

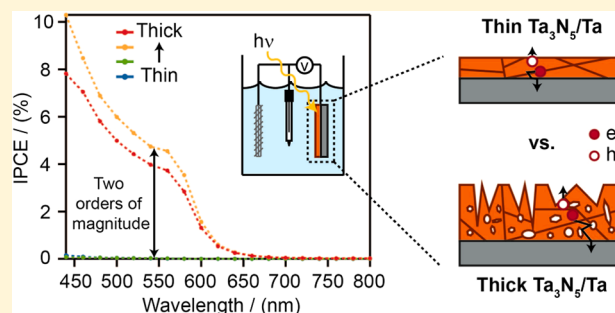
Effect of Film Morphology and Thickness on Charge Transport in Ta₃N₅/Ta Photoanodes for Solar Water Splitting

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S Supporting Information

ABSTRACT: Photoelectrochemical water splitting is one of many approaches being studied to harvest sunlight and produce renewable H₂. Tantalum nitride (Ta₃N₅) is a promising photoanode candidate as its band edges straddle the water redox potentials and it absorbs a large portion of the solar spectrum. However, reported photocurrents for this material remain far from the theoretical maximum. Previous results indicate Ta₃N₅ may be hindered by charge transport limitations attributed to poor bulk charge transport, charge transport across grain boundaries, and/or charge transfer across the interface at the back contact. The primary goal of this work was to study these mechanisms, especially bulk hole and electron transport, to determine which processes limit device efficiency. Crystalline thin films (60–780 nm) of Ta₃N₅ ($E_g = 2.1$ eV) on Ta foils were synthesized by oxidation of Ta metal in air at 550 °C and subsequent nitridation in NH₃ at 900 °C. Scanning electron microscopy revealed that thermal stresses and differences in the density of the phases resulted in the formation of porous, textured films with high surface area. Films were characterized by their photon absorption, crystal grain size, and electrochemically active surface area. Trends in photoactivity as a function of film thickness under broadband illumination as well as in the incident photon-to-current efficiency revealed that minority charge carrier (hole) and majority carrier (electron) transport both play important roles in dictating photoconversion efficiency in Ta₃N₅ films.



1.0. INTRODUCTION

Solar driven water splitting is a promising route for the generation of hydrogen in which intermittent solar energy can be stored long-term in the form of chemical bonds.¹ The complexity of the processes involved, namely, photon absorption and carrier collection coupled with catalysis, imposes many simultaneous constraints on the electrodes.² A system with high efficiency will likely have to incorporate a separate photocathode and photoanode in order to generate sufficient voltage to drive the reaction and maximize utilization of the solar spectrum. Several photocathode candidates have exhibited promising performance,^{3,4} but viable options for photoanodes are sparse. Tantalum nitride (Ta₃N₅) is an excellent candidate as the band positions are well matched to the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) redox potentials.⁵ Furthermore, red Ta₃N₅ has a band gap of 2.1 eV and thus absorbs in the visible.^{5,6} On the basis of the optical limit (complete absorption and 100% utilization of above band gap photons), a photocurrent of 12.5 mA/cm² is theoretically possible.⁷ Previous work to synthesize Ta₃N₅ includes nitridation of Ta₂O₅ powder,^{5,8,9} thermal oxidation and nitridation of Ta foils to yield thin films,^{6,10} sputtered thin films,¹¹ anodization of Ta foils to make nanotube arrays,¹² drop casting doped films from TaCl₅,¹³ atomic layer deposition,^{14,15} and fabrication of nanoparticles.^{16,17} The photoactivity of many of these samples has been measured

(under various conditions); even with a substantial applied bias, the highest reported photocurrents under visible light (intensity not specified) have been limited to ~4 mA/cm².⁶ The addition of a highly reversible redox couple such as Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ to circumvent issues with surface catalysis still yields photocurrents <7 mA/cm².⁶ In order to engineer this material to approach its optical limit, its fundamental limitations must be identified through careful study of its properties; previous work^{12,18} has pointed to possible issues with charge transport which we seek to investigate in the study herein.

Photoanode performance can potentially be hindered by several charge transport limitations, including poor (i) charge transport of both electrons (e⁻) and holes (h⁺) through the bulk of the material, (ii) charge transport of the two carriers across grain boundaries, (iii) charge transfer of electrons across the interface at the back contact, and (iv) charge transfer of holes across the semiconductor/liquid interface, i.e., catalytic water oxidation. The first limitation might arise in Ta₃N₅ due to many defect sites which act as recombination centers. The second limitation depends significantly on the synthesis of Ta₃N₅ which is usually accomplished by nitridation of tantalum oxides, resulting in a multicrystalline material with relatively

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small domains and thus many grain boundaries. The third issue is predicated on the fact that the optimal back contact must have a work function which closely matches the Fermi level of the semiconductor material and depends greatly on the atomic-scale structure of the interface. The fourth limitation involves the efficiency of water oxidation at the solid/liquid interface which can be significantly improved by adding an OER co-catalyst.^{18,19} The goal of this work is to gain insight into bulk hole and electron transport by studying the photoactivity of thin films of Ta₃N₅ as a function of thickness synthesized directly on Ta metal. This back contact is selected to help mitigate issue iii; the work function of polycrystalline Ta metal (4.25 eV)²⁰ is nearly ideal for matching up with the band structure of n-type Ta₃N₅ for which the conduction band (CB) is at 4.0 eV (−0.4 V vs NHE).⁵ To our knowledge, this work is the first to focus on studying these charge transport effects to explicitly identify limiting processes.

2.0. EXPERIMENTAL METHODS

2.1. Sample Preparation. Ta foils (10 mm × 10 mm × 0.5 mm, Alfa Aesar, 99.95% metals basis excluding Nb) were mechanically polished to yield a flat surface. The as-received foils were rough with features on the micrometer scale which had to be smoothed to facilitate the synthesis of uniform, thin films of Ta₃N₅. Electrochemical polishing is an alternate route²¹ that was explored, but the mechanically polished samples were more uniform and the process more scalable. Micrographs of the as-received, electropolished, and mechanically polished bare Ta foils are shown in Figure S1 (see the Supporting Information). Polished foils were cleaned by sequential sonication in acetone, isopropanol, and Milli-Q water. Ta₃N₅ thin films grown on Ta (denoted Ta₃N₅/Ta henceforth) were synthesized in a two-step process involving separate oxidation and nitridation steps. The thermal oxidation of Ta metal is well documented in the literature.^{22–24} Briefly, Ta foils were inserted into a hot tube furnace (single zone, Mellen Company) held at 550 °C and open to air. Since we found that metallic Ta does not readily nitride in NH₃, it is the oxide film thickness which dictates the final nitride thickness and for this reason we varied the oxidation time between 5 and 30 min. Nitridation was carried out by placing the samples in a sealed, continuous-flow tube furnace. A flow of 100 sccm Ar (Praxair, 99.999%) was maintained while the temperature was ramped to 900 °C at a rate of 10 °C/min. The sample was then held at 900 °C for 1 h while flowing 50 sccm NH₃ (Praxair, 99.995%) and subsequently cooled to room temperature in an Ar atmosphere. The nitridation conditions were identical regardless of initial oxide thickness, and the synthesis of oxide-free Ta₃N₅ was confirmed by X-ray diffraction (XRD) analysis of film crystallinity. Samples were produced in triplicate for imaging and so that fresh samples were available for photoelectrochemical measurements with broadband and monochromatic illumination.

2.2. Film Characterization. The morphology of the Ta₃N₅ films was imaged using scanning electron microscopy (SEM) (FEI XL30 Sirion, 5 kV and Phi 700 AES, 10 kV). The film thickness was also evaluated by SEM; the films supported on Ta foils were sheared to reveal a cross section which was mounted at approximately 90°, with some off-axis variation leading to a small error in the measurements. Each reported film thickness is the average of five separate measurements each on three different areas of the cross section. Ambient temperature XRD (Phillips PANalytical X'Pert Pro) using

Cu K α radiation ($\lambda = 1.54184$ Å) was employed to study the crystallinity of the films. Crystallite size was computed using the Scherrer equation,²⁵ assuming a shape factor of 0.9.

2.3. Electrochemical Testing. All electrochemical and photoelectrochemical testing was carried out in a Teflon compression cell with an exposed working electrode area of 0.5 cm², as shown in Figure S2 in the Supporting Information. Contact was made to the back of the Ta₃N₅/Ta working electrode using conductive copper tape. The measured ohmic drop in the 0.1 M KOH (pH 13.3) solution purged with N₂ was <67 Ω , and no correction was applied to the data. The remainder of the conventional three-electrode configuration consisted of a Pt wire counter electrode and a Ag/AgCl (4 M KCl) reference electrode (+0.965 V vs RHE). Data was collected using a potentiostat (Bio-Logic VSP). Relative electrochemical surface area was determined from capacitance measurements by cyclic voltammetry in the region between −0.25 and 0 V vs Ag/AgCl in 0.1 M KOH carried out in the dark. Under these conditions, all current is attributed to capacitive charging in this potential window due to the absence of any redox features. The scan rate was varied between 25 and 300 mV/s with a 30 s hold at each vertex to allow the current to decay to zero. The average value of the anodic current at −0.05 V vs Ag/AgCl and cathodic current at −0.20 V vs Ag/AgCl is reported. As expected for a charging process not limited by mass transfer, the relationship between scan rate and capacitive current was found to be linear. The illumination source for the study of photoactivity was a 1000 W xenon lamp (Newport) fitted with a water filter to reduce output in the IR region. When necessary, a neutral density filter (optical density of 0.3 at 632.8 nm, Newport) was used to uniformly reduce the output over all wavelengths. The light intensity and spectral distribution incident on the sample was measured prior to each experiment using an integrating sphere (International Light INS150) and spectroradiometer (International Light RPS900-W). A broadband illumination of 154 mW/cm² (integrated over $\lambda = 250$ –950 nm) was measured, corresponding to ~ 2 suns at $\lambda = 500$ nm. Monochromatic light (fwhm = 10.1 nm $\pm$ $\sigma = 0.3$) was obtained using a monochromator (74100 Oriel Cornerstone), and suitable cut-on filters were used to eliminate light from higher order diffractions. To determine the incident photon-to-current efficiency, each sample was held at constant potential while the wavelength of light was varied in 20 nm increments between 440 and 800 nm. The light was chopped at a frequency of 0.2 Hz and the dark current subtracted from the total current to yield actual photocurrent. An average value over five chopping cycles is reported.

3.0. RESULTS AND DISCUSSION

3.1. Film Thickness and Morphology. Cross-sectional images for the Ta₃N₅/Ta films of four different thicknesses are shown in Figure 1a–d. Despite an initially polished surface, the resulting films are textured and somewhat porous. The porosity is due to changes in density during the transformation from Ta ($\rho = 16.6$ g/cm³)⁸ to Ta₂O₅ ($\rho = 8.20$ g/cm³),²⁶ and finally to Ta₃N₅ ($\rho = 9.85$ g/cm³).²⁷ The formation of the porous structure was studied in more detail by synthesizing films on single crystal Si substrates (described in the Supporting Information) which are flatter and better defined than the Ta foils, allowing for more facile observation of changes in thickness and morphology. It was found that, while the thickness of the film expands by a factor of 2 during oxidation, the higher density of the Ta₃N₅ phase compared to the Ta₂O₅

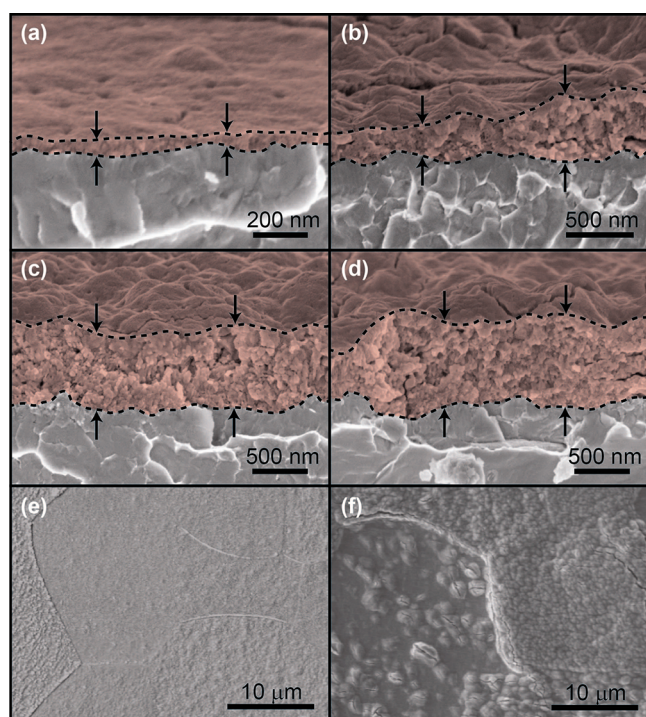


Figure 1. Cross-sectional SEM images of $\text{Ta}_3\text{N}_5/\text{Ta}$ films for average thicknesses of (a) 60 nm, (b) 260 nm, (c) 630 nm, and (d) 780 nm. The top-down images show the textured morphology for both (e) thin films (60 nm) and (f) thick films (780 nm).

phase results in the formation of void space rather than a decrease in film thickness upon nitridation (Figures S4 and S5, Supporting Information). The rough surface texture of the $\text{Ta}_3\text{N}_5/\text{Ta}$ samples is clearly evident in the top-down micrographs in Figure 1e and f which show differential growth patterns on the Ta grains. The surface texturing effect is more pronounced in thicker (Figure 1f) than in thinner (Figure 1e) films. We found that varying the oxidation temperature and nitridation conditions (NH_3 flow, time, and temperature) as well as attempting a simultaneous oxidation and nitridation procedure with a mixed stream of O_2 and NH_3 did not produce morphologies any more uniform or dense than those shown in Figure 1. Note as well in the cross-sectional views that there is a very sharp interface between the Ta_3N_5 and Ta but that there is no delamination, indicating good physical and electrical contact between the two phases. The resulting average film thicknesses (60, 260, 630, and 780 nm) are shown in Figure 2 as a function of oxidation time (5, 10, 15, and 30 min) where the large standard deviation can be attributed to the nonuniformity of the film thickness. The observed film growth rate is highly nonlinear; the initial slower growth is believed to be due to thermal conductivity, i.e., the heating time required for the sample to reach the temperature of the furnace (550 °C), while growth at longer times may be limited by diffusion of oxygen. It is clear, however, that the average thickness of the films spans the range of tens to hundreds of nanometers which should yield substantial differences in the charge carrier transport lengths.

3.2. Film Crystallinity. X-ray diffractograms for a set of four films are shown in Figure 3 and confirm the synthesis of phase-pure Ta_3N_5 with no TaON or Ta_2O_5 impurities based on reference spectra (PDF cards 00-004-0788 for Ta, 01-071-0639 for Ta_2O_5 , 01-071-0178 for TaON , and 01-079-1533 for Ta_3N_5). The peak at 38.6° corresponds to the underlying cubic

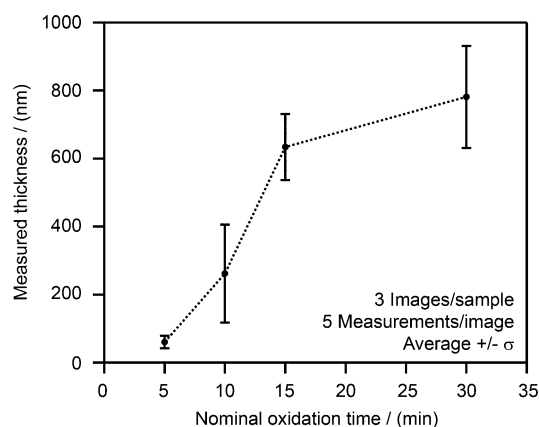


Figure 2. The measured Ta_3N_5 film thickness based on cross-sectional SEM images as a function of the nominal oxidation time. Thin films of tens to hundreds of nanometers have successfully been synthesized.

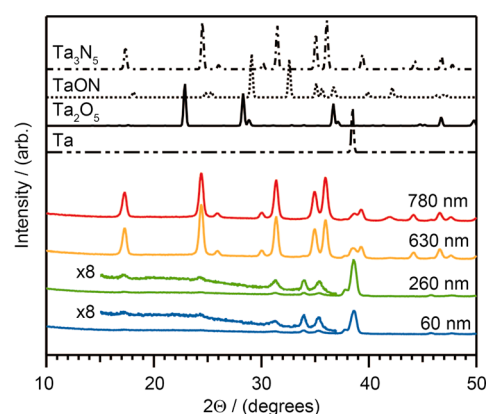


Figure 3. X-ray diffractograms for the films of four different thicknesses showing only peaks attributed to crystalline Ta_3N_5 or the underlying cubic Ta metal substrate.

Ta foil crystal structure. While the features at 17.3° , 24.3° , and 31.3° align with the reference spectra, the peaks indexed to the (130) and (113) diffractions which should be at 35.0° and 36.0° are shifted to lower angles for the two thinnest films. The origin of this shift is currently unknown. The Ta_3N_5 grain size for each film thickness was computed from the two most intense, unshifted peaks at 24.3° and 31.3° , corresponding to the (110) and (023) diffractions, using the Scherrer equation, and the results are shown in Table 1. The calculated crystallite size

Table 1. The Average Crystal Grain Size in the Films Calculated by Applying the Scherrer Equation to the Peaks at 24.3° and 31.3°

peak position	average crystallite size ($n = 3, \pm\sigma$)			
	780 nm	630 nm	260 nm	60 nm
24.3	18.7 ± 0.2	18.9 ± 0.1	15.0 ± 3.9	14.7 ± 1.5
31.3	19.3 ± 0.1	19.6 ± 0.1	14.5 ± 3.4	12.0 ± 2.2

varies between 12 and 19.6 nm with the thicker films exhibiting only slightly more long-range order. While the degree of crystallinity of a semiconductor material can potentially impact charge transport properties by means of trap states at the grain boundaries that act as recombination centers, the small differences in crystallinity found among these samples are

unlikely to factor significantly in any trends in electrode performance or charge transport.

3.3. Photoelectrochemistry. The first metric for film performance evaluated was the photocurrent generated under broadband illumination. Chopped ($f = 0.2$ Hz) cyclic voltammograms (scan rate = 10 mV/s) for 60, 260, 630, and 780 nm $\text{Ta}_3\text{N}_5/\text{Ta}$ films as well as a bare Ta foil are shown in Figure 4. A very important detail to note at this point is that

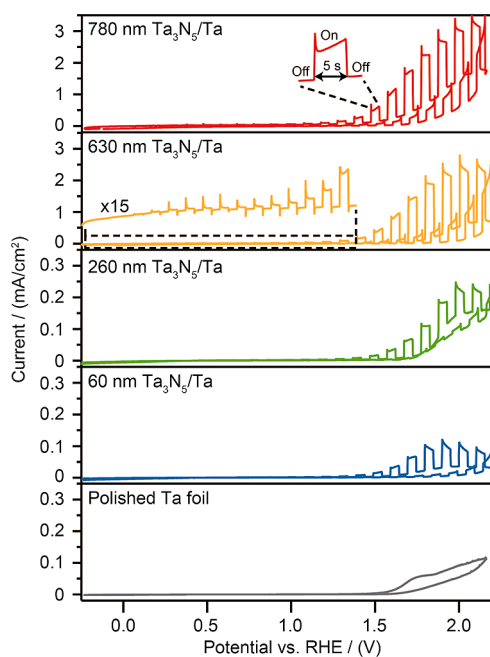


Figure 4. Chopped cyclic voltammograms for $\text{Ta}_3\text{N}_5/\text{Ta}$ films as well as a bare Ta foil under white light illumination. All films were photoactive with the two thickest films outperforming the two thinner films significantly (note the different current scales). Photocurrent may be the result of both water oxidation and oxidative photodegradation.

photocurrent is not necessarily the result of water oxidation. In fact, Ta_3N_5 is known to photodecompose through a process in which photogenerated holes oxidize the film itself, resulting in the release of N_2 , rather than oxidizing water.⁶ Addition of an OER co-catalyst such as IrO_2 has been shown to result in preferential shuttling of photogenerated h^+ to drive O_2 evolution rather than photodegradation and therefore stabilize the films.¹⁸ However, a co-catalyst was intentionally omitted in this study because even slight differences in coverage due to variation in the synthesis could result in effects which would convolute the study of charge transport. For example, a higher coverage on one film compared to another could provide a greater number of active sites for water oxidation or could result in decreased absorption in the Ta_3N_5 , since the catalysts are typically not optically transparent. Thus, we studied all films without any intentional modification of their surfaces. The photodegradation results in hysteresis of the photocurrent with progressive cycling; near-stable operation was achieved after five cycles (fifth cycle shown in Figure 4).

The onset of dark current for O_2 evolution and/or degradation is at 1.6 V vs RHE for both the nitride films and the bare Ta foil. The additional oxidative feature in the dark, centered at 1.7 V vs RHE, is attributed to electrochemical oxidation of exposed Ta metal, which may still be present in the nitrides due to cracks in the films. The onset of photocurrent

close to 0 V vs RHE for all films is consistent with the previously reported conduction band position at -0.4 V vs NHE for Ta_3N_5 .⁵ Of great interest was the finding that the photocurrents for the 630 and 780 nm films were both over an order of magnitude higher than those of the 60 and 260 nm films.

To investigate this result further, monochromatic illumination was used to directly calculate the incident photon-to-current efficiency (IPCE), analogous to an external quantum efficiency, which is shown in Figure 5 for an applied potential of

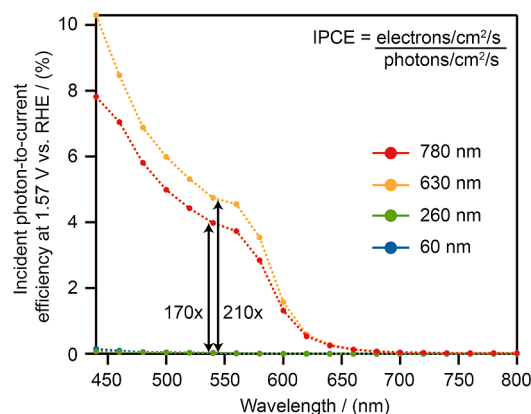


Figure 5. Incident photon-to-current efficiency for the $\text{Ta}_3\text{N}_5/\text{Ta}$ films of four different thicknesses. The 2 orders of magnitude higher activity of the 780 and 630 nm films compared to the 260 and 60 nm films is clearly evident.

1.57 V vs RHE. A second IPCE was also collected at a lower potential of 1.27 V vs RHE, shown in Figure S6 (Supporting Information), which reveals similar trends. The onset of significant photocurrent at ~ 620 nm (2 eV) is consistent with the published band gap of 2.1 eV.⁵ Consistent with the findings from broadband illumination, the IPCE at $\lambda = 540$ nm for the 780 and 630 nm films was significantly greater (approximately 170 and 210 times greater, respectively) than the IPCE of the 260 and 60 nm films. It is also interesting to note that, in comparing the two thicker films, the IPCE of the 630 nm film was 1.2 times higher than that of the thicker 780 nm film.

These trends in photoactivity and IPCE contain key information regarding the material properties of these Ta_3N_5 thin films. The following two possible explanations for these trends could be postulated: (i) differences in film thickness could impact photon absorption due to differences in optical path lengths for each sample, and (ii) differences in the film morphology and roughness could impact charge transport through the film. To investigate the first effect, we aimed to calculate an absorbed photon-to-current efficiency (APCE) for each sample. To do so, the value of the absorption coefficient as a function of wavelength is required for the Ta_3N_5 films. The manner in which they were grown, however, was not conducive to such a measurement as the opaque Ta substrates posed experimental challenges in studying the optical properties of the films. As an alternative, thin Ta_3N_5 films were synthesized on transparent quartz substrates and the optical properties studied by UV-vis absorption spectroscopy in transmission mode (see the Supporting Information for details, Figure S7). Though the synthetic route for Ta_3N_5 films on quartz very closely resembled the synthesis on Ta foils, precise values for APCE

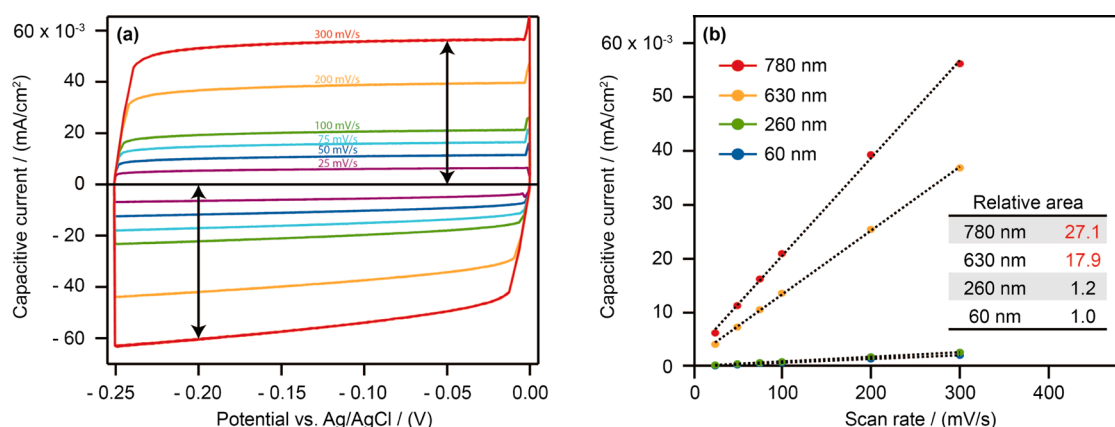


Figure 6. (a) Example cyclic voltammograms showing the capacitive current for the 780 nm film at six different scan rates from 25 to 300 mV/s. (b) Plot showing the linear relationship between the capacitive current and scan rate for all films. The relative electrochemically active surface areas (using the 60 nm as the baseline) are compiled in the inset table.

could not be extracted, as the syntheses are not (and cannot be) exactly the same. Nevertheless, the measured optical absorption in the transmissive samples did illustrate that absorption differences cannot be a dominant effect. An absorption coefficient of $6.2 \times 10^4 \text{ cm}^{-1}$ ($\sigma \sim 8 \times 10^3 \text{ cm}^{-1}$) at $\lambda = 540 \text{ nm}$ was estimated for Ta_3N_5 based on UV–vis absorption spectroscopy. Applying Beer's law, absorption accounts for a mere factor of 3.2 for the 780 nm film and 3.1 for the 630 nm film compared to the 60 nm film, and substantially less for the 260 nm film. Thus, differences in optical absorption cannot be expected to give rise to the photocurrent/IPCE trends described earlier.

There is, however, strong evidence that differences in surface area, a result of the morphological changes as a function of thickness, play a major role. The relative surface area of the Ta_3N_5 films was determined from the capacitive region of cyclic voltammograms, as shown in Figure 6 (representative sweeps for the 780 nm films are shown in Figure 6a). It is not possible to extract a value of the true electrochemical surface area per projected geometric area without an atomically flat Ta_3N_5 reference standard and detailed knowledge of the electronically accessible surface sites. However, assuming that the intrinsic specific surface capacitance of all Ta_3N_5 films is approximately the same, the relative surface area of the films can be determined. The 630 and 780 nm films are 17.9 and 27.1 times higher in surface area, respectively, than the 60 nm film. The increased area arises not only from higher surface roughness but also from cracks which form in the thicker films. The differences in surface area have important ramifications for charge transport, as discussed below.

3.4. Charge Transport. To put these results into context, it is instructive to consider diagrams showing the movement of photogenerated e^- and h^+ in the material, as shown in Figure 7. The first image in Figure 7a is representative of many of the previous Ta_3N_5 films made by depositing a powder on an electrode. The high surface area results in very short distances the photogenerated h^+ must travel to reach the reactive sites at the semiconductor/electrolyte interface. However, the lack of long-range crystallinity and very high porosity leads to a tortuous path for e^- transport. A thick, highly crystalline film, as shown in Figure 7b, can remedy the majority carrier transport issue by providing a continuous, less-defected path for e^- movement to the back contact, but it does so to the detriment of the minority carrier transport, as only a small fraction of the

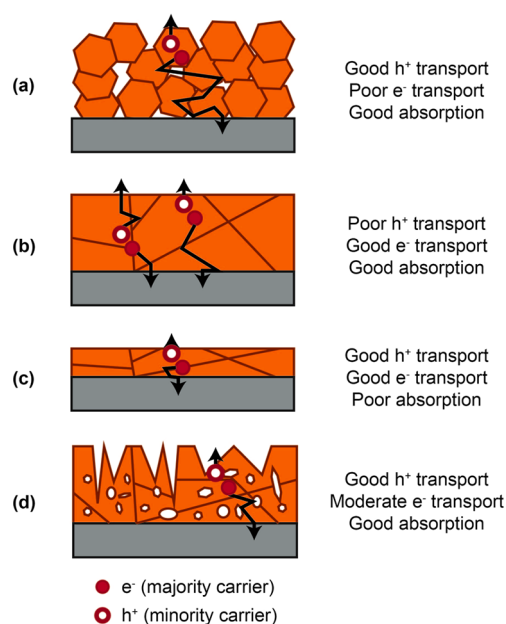


Figure 7. Schematics showing the effect of film geometry and structure on electron and hole transport for supported Ta_3N_5 in the form of (a) powder films, (b) thick crystalline films, (c) thin crystalline films, and (d) thick, rough crystalline films.

photogenerated charge carriers will be produced near the solid/liquid interface. Collection of photogenerated h^+ near the surface is still facile, but carriers generated deeper in the material have to travel much further than the average hole diffusion length. A thin crystalline film geometry as illustrated in Figure 7c solves this problem; the distances that the photogenerated carriers must travel are now small for both h^+ and e^- , leading in theory to a high APCE. Presumably, photon absorption in such a film will likely be limited, resulting in a low IPCE, so methods to increase the path length of light through the material would be required.

On the basis of the illustrative examples of Figure 7a–c, we are in a better position to describe the phenomena observed in the $\text{Ta}_3\text{N}_5/\text{Ta}$ films synthesized in this work. The thinner films (60 and 260 nm) are in the regime of thin, conformal films best represented by Figure 7b. The data supports this point of view as (i) both films have a similar, low surface area, as shown in Figure 6b, and (ii) both films exhibit nearly identical

photoactivity; the extra photon absorption in the thicker 260 nm film has little effect on overall efficiency, leading us to conclude that hole transport is likely a limiting process in both of these films.

The surface area measurements of Figure 6b indicate that the thicker films likely have a different film morphology, akin to that shown in Figure 7d. The highly textured surface and porosity of the thicker films means that a much larger fraction of the photogenerated e^-/h^+ pairs is produced near the solid/liquid interface, significantly improving h^+ collection. This translates to a 1–2 orders of magnitude increase in photoactivity of the two thicker films (780 and 630 nm) compared to the thinner films (60 and 260 nm). The fact that photocurrents appear to scale primarily with surface area, rather than with thickness and therefore with e^- transport lengths, points to h^+ transport as a fundamental limiting process in n-type Ta_3N_5 . Further evidence in support of this conclusion is the steep, continuous rise in the IPCE (Figure 5) at wavelengths above the band gap; this suggests that charge carriers generated by higher energy photons, which are absorbed closer to the top surface of the films as we employed front-side illumination, are collected more efficiently even if the e^- must travel further to reach the Ta back contact.

Hole transport, however, does not account for all of the observed trends in photoactivity. As noted earlier, in comparing the two thicker films (630 and 780 nm) to one another, the 780 nm film has a slightly lower activity than the 630 nm film. On the basis of the discussion above relating higher surface area to improved hole transport, one would expect the 780 nm film to perform better; another limiting mechanism must be at play. The data suggest that e^- transport begins to play a more important role for thicker films in which most of the photons are absorbed in the region closest to the light source (at the top of the film). Our experimentally determined absorption coefficients described earlier suggest that, for above band gap photons, 90% should be absorbed within the topmost 370 nm of the film. Any additional thickness (irrespective of the morphology) simply adds resistance for majority carriers to traverse between the site of photon absorption and the back contact. Thus, for the 780 nm sample, even though the higher surface area allows for improved hole transport, the increased path length for majority carriers (electrons) counteracts those benefits and leads to decreased performance compared to the 630 nm film.

Both hole transport and electron transport thus play important roles in Ta_3N_5 thin films, processes that depend greatly on film thickness and morphology. In order to approach the 12.5 mA/cm² theoretical limit for this material, an emphasis needs to be placed on designing electrodes which minimize the distance for h^+ transport or employ strategies to improve the minority charge carrier diffusion length without adversely affecting e^- transport.

4.0. CONCLUSIONS

Ta_3N_5 films of different thicknesses were synthesized via thermal oxidation and nitridation of Ta foils. All photoanodes were active under both broadband and monochromatic illumination, but thicker films exhibited much higher photocurrents than would be expected based solely on enhanced absorption. Their morphological differences, specifically large changes in surface area, played a significant role in governing photoelectrode activity, leading to the conclusion that both h^+ and e^- transport can be fundamental limiting processes in these

films. Control of the morphology and thickness of the films can allow for the development of devices with improved photoconversion efficiency.

■ ASSOCIATED CONTENT

Supporting Information

SEM images of as-received unpolished, mechanically polished, and electropolished bare Ta foil substrates are provided. A description and image of the compression cell used for all electrochemical testing is shown for clarity. The synthesis, characterization, and UV–vis absorption spectroscopy of thin films of Ta_3N_5 on quartz and Si is detailed along with the calculation of the absorption coefficient at $\lambda = 540$ nm. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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