidation are synergistically responsible for the performance degradation of Ta_3N_5 , and the latter is even more crucial than the former.

The surface chemical compositions of Ta_3N_5 photoanodes before and after the PEC tests were further evaluated by XPS analysis. The binding energies were calibrated using the adventitious C 1s peak at 284.8 eV. As shown in Fig. 6a, Ta 4f_{7/2} and Ta 4f_{5/2} peaks are centered at ca. 24.5 and 26.3 eV, respectively, corresponding to Ta⁵⁺ in Ta_3N_5 [4,23,29,36]. The used photoanode shows Ta 4f_{7/2} and Ta 4f_{5/2} peaks at 26.0 and 27.7 eV, respectively, which can be assigned to Ta⁵⁺ in Ta_2O_5 [4,6,10]. Meanwhile, the Ta 4f_{7/2} peak of Ta_3N_5 at 24.5 eV remains but shows much weaker intensity. As shown in Fig. 6b, N 1s peak at 395.9 eV assigned to Ta_3N_5 is remarkably reduced after the PEC tests [24], indicative of the decreased N content. Moreover, the Ta 4p_{3/2} signal of Ta_3N_5 located at 403.1 eV also weakens [23–25], which is probably related to the formation of surface oxide layers on Ta_3N_5 via the electrochemical and hole-induced oxi-

Figure 5 Transient photocurrent responses of T-162 at E_{oc} (a) and 1.23 V vs. RHE (b). LSV curves of (c) T-162, (d) T-27 and (e) T-270. (f) Photocurrent degradation of the Ta_3N_5 photoanodes at 1.23 V vs. RHE.

Figure 6 XPS spectra of T-162 before and after PEC tests: (a) Ta 4f, (b) N 1s.

dative decomposition ($2\text{Ta}_3\text{N}_5 + 30\text{h}^+ + 30\text{OH}^- \rightarrow 3\text{Ta}_2\text{O}_5 + 5\text{N}_2 + 15\text{H}_2\text{O}$; $2\text{N}^{3-} + 6\text{h}^+ \rightarrow \text{N}_2$) [36,37]. In addition, the slight peak shifts detected for N 1s, Ta 4p and Ta 4f to higher binding energies suggest certain changes in the chemical environment of N and Ta atoms due to the surface deterioration of Ta₃N₅. The XPS survey spectra and chemical compositions of the original and used T-162 are shown in Fig. S9a, which reveals the increased surface oxygen content in the Ta₃N₅ film after the long-term PEC reactions. The above results further confirm the performance degradation of Ta₃N₅ originated from its surface oxidation in electrolyte under higher anodic potential than E_{oc} and strong light irradiation (Fig. S9b).

To remove the surface oxide layer and recover the PEC performance, the used Ta₃N₅ samples were subjected to NH₃ nitridation at 900°C for 2 h. Fig. S10a shows that the photocurrent density of T-162 at 1.23 V vs. RHE decreased from ca. 0.81 to 0.18 mA cm⁻², and encouragingly recovered to 0.27 mA cm⁻² after the regeneration treatment but still much lower than the initial state. The other used photoanodes (Fig. S10b) also show rapid photocurrent decays higher than 50% within 10 min at 1.23 V vs. RHE. As shown in Fig. S10c–e, the recovered photoanodes exhibit a notably improved photoactivity, but unfortunately they are still much inferior to the original counterparts. Even so, the recovered T-270 shows higher PEC stability than the original electrode (Fig. S10f), implying the formation of a thin passivation layer on the Ta₃N₅ surface that can protect it from photocorrosion at high anodic potentials. Therefore, it can be concluded that the PEC performance of the deteriorated Ta₃N₅ photoanodes can be only partially recovered *via* thermal nitridation, which is probably related to the long-term high-temperature NH₃ treatment on Ta₃N₅ photoanodes

[36]. Besides, although the surface oxide layer could be removed after nitridation (Fig. S11), the composition and microstructure of the resultant layer may be different with the original state and thus it can also be responsible for the irreparable PEC performance.

Enhanced PEC performance and mechanism insights

According to the above results and previous studies [8–10], the unsatisfactory photostability of Ta₃N₅ can be attributed to its poor chemical stability, surface self-oxidation by the agglomerated holes and particularly the electrochemical oxidation at high anodic potentials. To further improve the PEC performance and stability, the Ta₃N₅ photoanodes were modified by colloidal Co(OH)_x. As shown in Fig. 7a, CT-162 exhibits a much higher PEC performance over the entire applied potential range and a 2.7-fold enhancement of photocurrent at 1.23 V vs. RHE is achieved ($\sim 2.96 \text{ mA cm}^{-2}$), as compared with the bare T-162 (0.81 mA cm^{-2}). More importantly, the stability of CT-162 is remarkably enhanced, suggesting that Co(OH)_x has strong hole collection ability to accelerate OER kinetics and thereby efficiently suppresses the surface oxidation of Ta₃N₅ [13,14,38,39]. The wavelength-dependent IPCE curves (Fig. 7b) shows higher IPCE values on CT-162 than T-162 in the range of 400–500 nm. The maximum IPCE value of CT-162 is $\sim 27.4\%$ at 400 nm, which is nearly 3.3 times that of T-162 ($\sim 8.2\%$) and also superior to most of the reported Ta₃N₅-based photoanodes (Table S1). Meanwhile, the ABPE of T-162 increases from $\sim 0.04\%$ to 0.18% after the Co(OH)_x modification (Fig. S12), suggesting a substantially improved solar-energy conversion efficiency. From Fig. 7c, it can be seen that CT-162 has a higher electron collection ability than T-162 due to its larger ΔE_{oc} . EIS Nyquist plots in Fig. 7d

Figure 7 (a) LSV, (b) IPCE, (c) E_{oc} , (d) EIS, (e) Mott-Schottky, (f, g) CV and (h) ΔJ - v plots of T-162 and CT-162. (i) Typical TEM image of the Co(OH)_x -modified Ta_3N_5 NAs.

reveal a much smaller R_{ct} value of CT-162 than that of T-162, indicating lower electric resistance and faster charge transport across the photoanode/electrolyte interface. As shown in Fig. 7e, the slope of Mott-Schottky curve is notably reduced after Co(OH)_x loading, indicating a higher charge-carrier concentration (N_D) of CT-162 ($5.17 \times 10^{13} \text{ cm}^{-3}$) than that of T-162 ($2.65 \times 10^{13} \text{ cm}^{-3}$). The relative electrochemically active surface areas (ECSAs) of the photoanodes were evaluated by the double layer capacitances (C_{dl}) via measuring the CV curves in non-Faraday region (Fig. 7f and g) [19,40]. The C_{dl} can be estimated from the difference values (ΔJ) between anode current (J_a) and cathode current (J_c) at 0.35 V in the CV curves with different scan rates (v). As shown in Fig. 7h,

the linear slopes of ΔJ - v plots equal to twice the C_{dl} value are used to determine the ECSAs of T-162 and CT-162. It is evidenced that the introduction of Co(OH)_x can considerably increase the specific surface area and active sites of the porous Ta_3N_5 photoanode. Fig. 7i shows the typical TEM image of $\text{Co(OH)}_x/\text{Ta}_3\text{N}_5$ composite structure: 2D wrinkled Co(OH)_x nanoflakes closely anchored on the 3D interconnected porous Ta_3N_5 NAs. After the PEC test, such a characteristic composite structure still remains with close interfacial contact between Co(OH)_x and Ta_3N_5 , as shown in Fig. S13a and b. The selected-area electron diffraction (SAED) pattern (Fig. S13c) and high-resolution TEM (HRTEM) image (Fig. S13d) can further suggest the good crystallinity of Co(OH)_x (JCPDS card

No. 30-0443), in consistent with the XRD results (Fig. S14). The EDS mapping images (Fig. S13e) reveal not only the closely coupled $\text{Co}(\text{OH})_x/\text{Ta}_3\text{N}_5$ nanocomposite but also the uniform coating of $\text{Co}(\text{OH})_x$ on the porous Ta_3N_5 . Therefore, the enhanced PEC performance of CT-162 can be readily attributed to the increased surface active sites, charge-carrier concentration and the significantly boosted charge separation and water oxidation dynamics.

To further clarify the enhanced PEC properties of CT-162, the specific role of $\text{Co}(\text{OH})_x$ in PEC water-oxidation reaction was investigated. As is well known, the $\text{Co}(\text{OH})_x$ on the photoanodes can be oxidized into CoOOH by the photogenerated holes with strong oxidation ability, which has been widely employed to enhance the PEC performance *via* depositing MOOH ($\text{M} = \text{Co}, \text{Ni}, \text{Fe}$) co-catalysts on the photoanodes [41–44]. Herein, CoOOH acts as an efficient co-catalyst for hole extraction and collection to facilitate the PEC water oxidation reactions on the photoanodes, and simultaneously it will be reduced back to $\text{Co}(\text{OH})_x$ [45,46]. To determine the *in-situ* conversion of $\text{Co}(\text{OH})_x$ into CoOOH by light-induced holes, the bias-free photocurrent response of CT-162 was monitored. Considering that the performance degradation of bare T-162 at E_{oc} is nearly negligible, the conspicuous photocurrent decay at the first 3 min can be explained by the decrease in the available holes for OER due to the hole-induced $\text{Co}(\text{OH})_x$ -to- CoOOH transformation (Fig. 8a). After 6 min of light irradiation, the photocurrent responses gradually reach a stable state, suggesting that the interfacial CoOOH is saturated and the surface cyclic $\text{Co}^{2+}/\text{Co}^{3+}$ mediator is well established (inset of Fig. 8a). During the PEC reactions, the redox between Co^{2+} and Co^{3+} can accelerate the charge distribution, migration and separation. It is worth men-

tioning that the steady photocurrent density of CT-162 ($\sim 413 \mu\text{A cm}^{-2}$) is 16.5 times that of T-162 ($\sim 25 \mu\text{A cm}^{-2}$), highlighting the remarkable contribution of $\text{Co}(\text{OH})_x/\text{CoOOH}$ co-catalyst shell to the PEC water-splitting process. But no obvious XRD signals of CoOOH phase were detected on the composite photoanode after PEC tests (Fig. S14), which can be attributed to the low content of CoOOH layer and a reversible CoOOH -to- $\text{Co}(\text{OH})_x$ reaction [47]. Thus, the *in-situ* grown dual-layer $\text{Co}(\text{OH})_x/\text{CoOOH}$ shell on porous Ta_3N_5 NAs serves as a hole extraction and storage layer that can not only inhibit the surface hole accumulation but also promote the charge separation, thus remarkably enhancing the PEC performance and stability, as illustrated in Fig. 8b.

CONCLUSIONS

In summary, 3D interconnected porous Ta_3N_5 NAs with controlled film thickness were precisely fabricated by a two-step strategy including galvanostatic anodization and NH_3 nitridation. The unique porous NAs can endow the Ta_3N_5 films with beneficial structure adherence, interfacial charge transfer and light harvesting. The optimal thickness of nanoporous Ta_3N_5 films for PEC water splitting is ca. 900 nm, attributed to the synergy of advantageous light absorption and charge separation. The electrochemical oxidation at high anodic potentials is the more crucial reason for the performance degradation of Ta_3N_5 than hole-induced self-oxidation. Thermal nitridation can recover the PEC performance of the used Ta_3N_5 photoanodes but it is still much inferior to the initial states. As a hole extraction and collection layer, $\text{Co}(\text{OH})_x/\text{CoOOH}$ was *in-situ* deposited on Ta_3N_5 NAs and significantly improved the PEC performance and stability. This work paves an avenue for the controllable synthesis of 3D interconnected nanoporous films with

Figure 8 (a) Bias-free photocurrent responses of CT-162 and the corresponding changes of $\text{Co}(\text{OH})_x$ layer. (b) Possible mechanism of PEC water-splitting process over the CT-162 photoanode.

beneficial light harvesting and charge separation for efficient PEC water splitting. Further, the development of Ta₃N₅-based photoanodes can be focused on improving the bias-free PEC performance and the stability at high applied potentials through microstructure control and surface engineering strategies.

Received 3 September 2020; accepted 1 December 2020;
published online 9 February 2021

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Acknowledgements This work was financially supported by the National Natural Science Foundation of China (51774145, 51872317 and 21835007), and China Postdoctoral Science Foundation (2019M661644). The first author also thanks the China Scholarship Council (CSC) for financial support.

Author contributions Zhu H and Li B guided the project. Wang Q designed and performed the experiments; Zhang L and Shi J helped with the data analysis; Wang Q wrote the paper with support from Zhang L, Zhu H, Li B and Shi J. All authors contributed to the general discussion.

Conflict of interest The authors declare no competing financial interests.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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用于光电化学分解水的三维贯通纳米多孔Ta₃N₅薄膜: 厚度调控与稳定性研究

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摘要 太阳能光电化学分解水是一种理想的绿色制氢技术, 而设计高效、稳定的光阳极是目前面临的巨大挑战。考虑到薄膜厚度及其微观结构是影响光阳极性能的关键因素, 本文采用恒电流阳极氧化-NH₃氮化法制备出厚度精准可控的三维贯通纳米多孔Ta₃N₅薄膜光阳极。结果表明, Ta₃N₅厚度为900 nm时具有最高的光电解水性能, 这源于其最优的光吸收和电荷分离效率。相比空穴自氧化, 高偏压下的电催化氧化会造成更严重的性能衰减。NH₃氮化可去除Ta₃N₅表面氧化层, 但仅能部分恢复其性能, 而原位负载的Co(OH)_x/CoOOH双层助催化剂则显著提高了Ta₃N₅的光电化学性能及稳定性。本文提出通过厚度调控和表面修饰优化光吸收、空穴转移和电荷分离, 为高效、稳定的纳米多孔Ta₃N₅基光阳极的可控制备提供了新策略。