

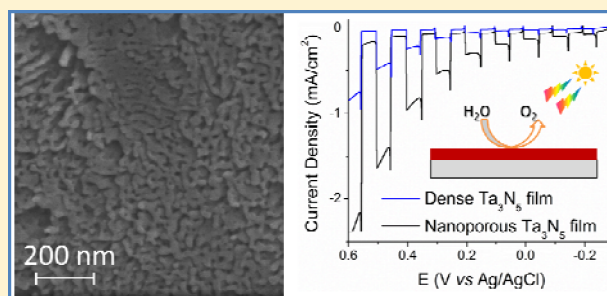
# Nanostructured Ta<sub>3</sub>N<sub>5</sub> Films as Visible-Light Active Photoanodes for Water Oxidation

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## Supporting Information

**ABSTRACT:** Nanostructured Ta<sub>3</sub>N<sub>5</sub> photoanodes (band gap of ~2.0 eV) were synthesized via a two-step process: first, nanocolumnar Ta<sub>2</sub>O<sub>5</sub> films were deposited by evaporation of tantalum metal in a vacuum chamber in a low pressure oxygen ambient followed by heating in an ammonia gas flow to convert Ta<sub>2</sub>O<sub>5</sub> into orthorhombic Ta<sub>3</sub>N<sub>5</sub>. Under Xe lamp irradiation (~73 mW/cm<sup>2</sup>), a 100 nm nanoporous Ta<sub>3</sub>N<sub>5</sub> electrode achieved an anodic photocurrent of ~1.4 mA/cm<sup>2</sup> at +0.5 V versus Ag/AgCl in 1 M KOH solution. By comparison, a dense film achieved ~0.4 mA/cm<sup>2</sup> clearly illustrating the importance of nanostructuring for improving the performance of Ta<sub>3</sub>N<sub>5</sub> photoanodes. However, Ta<sub>3</sub>N<sub>5</sub> films suffered from inherent self-oxidation under light illumination, and application of a cobalt cocatalyst layer was found to improve the stability as well as photocatalytic activity of the Ta<sub>3</sub>N<sub>5</sub> films.



## INTRODUCTION

Recent calculations show that using just a small fraction of the energy from the sunlight reaching our planet can meet the world energy demand.<sup>1</sup> However, it has proven to be extremely challenging to find ways to economically convert solar energy into usable forms. The cost-effective production of hydrogen fuel from sunlight and water is therefore considered one of the “Holy Grails” of chemistry.<sup>2</sup> One method is photoelectrochemical (PEC) water splitting using a photocatalyst. In a single-semiconductor, unbiased PEC system, catalyzing the water electrolysis process requires the material to have band edge positions (the top of the valence band and the bottom of conduction band) that straddle the water oxidation and proton reduction potentials while providing appropriate overpotentials for acceptable kinetics in driving the evolution of hydrogen and oxygen. In addition, to efficiently collect the incident sunlight energy, it is necessary that the band gap ( $E_g$ ) of the material be narrow enough ( $E_g < 3.0$  eV) to harvest a sizable fraction of the visible region of the solar spectrum.<sup>3</sup> Fujishima and Honda<sup>4</sup> first suggested the occurrence of water splitting in a Pt–TiO<sub>2</sub> electrochemical cell in 1972, and since this pioneering work there have been several studies regarding the synthesis and fabrication of long-lived, inexpensive photocatalysts that can utilize sunlight to produce hydrogen using water as the feed stock. However, these materials are either unstable or not sufficiently efficient.

Ta<sub>3</sub>N<sub>5</sub> is a promising candidate as a photocatalyst for a single semiconductor system due to its visible-light absorption up to 600 nm ( $E_g \approx 2.1$  eV), thermodynamically appropriate band edge positions for the water splitting process,<sup>3,5–9</sup> and its

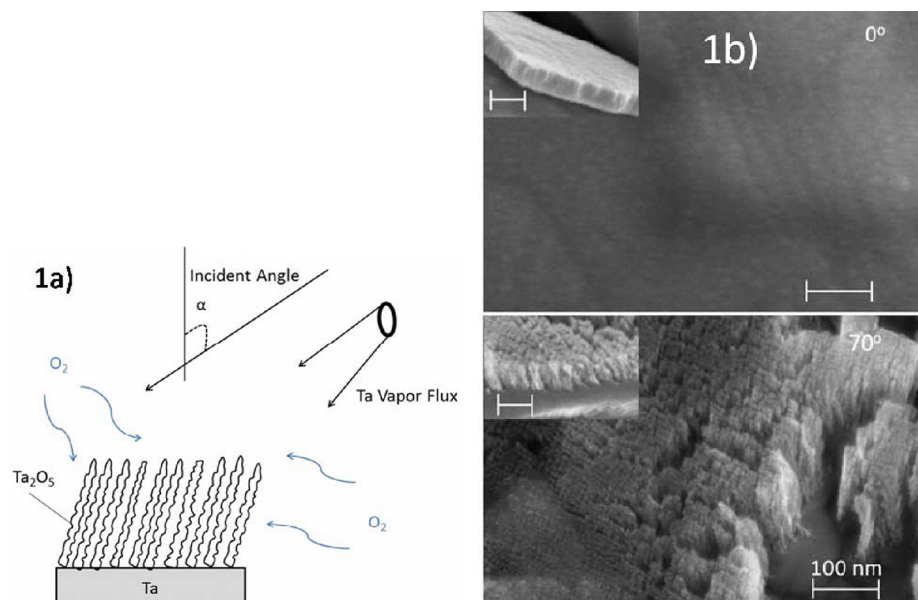
maximum theoretical photoconversion (AM 1.5 global solar illumination) of 15.9%.<sup>10</sup> There have been several studies on Ta<sub>3</sub>N<sub>5</sub> particles as photocatalysts for hydrogen or oxygen evolution under visible light in the presence of sacrificial agents, but few studies evaluating the PEC performance of Ta<sub>3</sub>N<sub>5</sub> thin films.<sup>11–17</sup> The fabrication and PEC performance of Ta<sub>3</sub>N<sub>5</sub> films by a radio frequency sputtering technique<sup>3</sup> (dense films) or anodization<sup>9</sup> (nanotubular films) has been reported. However, from these studies, it is difficult to see whether nanostructuring is necessary to improve the PEC performance of Ta<sub>3</sub>N<sub>5</sub>. For this reason, we have employed a single technique to synthesize Ta<sub>3</sub>N<sub>5</sub> films having either dense or porous structure to understand this difference.

Our growth of nanostructured Ta<sub>3</sub>N<sub>5</sub> films for photoelectrocatalysis takes place via a two-step process: first, we grow porous Ta<sub>2</sub>O<sub>5</sub> films by evaporation of tantalum metal in a vacuum chamber at a glancing angle with a low pressure ambient of oxygen ( $3 \times 10^{-6}$  Torr of O<sub>2</sub>) [this process is referred to as reactive ballistic deposition (RBD) at a glancing angle] followed by a nitridation step in a tube furnace containing an ammonia atmosphere. A key factor for synthesizing high surface area films via RBD is the limitation of adatom surface diffusion during film growth. For Ta<sub>2</sub>O<sub>5</sub>, when the growth surface is near room temperature (or below), surface diffusion is restrained and porous nanostructured surfaces can be generated. This growth process is described

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**Figure 1.** (a) Schematic of the reactive ballistic deposition (RBD) technique. Nanocolumnar  $\text{Ta}_2\text{O}_5$  films are grown by evaporating Ta at a glancing angle on a Ta substrate in the presence of oxygen as the reactive gas. (b) SEM images of as-deposited  $\text{Ta}_2\text{O}_5$  films on Ta foils at varying deposition angles:  $\alpha = 0^\circ$  (right, above) and  $70^\circ$  (right, bottom). All scale bars including the inset are 100 nm.

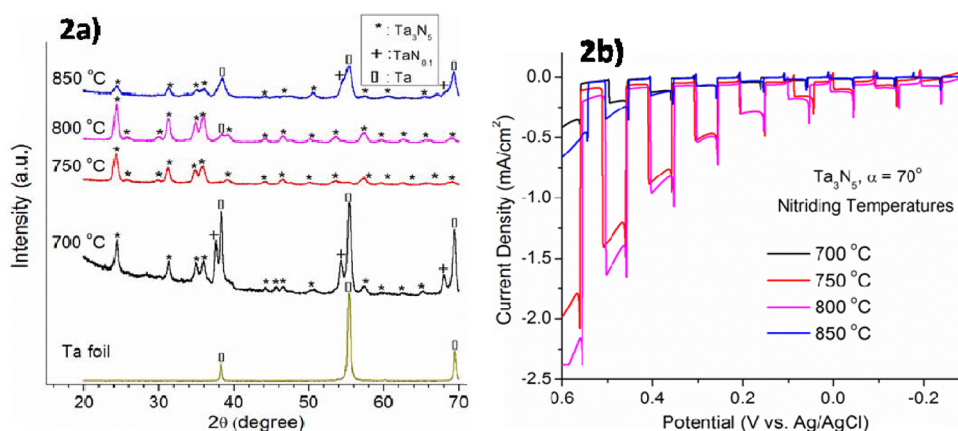
as “hit-and-stick” or ballistic deposition (BD).<sup>18</sup> In this scenario, vapor phase atoms or molecules travel from their source along straight-line trajectories to the deposition surface where they are incorporated in close proximity to their original landing sites.<sup>18</sup> At oblique angles of metal deposition, topographically elevated points, created stochastically during the initial growth, preferentially intercept the incoming vapor-phase atoms while shadowing lower regions.<sup>19</sup> This self-shadowing growth process can result in very porous nanocolumnar films. Brett et al.<sup>20</sup> have grown highly engineered and ordered films using ballistic deposition at glancing deposition angles to create arrays of micrometer-length nanocolumns, -zigzags, and -helices. This growth technique [without a reactive gas such as oxygen, ethylene, etc.] is sometimes referred to as glancing angle deposition (GLAD), and it has been the subject of two recent reviews by Abelman and Lodder<sup>19</sup> as well as Hawkeye and Brett.<sup>21</sup>

The capabilities of ballistic deposition can be extended further via addition of a reactive ambient ( $\text{O}_2$ ,  $\text{C}_2\text{H}_4$ , etc.) as described by Dohnálek and Kay in their pioneering paper.<sup>22</sup> By this method, metal-compound thin films are grown by reaction of the metallic adatoms and the adsorbed ambient gas. As suggested above, this technique is referred to as reactive ballistic deposition (RBD).<sup>22,23</sup> BD or RBD has been used to grow highly structured films from a wide variety of materials including Pd,<sup>24</sup> Cr,<sup>25</sup> Cu,<sup>25</sup> Fe,<sup>26</sup> Ti,<sup>27</sup>  $\text{TiO}_2$ ,<sup>28–31</sup> Mn,<sup>32</sup>  $\text{MgO}$ ,<sup>22</sup>  $\text{Ta}_2\text{O}_5$ ,<sup>33,34</sup>  $\text{WO}_3$ ,<sup>33</sup>  $\text{SiO}_x$ ,<sup>35,36</sup>  $\text{MgF}_2$ ,<sup>32</sup>  $\text{CaF}_2$ ,<sup>32</sup>  $\text{TiC}$ ,<sup>37–39</sup> and  $\text{Fe}_2\text{O}_3$ .<sup>40,41</sup> The resulting films often have optical, electronic, magnetic, and chemi-physical surface properties that can differ from dense, nonstructured films of similar composition. Detailed studies of RBD grown hematite,<sup>40</sup> Ti doped-hematite,<sup>41</sup> Si doped-hematite,<sup>42</sup> nanostructured  $\text{BiVO}_4$ ,<sup>43</sup> and Mo and W incorporated nanostructured  $\text{BiVO}_4$ <sup>44</sup> films for photoelectrochemical applications have recently been reported. During the course of our investigation, we found that the  $\text{Ta}_3\text{N}_5$  films suffered from serious photocorrosion while being tested in 1 M KOH, which was not reported earlier.<sup>9</sup> Interestingly, a simple cobalt surface

treatment was found to improve the photocurrent stability as well as boost the PEC performance of the  $\text{Ta}_3\text{N}_5$  films. The use of cobalt-based cocatalysts for various photoelectrodes<sup>45–52</sup> is promising due to the abundance of cobalt as compared to commonly used cocatalysts such as  $\text{IrO}_2$  or Pt. Also, oxygen detection experiments were carried out to calculate the contribution of the actual water oxidation in the overall observed photocurrent of the  $\text{Ta}_3\text{N}_5$  photoanodes.

## EXPERIMENTAL SECTION

**Film Preparation.** RBD  $\text{Ta}_2\text{O}_5$  films were deposited on Ta foil substrates at room temperature by evaporating tantalum metal in a background of  $\text{O}_2$  (partial pressure of  $\text{O}_2 \approx 3 \times 10^{-6}$  Torr) as a reactive gas under high vacuum conditions. Before film growth was started, the vacuum chamber was pumped to  $\sim 5 \times 10^{-8}$  Torr. For a typical film synthesis, pieces of  $1 \text{ cm} \times 2 \text{ cm}$  Ta substrates were cut from a larger  $25 \mu\text{m}$  thick Ta foil (99.95%, Alfa Aesar), and then sonicated in alcohol and acetone for  $\sim 10$  min each before being rinsed with deionized water. The Ta substrate was then dried in a gentle  $\text{N}_2$  flow before loading on a substrate holder positioned within the vacuum chamber. A home-built evaporator was used to evaporate Ta from a 0.125 in. diameter Ta rod (3N8 purity, ESPI). The sample holder was  $\sim 6$  in. from the evaporating source and could be rotated to a target deposition angle,  $\alpha$ , which is the angle between the direction normal to the Ta foil substrate and the evaporant flux (see Figure 1a for a schematic of the RBD technique). The evaporating tantalum flux was measured using a quartz crystal microbalance (QCM). From this flux value and the deposition angle, the deposition time required for a desired film thickness was determined. The chamber was then backfilled with  $\text{O}_2$  gas (99.99%, Matheson) to  $\sim 3 \times 10^{-6}$  Torr using a leak valve. Thermal nitridation in an ammonia environment of the as-deposited  $\text{Ta}_2\text{O}_5$  films was carried out in a tube furnace (OTF-1200X, MTI) at temperatures ranging from 700 to 850  $^\circ\text{C}$  for 8 h. A gas flow controller (Alicat Scientific) was employed to control the rate of  $\text{NH}_3$  gas (Anhydrous 99.99%, Matheson) flowing through a



**Figure 2.**  $\text{Ta}_3\text{N}_5$  films obtained at various nitriding temperatures. (a) XRD patterns (curves are offset) with a Ta substrate after nitridation included. (b) Chopped light PEC performance in 1 M KOH using full spectrum illumination ( $\sim 73 \text{ mW/cm}^2$  xenon lamp).

3 in.-diameter quartz tube at the rate of 100 mL/min at a pressure slightly above atmospheric by bubbling the effluent gas flow through a water reservoir. Before the samples were heated, the tube furnace was purged with  $\text{NH}_3$  for 1 h. The samples were then heated from room temperature to the desired annealing temperatures with a temperature ramp rate of  $3 \text{ }^\circ\text{C/min}$ , and finally allowed to cool naturally after the desired nitridation duration was reached. The cobalt treatment was carried out by submerging  $\text{Ta}_3\text{N}_5$  films in 0.1 M  $\text{Co}(\text{NO}_3)_2$  (99.999% purity, Alfa Aesar) for  $\sim 10$  min followed by rinsing with deionized water.

**Film Characterization.** XRD data were acquired with a Bruker D8 diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) with detector scan mode with an incident angle of  $2^\circ$  at a scan speed of  $6 \text{ deg/min}$ . SEM images were taken using a Zeiss FE-SEM at a 5 kV focus voltage. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos AXIS X-ray photoelectron spectrometer with Mono Al radiation. The atomic ratios were calculated using CasaXPS software with each element's relative sensitivity factors specific to the Kratos XPS. The diffuse reflectance spectroscopy (DRS) measurements were performed using a Varian Cary 500 UV-vis-NIR spectrophotometer with a Labsphere DR-CA-5500 integrating sphere. The film absorbance was calculated from the corresponding reflectance by assuming that the sum of the film's reflectance and absorbance was 100%. High-resolution transmission electron microscopy (HRTEM) images were collected using a JEOL 2010F transmission electron microscope operated at 200 kV.

**Photoelectrochemical Testing.** A three-electrode electrochemical cell controlled by a potentiostat (CHI 660D, CH Instruments) was employed for PEC testing of the  $\text{Ta}_3\text{N}_5$  films as photoanodes for water oxidation. The cell contained a Ag/AgCl reference electrode and a Pt wire counter electrode. The  $\text{Ta}_3\text{N}_5$  film on the Ta substrate acted as the working electrode with an illuminated area of  $\sim 0.21 \text{ cm}^2$  exposed to an aqueous 1 M KOH solution, which was purged with  $\text{N}_2$  gas for  $\sim 30$  min prior to testing. Linear sweep voltammetry scans were obtained with a scan rate of  $0.025 \text{ V/s}$  from negative to positive potentials. Electrochemical impedance spectroscopy (EIS) measurements were carried out on a dense  $\text{Ta}_3\text{N}_5$  film (the corresponding  $\text{Ta}_2\text{O}_5$  film was deposited at normal incidence ( $\alpha = 0^\circ$ )) using the ideal semiconductor model<sup>53</sup> to obtain the Mott–Schottky plot at various frequencies. All electrochemical experiments were performed at room temperature. IPCE data

were taken by employing a monochromator (Newport), and the light intensity at each selected wavelength was measured by an optical power meter (1916-C, Newport) equipped with a photodiode (818-UV, Newport). The following equation was used for calculating IPCE values:

$$\text{IPCE} = [1240 * i_p / (\lambda * E_\lambda)] * 100\% \quad (1)$$

where  $i_p$  ( $\mu\text{A}$ ) is the steady-state photocurrent and  $E_\lambda$  ( $\mu\text{W}$ ) is the light power measured at the position of the film surface corresponding to a selected wavelength  $\lambda$  (nm). The spot of the incident light at the selected wavelength was adjusted to be within the O-ring area where the film was exposed to the 1 M KOH electrolyte. The overall applied-bias photon-to-current efficiency (ABPE)<sup>54</sup> (in 1 M KOH) was measured by using the two-electrode configuration cell with the Pt wire as the counter electrode and the  $\text{Ta}_3\text{N}_5$  film as working electrode. The following equation was used for calculating ABPE values:

$$\text{ABPE} = j_{\text{ph}} * (1.23 - V_{\text{bias}}) / P_{\text{total}} \quad (2)$$

where  $j_{\text{ph}}$  ( $\text{mA/cm}^2$ ) is the steady-state photocurrent density under the applied voltage  $V_{\text{bias}}$  (V) between the two electrodes (with a scan rate of  $0.025 \text{ V/s}$  from positive to negative potentials), and  $P_{\text{total}}$  ( $\text{mW/cm}^2$ ) is the incident illumination power density. A xenon lamp (Newport) was utilized as the light source with a white-light intensity of  $\sim 73 \text{ mW/cm}^2$  measured by a thermopile detector with the spectrum response from 0.19 to  $10.6 \text{ }\mu\text{m}$  (Newport, 818P-020-12). A visible light cutoff filter (cutoff 420 nm, Newport) was employed to achieve visible light illumination.

#### Ring Collection/Substrate Generation Measurements.

Scanning electrochemical microscopy (SECM) was used to measure the faradaic efficiency of the  $\text{Ta}_3\text{N}_5$  films for water oxidation under irradiation.<sup>50</sup> A Au ring coated around an optical fiber (SFS200/200G, Fiberguide Industries, Inc., Long Hill, NJ) was used as a ring electrode.<sup>55</sup> The optical fiber has a diameter of  $200 \text{ }\mu\text{m}$ , and  $\text{SiO}_2$  and Au were coated around the optical fiber with thicknesses of  $\sim 10$  and  $20 \text{ }\mu\text{m}$ , respectively. The Au ring was coated with a borosilicate glass (capillary tubing, #27-32-1, FHC Inc., Bowdoin, ME) resulting in a final diameter of about  $500 \text{ }\mu\text{m}$ . Cyclic voltammetry (CV) of the ring (Figure S9a) shows the prepared electrode had no severe leakage, which is often observed for rings coated around the optical fiber. For the oxygen reduction reaction (ORR) at the ring, Pt was electrochemically deposited by repeated cyclic

voltammetry from 0.2 to  $-0.7$  V for three cycles at a scan rate of 20 mV/s in a 10 mM  $\text{H}_2\text{PtCl}_6$  and 0.1 M  $\text{Na}_2\text{SO}_4$  aqueous solution. After the Pt deposition, distinctive hydrogen adsorption/desorption peaks appeared in the CV of the Pt plated Au ring (Figure S9b).

For the substrate generation/ring collection measurements, a SECM (model 900B, CH Instruments, Austin, TX) and a linear inchworm actuator (T-LA28A, Zaber Technologies Inc., Vancouver, Canada) were used. A Xe lamp (XBO 150 W, Osram, Munich, Germany) was used with the full output as a light source. Ferrocenemethanol (FcMeOH) (97%, Sigma-Aldrich), NaOH (97%, Fisher Scientific, Pittsburgh, PA),  $\text{H}_2\text{PtCl}_6$  (99.9%, Alfa Aesar, Ward Hill, MA), and  $\text{Na}_2\text{SO}_4$  (99.0%, Sigma-Aldrich, St. Louis, MO) were used as received.

## RESULTS

**Fabrication and Characterization of  $\text{Ta}_2\text{O}_5$  Films by RBD.** Figure 1a illustrates the preparation of  $\text{Ta}_2\text{O}_5$  films by the RBD technique, and two typical types of morphologies of the as-deposited  $\text{Ta}_2\text{O}_5$  films are presented in Figure 1b; both were grown in an ambient of  $3 \times 10^{-6}$  Torr  $\text{O}_2$ , but one was deposited at a glancing angle of  $70^\circ$  ( $\alpha = 70^\circ$ ), while the other was deposited at normal incidence ( $\alpha = 0^\circ$ ). Nanocolumnar structure is observed for the film deposited at  $\alpha = 70^\circ$ , while a densely packed film without nanostructured features is seen for the deposition at  $\alpha = 0^\circ$ . The as-deposited  $\text{Ta}_2\text{O}_5$  films are amorphous as confirmed by using quartz substrates instead of Ta foils (Figure S1).

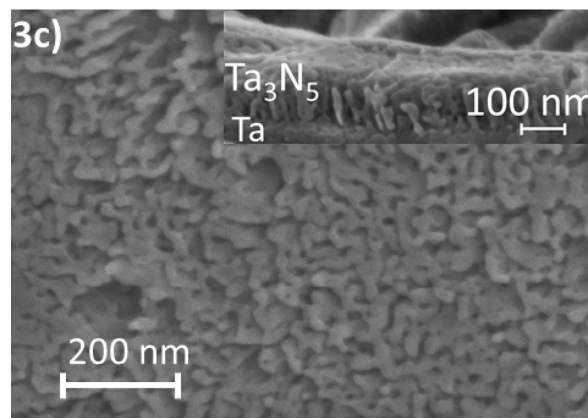
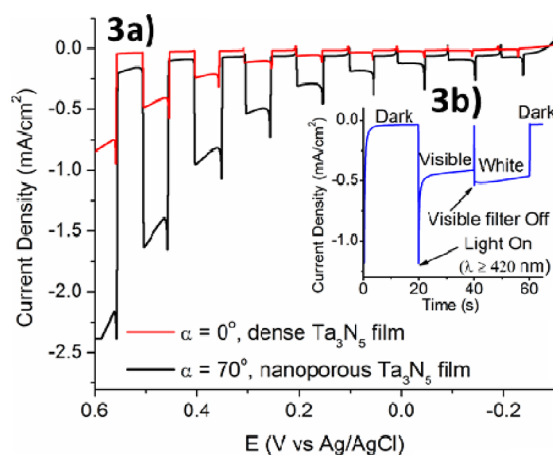
### Nitriding Temperature Effects on PEC Performance.

After deposition by RBD at  $70^\circ$  glancing incidence, 100 nm-thick  $\text{Ta}_2\text{O}_5$  films were nitrided in a heated tube furnace filled with a 100 mL/min flow of  $\text{NH}_3$  for 8 h at slightly above atmospheric pressure to convert the amorphous  $\text{Ta}_2\text{O}_5$  to crystalline  $\text{Ta}_3\text{N}_5$ .

The X-ray diffraction (XRD) data shown in Figure 2a indicate that the  $\text{Ta}_3\text{N}_5$  orthorhombic phase (PDF #01-072-0813) appears at  $700^\circ\text{C}$ . This is a lower temperature than that reported earlier for converting micrometer-sized- $\text{Ta}_2\text{O}_5$  particles to  $\text{Ta}_3\text{N}_5$  ( $850\text{--}900^\circ\text{C}$ ).<sup>17</sup> However, our results are in agreement with earlier studies, suggesting that nanostructuring of the  $\text{Ta}_2\text{O}_5$  films can assist in lowering the required nitriding temperature.<sup>9,56</sup> Over the temperature range  $700\text{--}800^\circ\text{C}$ , Figure 2b shows the photoactivity of the  $\text{Ta}_3\text{N}_5$  films increased with increasing temperature, probably due to the effectiveness of higher annealing temperatures in the conversion of  $\text{Ta}_2\text{O}_5$  ( $E_g \approx 4.0$  eV<sup>57</sup>) into crystallized  $\text{Ta}_3\text{N}_5$  ( $E_g \approx 2.1$  eV<sup>3,57</sup>), which has higher photocatalytic activity in the visible region. The films nitrided at  $800^\circ\text{C}$  have the highest photocurrents over the investigated temperature range ( $700\text{--}850^\circ\text{C}$ ), reaching 1.4 mA/cm<sup>2</sup> at +0.5 V vs Ag/AgCl (pH 13.6) or +1.5 V vs RHE (reversible hydrogen electrode). In Figure 2a, films nitrided at  $850^\circ\text{C}$  have significant peaks assigned to tantalum metal. We hypothesize that at high temperature the decomposition of  $\text{NH}_3$  to  $\text{H}_2$  and  $\text{N}_2$ <sup>11,58</sup> is sufficiently rapid that during the nitridation process  $\text{H}_2$  from the  $\text{NH}_3$  decomposition at high temperature acts to reduce  $\text{Ta}^{5+}$  on the surface of  $\text{Ta}_2\text{O}_5$  or  $\text{Ta}_3\text{N}_5$  to lower oxidation states (such as those found in Ta or  $\text{TaN}_{0.1}$ ). The failure to obtain a well-crystallized  $\text{Ta}_3\text{N}_5$  phase employing an  $850^\circ\text{C}$  nitridation temperature resulted in a lower photocatalytic activity as compared to similar films nitrided at  $750$  and  $800^\circ\text{C}$ . Typical morphologies for dense and nanoporous  $\text{Ta}_3\text{N}_5$  films prepared at various nitriding temperatures and a high-resolution transmission electron

microscopy image of a  $\text{Ta}_2\text{O}_5$  film after  $800^\circ\text{C}$  nitridation are shown in Figures S1, S2. Longer nitridation at  $700$  and  $800^\circ\text{C}$  (15 h instead of 8 h) was also investigated (Figures S3, S4), and thus nitridation at  $800^\circ\text{C}$  for 8 h was chosen as optimal condition for further analysis.

To better understand the photocatalytic improvement of nanoporous  $\text{Ta}_3\text{N}_5$  films as compared to densely packed ones, two  $\text{Ta}_3\text{N}_5$  films were prepared at the same deposition (100 nm thickness) and nitridation conditions ( $800^\circ\text{C}$ , 8 h) except for deposition angle during  $\text{Ta}_2\text{O}_5$  deposition: one film was deposited at  $\alpha = 0^\circ$  to produce a dense film and the other at  $\alpha = 70^\circ$  to produce a nanoporous film. In similar PEC tests, the  $\text{Ta}_3\text{N}_5$  porous film had a photocurrent  $\sim 3$  times higher than the dense film (Figure 3a). As compared to a dense film of the

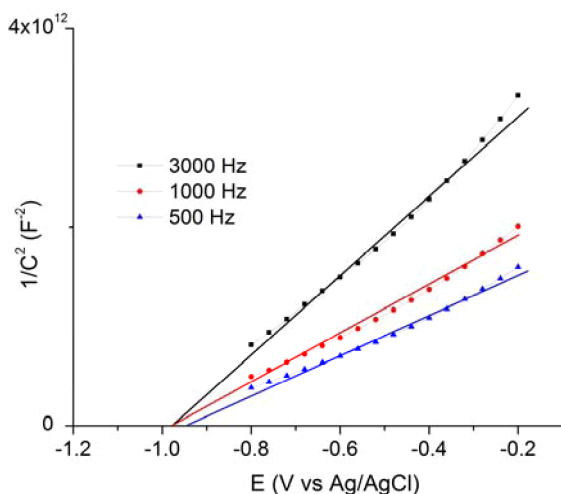


**Figure 3.** (a) Chopped light experiments using full spectrum illumination ( $\sim 73$  mW/cm<sup>2</sup> xenon lamp) in 1 M KOH for 100 nm nanoporous and dense  $\text{Ta}_3\text{N}_5$  films. (b) Chronoamperometry of the nanoporous film under 0.5 V vs Ag/AgCl. (c) Top view and cross-sectional (inset) SEM images of the nanoporous  $\text{Ta}_3\text{N}_5$  film.

same thickness, the nanoporous film has a more open structure that increases the likelihood of the photogenerated holes reaching the solid–liquid interface (shorter transport pathway) rather than recombining with the electrons within the bulk film, which benefits the PEC performance. The contribution from the visible portion of the whole spectrum for a 100 nm nanoporous  $\text{Ta}_3\text{N}_5$  film is estimated to be  $\sim 80\%$  by calculating the ratio between the steady-state photocurrent value from the visible region and from the whole spectrum (white-light illumination) (Figure 3b).

The Ta<sub>3</sub>N<sub>5</sub> film thickness was estimated from a cross-sectional scanning electron microscopy (SEM) image of a Ta<sub>3</sub>N<sub>5</sub> film prepared at 800 °C (Figure 3c) to be ~100 nm, essentially the same as the original RBD Ta<sub>2</sub>O<sub>5</sub> film. This result is somewhat consistent with earlier studies on the pseudomorphic transformation of Ta<sub>2</sub>O<sub>5</sub> into Ta<sub>3</sub>N<sub>5</sub>,<sup>7</sup> although the feathery structure of RBD Ta<sub>2</sub>O<sub>5</sub> is lost after the nitridation process. It is also observed that only the Ta<sub>2</sub>O<sub>5</sub> layer was nitridated and not the Ta substrate underneath.<sup>3,8</sup> This confirms the advantage of using Ta foils as stable substrates for the synthesis of nanostructured Ta<sub>3</sub>N<sub>5</sub> films as well as their utility as an electrical contact for the Ta<sub>3</sub>N<sub>5</sub> electrodes for PEC applications.

A Mott–Schottky (MS) plot (Figure 4) was obtained by EIS measurements using frequencies ranging from 500 to 3000 Hz



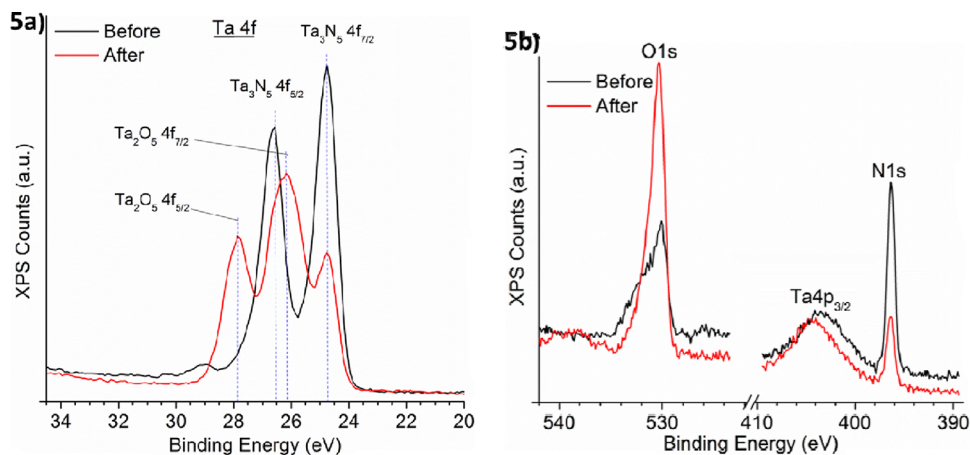
**Figure 4.** MS plots derived from EIS performed at various frequencies in 1 M KOH for a 100 nm dense Ta<sub>3</sub>N<sub>5</sub> film.

in 1 M KOH (pH = 13.6). In this case, a dense film was used to more accurately represent the planar electrode assumed by the model RC circuit to generate the MS plots from the impedance data. The MS plot confirms the n-type behavior of Ta<sub>3</sub>N<sub>5</sub> semiconductor electrodes. By taking the intercept between the linear fit to the MS plot and the potential axis, the flat band potential ( $E_{fb}$ ) of our Ta<sub>3</sub>N<sub>5</sub> films was estimated to be ~−1.05 V vs Ag/AgCl or ~−0.85 V vs NHE at pH = 13.6.

A light chopping experiment near this potential was also carried out to estimate the transient photoanodic current onset potential of this Ta<sub>3</sub>N<sub>5</sub> film, and a similar value was obtained (Figure S7). This finding is consistent with earlier studies reporting the flat band potential of Ta<sub>3</sub>N<sub>5</sub> films and confirms that the conduction band edge of Ta<sub>3</sub>N<sub>5</sub> is more negative than the proton reduction potential (~−0.8 V vs NHE) at pH 13.6,<sup>8,57</sup> making Ta<sub>3</sub>N<sub>5</sub> a theoretically possible material for an unbiased, single PEC water splitting system. However, Figure 2b showed the photocurrent is negligible at ~−0.3 V vs Ag/AgCl, suggesting that in fact few electrons are produced at potentials for water reduction.

**Ta<sub>3</sub>N<sub>5</sub> Film's Photocorrosion and the Cobalt Surface Treatment To Improve the Photostability.** Figure 3b (and later Figure 7a) indicates the fresh Ta<sub>3</sub>N<sub>5</sub> electrode undergoes significant degradation under illumination in 1 M KOH despite its high initial photocurrent. This photocorrosion can be explained by the oxidation of the nitrogen anions on the electrode surface to N<sub>2</sub> by photogenerated holes during the course of light illumination as is often found with oxynitrides with d<sup>0</sup> electronic configuration, for which a small amount of gaseous N<sub>2</sub> can be observed during the initial portions of photocatalytic tests.<sup>59</sup> In comparing the Ta<sub>3</sub>N<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> band edge positions,<sup>57</sup> the conduction band (CB) of Ta5d orbitals is unchanged; however, the valence band (VB) position of Ta<sub>3</sub>N<sub>5</sub> (the top of the VB is the N2p orbital,  $E_{VB} \approx 1.58$  V vs NHE at pH = 0) is much closer to the water oxidation potential than the VB of Ta<sub>2</sub>O<sub>5</sub> (the top of the VB is the O2p orbital,  $E_{VB} \approx 3.39$  V vs NHE at pH = 0). As photogenerated holes are trapped at the VB edge, the more negative (on an electrochemical scale) VB of Ta<sub>3</sub>N<sub>5</sub> as compared to Ta<sub>2</sub>O<sub>5</sub> results in a decrease in the holes' oxidation power, making the water oxidation reaction less preferred,<sup>60</sup> leading to photocorrosion of the film instead. A dark scan of a typical Ta<sub>3</sub>N<sub>5</sub> film (Figure S8) shows the oxidation of the Ta<sub>3</sub>N<sub>5</sub> film happens at a lower potential than the thermodynamic onset potential for the oxidation of water. This implies that photocorrosion will occur unless the water oxidation reaction is made much more favorable kinetically.

XPS measurements were carried out to investigate the surface composition and chemical nature of the Ta<sub>3</sub>N<sub>5</sub> films (all nitridated at 800 °C for 8 h) before and after PEC testing. Two areas of the same Ta<sub>3</sub>N<sub>5</sub> film were analyzed, one with and the



**Figure 5.** XPS spectra of a Ta<sub>3</sub>N<sub>5</sub> film before and after full spectrum illumination for 30 min in 1 M KOH at +0.5 V vs Ag/AgCl. (a) Ta4f; (b) O1s, Ta4p, N1s. The corresponding Ta<sub>2</sub>O<sub>5</sub> film was 100 nm thick and grown at 70° deposition angle by RBD prior to nitridation.

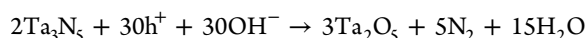
other without exposure to the full spectrum of a xenon lamp ( $\sim 73 \text{ mW/cm}^2$ ) for 30 min in 1 M KOH at +0.5 V vs Ag/AgCl (Figure 5).

The binding energies were calibrated by using the contaminating carbon C1s peak at 284.5 eV as a standard. In Figure 5a, the original  $\text{Ta}_3\text{N}_5$  film has  $\text{Ta}4f_{7/2}$  and  $\text{Ta}4f_{5/2}$  features, which are assigned to  $\text{Ta}^{5+}$  in  $\text{Ta}_3\text{N}_5$ ,<sup>3,57</sup> while the film after light illumination has  $\text{Ta}4f_{7/2}$  and  $\text{Ta}4f_{5/2}$  peaks at 27.8 and 26.2 eV, respectively, corresponding to  $\text{Ta}^{5+}$  in  $\text{Ta}_2\text{O}_5$ .<sup>57,61</sup> Also, after illumination, the  $\text{Ta}4f_{7/2}$  peak (at 24.7 eV, assigned to  $\text{Ta}_3\text{N}_5$ ) remained but showed lower intensity. In Figure 5b, the intensity of the O1s peak increased after illumination while the intensity of the N1s peak decreased. The changes in XPS spectra as well as the change of atomic ratios (O/Ta increased while N/Ta decreased (Table 1)), all indicate the oxidation of

**Table 1. Atomic Ratios of O/Ta, N/Ta, and Co/Ta on the Cobalt-Treated  $\text{Ta}_3\text{N}_5$  Film Surface before and after Full-Spectrum Light Irradiation ( $\sim 73 \text{ mW/cm}^2$ ) for 30 min at +0.5 V vs Ag/AgCl in 1 M KOH**

XPS measurement on film surface	atomic ratios	O/Ta	N/Ta	Co/Ta
untreated $\text{Ta}_3\text{N}_5$ films	before	1.27	1.23	
	after 30 min illumination	2.08	0.42	
cobalt-treated $\text{Ta}_3\text{N}_5$ films	before	1.50	1.92	0.42
	after 30 min illumination	2.09	1.26	0.22

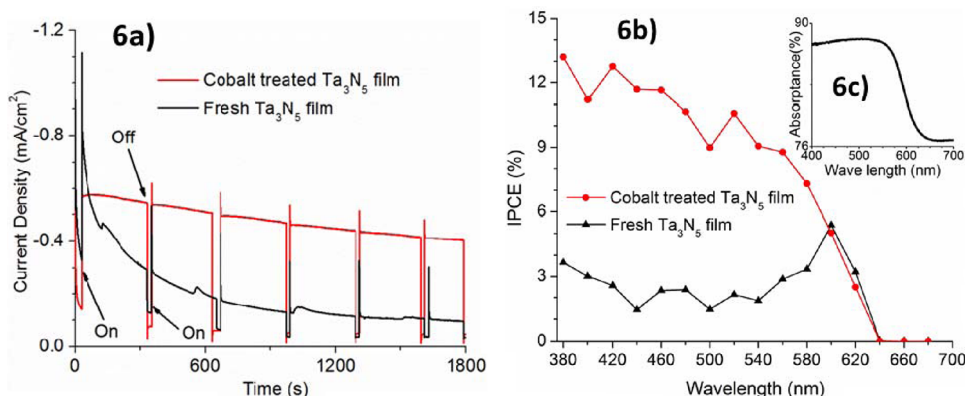
the  $\text{Ta}_3\text{N}_5$  electrode surface by photogenerated holes<sup>3,8</sup> under light irradiation:



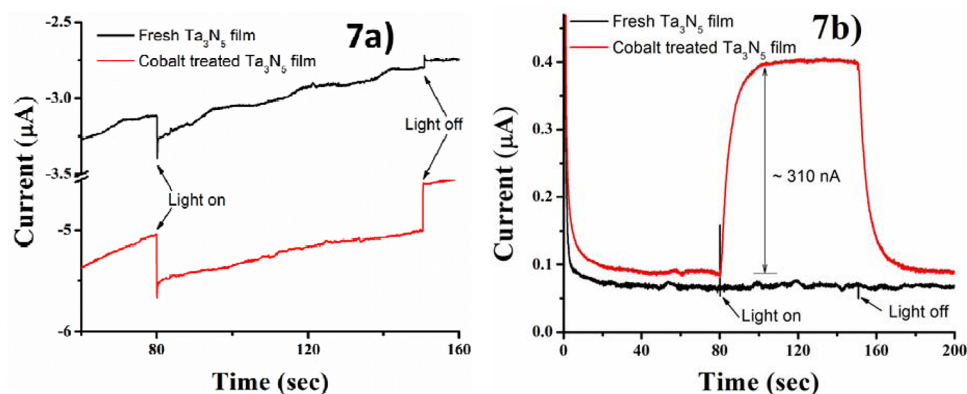
The PEC performance improvement and suppression of the oxidation of  $\text{Ta}_3\text{N}_5$  films under illumination has been studied by loading  $\text{IrO}_2$ <sup>3</sup> or  $\text{Pt}^{12}$  as electrocatalysts. Recently, the use of cobalt-based electrocatalysts to improve the PEC performance of various photoanodes has been given attention because cobalt is inexpensive and abundant.<sup>45–52</sup> In a study by Kay et al.<sup>46</sup> regarding a cobalt surface treatment of  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{Co}^{2+}$  was adsorbed on the  $\text{Fe}_2\text{O}_3$  electrode by simply submerging the electrode in a dilute  $\text{Co}(\text{NO}_3)_2$  aqueous solution.

Here, we attempted a similar approach;  $\text{Co}^{2+}$  was adsorbed on the film surface by submerging the fresh  $\text{Ta}_3\text{N}_5$  films in a 0.1 M  $\text{Co}(\text{NO}_3)_2$  solution for  $\sim 10$  min followed by rinsing with deionized water prior to PEC testing. Figure 6a illustrates the improved stability of the cobalt-treated  $\text{Ta}_3\text{N}_5$  film under visible illumination. The existence of transient spikes during intermittent illumination has also been observed for  $\text{Fe}_2\text{O}_3$  films and can be a result of recombination or the back reaction of photogenerated species (oxy or hydroxyl) on the surface.<sup>62–64</sup> Although the current drops slightly over time, the photocurrent remains clearly higher than that of the untreated  $\text{Ta}_3\text{N}_5$  film. This behavior is consistent with the result for the cobalt treatment of  $\alpha\text{-Fe}_2\text{O}_3$ <sup>46</sup> and suggests that the surface cobalt sites facilitate the water oxidation reaction and inhibit to some extent the film's self-oxidation by photogenerated holes. For the same reason, higher, more stable photocurrents of the cobalt-treated  $\text{Ta}_3\text{N}_5$  films resulted in an IPCE enhancement (Figure 6b). Diffuse reflectance spectroscopy measurements are shown in Figure 6c in which the onset wavelength of the film is  $\sim 620$  nm indicating  $E_g \approx 2.0$  eV. This value is in agreement with earlier studies<sup>3,9</sup> and also with the onset wavelength from IPCE measurements (Figure 6b) and that of pristine  $\text{Ta}_3\text{N}_5$  photoanodes for water oxidation (Figure S5). These IPCE values are similar to those observed by Feng et al.<sup>9</sup> for  $\text{Ta}_3\text{N}_5$  nanotubes. Since stability was not discussed in their work, those values may represent the initial high performance of the films prior to degradation. The applied-bias photon-to-current efficiency (ABPE) was measured to calculate our cell's overall solar energy efficiency using a two-electrode configuration in 1 M KOH. The ABPE values at 0.5 V vs a Pt counter electrode for 100 nm-thick nanoporous  $\text{Ta}_3\text{N}_5$  films before and after the cobalt loading are 0.04% and 0.24%, illustrating the enhancement of the overall PEC performance by the cobalt treatment.

As shown in Table 1, on the cobalt-treated  $\text{Ta}_3\text{N}_5$  film after illumination the O content increased by 39%, while the N content decreased by 34% as compared to the values of 64% and 67%, respectively, for the untreated  $\text{Ta}_3\text{N}_5$  films. This comparison suggests the suppression of  $\text{Ta}_3\text{N}_5$  oxidation by the adsorbed cobalt on the film surface. The cobalt content of the treated films decreased after PEC testing, which might be due to the removal of some excess cobalt during testing or the instability of the cobalt on the surface of the film as mentioned earlier in the study involving the cobalt-treated hematite



**Figure 6.** (a) Amperometric  $i-t$  curve for nanoporous  $\text{Ta}_3\text{N}_5$  films with and without cobalt treatment in 1 M KOH at +0.5 V vs Ag/AgCl under visible illumination. (b) IPCE comparison of  $\text{Ta}_3\text{N}_5$  films with and without cobalt surface treatment in 1 M KOH at +0.2 V vs Ag/AgCl. (c) Absorbance spectrum calculated from the diffuse reflectance of a  $\text{Ta}_3\text{N}_5$  film on Ta foil. The corresponding  $\text{Ta}_2\text{O}_5$  films were 100 nm thick and grown at  $70^\circ$  deposition angle by RBD prior to nitridation. The light source is a  $\sim 73 \text{ mW/cm}^2$  xenon lamp.



**Figure 7.** (a) Photooxidation current of 100 nm nanoporous  $\text{Ta}_3\text{N}_5$  films measured in 0.1 M NaOH at 0.5 V vs Ag/AgCl. The UV–visible irradiation was switched on from 80 to 150 s. (b) Collected current at the Pt RDE tip electrode 30  $\mu\text{m}$  above the  $\text{Ta}_3\text{N}_5$  films. The tip electrode was held at  $-0.4$  V vs Ag/AgCl for the diffusion limited ORR.

photoanode.<sup>47</sup> We note that the current cobalt treatment may be not the final solution for the instability issue; further investigation is needed regarding how to load stable electrocatalysts on the  $\text{Ta}_3\text{N}_5$  surface. Recently, two studies have appeared reporting on the stability and PEC enhancement of  $\text{Ta}_3\text{N}_5$  films by the loading of  $\text{Co}_3\text{O}_4$  via immersing the films in either  $\text{Co}_3\text{O}_4$  nanoparticles<sup>55</sup> or  $\text{Co}(\text{OH})_x$  colloidal solutions followed by 300 °C calcination in air.<sup>52</sup> The presence of  $\text{Co}^{2+}$  on our cobalt-treated  $\text{Ta}_3\text{N}_5$  film is shown in Figure S8.

To further study the  $\text{Ta}_3\text{N}_5$  films' photocorrosion, scanning electrochemical microscopy (SECM) was employed to ascertain the origin of the current generated from  $\text{Ta}_3\text{N}_5$  photoanodes (i.e., water oxidation versus photocorrosion). Details of the experimental setup can be found in the Experimental Section. Briefly, during illumination a fiber optic with a platinum-plated Au ring was placed 30  $\mu\text{m}$  above the  $\text{Ta}_3\text{N}_5$  films to detect generated oxygen by measuring the current at the ring corresponding to the oxygen reduction reaction (ORR). When this current is compared to the oxidation current measured at the  $\text{Ta}_3\text{N}_5$  anode, a collection efficiency can be calculated. The collection efficiency is defined as the ratio of the ring current (collection) and the photo-oxidation current (generation).

As shown in Figure 7a, a photo-oxidation current at the cobalt-treated nanoporous  $\text{Ta}_3\text{N}_5$  film held stable at  $\sim 470$  nA at 0.5 V vs Ag/AgCl. The estimated current density based on the irradiation area ( $4 \times 10^{-4}$   $\text{cm}^2$ ) was  $\sim 1$   $\text{mA}/\text{cm}^2$ , on the same order as that shown in Figure 2b. The photo-oxidation current from the untreated  $\text{Ta}_3\text{N}_5$  film decreased from 150 to 60 nA, while the current collected at the ring electrode was near zero (indicating little or no oxygen evolution). However, for the cobalt-treated film, the generation current was 470 nA, and the collection current was  $\sim 310$  nA. The overall collection efficiency was thus calculated to be 67% for the cobalt-treated film, where the theoretical maximum collection efficiency (for a tip–substrate distance of 30  $\mu\text{m}$ ) was determined to be 87%.<sup>55</sup> Thus, the faradaic efficiency of the cobalt-treated nanoporous  $\text{Ta}_3\text{N}_5$  electrode for water oxidation is  $\sim 77\%$ .

## CONCLUSIONS

Nanostructured  $\text{Ta}_3\text{N}_5$  films have been prepared via reactive ballistic deposition (RBD) followed by a nitridation step over a temperature range of 700–850 °C, for which  $\text{Ta}_3\text{N}_5$  films nitrided at 800 °C showed the highest photocurrents in 1 M KOH. The photocatalytic activity of a nanoporous  $\text{Ta}_3\text{N}_5$  film

prepared at a 70° glancing angle is 3 times higher than a dense film of similar thickness, confirming the advantage of using nanostructured  $\text{Ta}_3\text{N}_5$  for photoelectrochemical water oxidation. Additionally, XPS measurements revealed that the degradation of  $\text{Ta}_3\text{N}_5$  films during water oxidation testing is from the film's oxidation by photogenerated holes. SECM measurements found a faradaic efficiency for water oxidation of  $\sim 77\%$  for cobalt-treated 100 nm nanostructured  $\text{Ta}_3\text{N}_5$  film, confirming the suppression of the films' photocorrosion by this simple cobalt surface treatment.

## ASSOCIATED CONTENT

### Supporting Information

Details of experimental methods, XRD patterns, and the PEC performance of  $\text{Ta}_3\text{N}_5$  films nitrided for 15 h, IPCE measurements, estimation of onset potential, a dark scan of a  $\text{Ta}_3\text{N}_5$  film, and XPS spectra as indicated in the text, as well as cyclic voltammograms of the tip electrodes used in the SECM measurements. 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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## REFERENCES

- (1) Kamat, P. V. *J. Phys. Chem. C* **2007**, *111*, 2834–2860.
- (2) Bard, A. J.; Fox, M. A. *Acc. Chem. Res.* **1995**, *28*, 141–145.

- (3) Yokoyama, D.; Hashiguchi, H.; Maeda, K.; Minegishi, T.; Takata, T.; Abe, R.; Kubota, J.; Domen, K. *Thin Solid Films* **2010**, *519*, 2087–2092.
- (4) Fujishima, A.; Honda, K. *Nature* **1972**, *238*, 37–38.
- (5) Hara, M.; Chiba, E.; Ishikawa, A.; Takata, T.; Kondo, J. N.; Domen, K. *J. Phys. Chem. B* **2003**, *107*, 13441–13445.
- (6) Tabata, M.; Maeda, K.; Higashi, M.; Lu, D.; Takata, T.; Abe, R.; Domen, K. *Langmuir* **2010**, *26*, 9161–9165.
- (7) Lu, D.; Hitoki, G.; Katou, E.; Kondo, J. N.; Hara, M.; Domen, K. *Chem. Mater.* **2004**, *16*, 1603–1605.
- (8) Ishikawa, A.; Takata, T.; Kondo, J. N.; Hara, M.; Domen, K. *J. Phys. Chem. B* **2004**, *108*, 11049–11053.
- (9) Feng, X.; LaTempa, T. J.; Basham, J. I.; Mor, G. K.; Varghese, O. K.; Grimes, C. A. *Nano Lett.* **2010**, *10*, 948–952.
- (10) Murphy, A. B.; Barnes, P. R. F.; Randeniya, L. K.; Plumb, I. C.; Grey, I. E.; Horne, M. D.; Glasscock, J. A. *Int. J. Hydrogen Energy* **2006**, *31*, 1999–2017.
- (11) Lee, Y.; Nukumizu, K.; Watanabe, T.; Takata, T.; Hara, M.; Yoshimura, M.; Domen, K. *Chem. Lett.* **2006**, *35*, 352–353.
- (12) Yuliati, L.; Yang, J.-H.; Wang, X.; Maeda, K.; Takata, T.; Antonietti, M.; Domen, K. *J. Mater. Chem.* **2010**, *20*, 4295–4298.
- (13) Hitoki, G.; Takata, T.; Kondo, J. N.; Hara, M.; Kobayashi, H.; Domen, K. *Chem. Commun.* **2002**, 1698–1699.
- (14) Ho, C.-T.; Low, K.-B.; Klie, R. F.; Maeda, K.; Domen, K.; Meyer, R. J.; Snee, P. T. *J. Phys. Chem. C* **2011**, *115*, 647–652.
- (15) Ho, C.-T.; Low, K.-B.; Jash, P.; Shen, H.; Snee, P. T.; Meyer, R. J. *Chem. Mater.* **2011**, *23*, 4721–4725.
- (16) Higashi, M.; Domen, K.; Abe, R. *Energy Environ. Sci.* **2011**, *4*, 4138–4147.
- (17) Hitoki, G.; Ishikawa, A.; Takata, T.; Kondo, J. N.; Hara, M.; Domen, K. *Chem. Lett.* **2002**, *31*, 736–737.
- (18) Family, F. *J. Stat. Phys.* **1996**, *83*, 1255–1259.
- (19) Abelmann, L.; Lodder, C. *Thin Solid Films* **1997**, *305*, 1–21.
- (20) Robbie, K.; Sit, J. C.; Brett, M. J. *J. Vac. Sci. Technol., B* **1998**, *16*, 1115–1122.
- (21) Hawkeye, M. M.; Brett, M. J. *J. Vac. Sci. Technol., A* **2007**, *25*, 1317–1335.
- (22) Dohnálek, Z.; Kimmel, G. A.; McCready, D. E.; Young, J. S.; Dohnáková, A.; Smith, R. S.; Kay, B. D. *J. Phys. Chem. B* **2002**, *106*, 3526–3529.
- (23) Flaherty, D. W.; Hahn, N. T.; May, R. A.; Berglund, S. P.; Lin, Y.-M.; Stevenson, K. J.; Dohnálek, Z.; Kay, B. D.; Mullins, C. B. *Acc. Chem. Res.* **2012**, *45*, 434–443.
- (24) Kim, J.; Dohnálek, Z.; Kay, B. D. *Surf. Sci.* **2005**, *586*, 137–145.
- (25) Robbie, K.; Friedrich, L. J.; Dew, S. K.; Smy, T.; Brett, M. J. *J. Vac. Sci. Technol., A* **1995**, *13*, 1032–1035.
- (26) Liu, F.; Umlor, M. T.; Shen, L.; Weston, J.; Eads, W.; Barnard, J. A.; Mankey, G. J. *J. Appl. Phys.* **1999**, *85*, 5486–5488.
- (27) Sit, J. C.; Vick, D.; Robbie, K.; Brett, M. J. *J. Mater. Res.* **1999**, *14*, 1197–1199.
- (28) Krause, K. M.; Taschuk, M. T.; Harris, K. D.; Rider, D. A.; Wakefield, N. G.; Sit, J. C.; Buriak, J. M.; Thommes, M.; Brett, M. J. *Langmuir* **2009**, *26*, 4368–4376.
- (29) Colgan, M. J.; Djurfors, B.; Ivey, D. G.; Brett, M. J. *Thin Solid Films* **2004**, *466*, 92–96.
- (30) Flaherty, D. W.; Dohnálek, Z.; Dohnáková, A.; Arey, B. W.; McCready, D. E.; Ponnusamy, N.; Mullins, C. B.; Kay, B. D. *J. Phys. Chem. C* **2007**, *111*, 4765–4773.
- (31) Lin, Y.-M.; Abel, P. R.; Flaherty, D. W.; Wu, J.; Stevenson, K. J.; Heller, A.; Mullins, C. B. *J. Phys. Chem. C* **2011**, *115*, 2585–2591.
- (32) Robbie, K.; Brett, M. J.; Lakhtakia, A. *Nature* **1996**, *384*, 616–616.
- (33) Motohiro, T.; Taga, Y. *Appl. Opt.* **1989**, *28*, 2466–2482.
- (34) Rico, V.; Borrás, A.; Yubero, F.; Espinós, J. P.; Frutos, F.; González-Elipe, A. R. *J. Phys. Chem. C* **2009**, *113*, 3775–3784.
- (35) Messier, R.; Venugopal, V. C.; Sunal, P. D. Origin and evolution of sculptured thin films. The 46th international symposium of the American Vacuum Society, 2000.
- (36) Seto, M. W.; Robbie, K.; Vick, D.; Brett, M. J.; Kuhn, L. J. *Vac. Sci. Technol., B* **1999**, *17*, 2172–2177.
- (37) Flaherty, D. W.; Hahn, N. T.; Ferrer, D.; Engstrom, T. R.; Tanaka, P. L.; Mullins, C. B. *J. Phys. Chem. C* **2009**, *113*, 12742–12752.
- (38) Flaherty, D. W.; May, R. A.; Berglund, S. P.; Stevenson, K. J.; Mullins, C. B. *Chem. Mater.* **2009**, *22*, 319–329.
- (39) May, R. A.; Flaherty, D. W.; Mullins, C. B.; Stevenson, K. J. *J. Phys. Chem. Lett.* **2010**, *1*, 1264–1268.
- (40) Hahn, N. T.; Ye, H.; Flaherty, D. W.; Bard, A. J.; Mullins, C. B. *ACS Nano* **2010**, *4*, 1977–1986.
- (41) Hahn, N. T.; Mullins, C. B. *Chem. Mater.* **2010**, *22*, 6474–6482.
- (42) Chemelewski, W. D.; Hahn, N. T.; Mullins, C. B. *J. Phys. Chem. C* **2012**, *116*, 5255–5261.
- (43) Berglund, S. P.; Flaherty, D. W.; Hahn, N. T.; Bard, A. J.; Mullins, C. B. *J. Phys. Chem. C* **2011**, *115*, 3794–3802.
- (44) Berglund, S. P.; Rettie, A. J. E.; Hoang, S.; Mullins, C. B. *Phys. Chem. Chem. Phys.* **2012**, *14*, 7065–7075.
- (45) Kanan, M. W.; Nocera, D. G. *Science* **2008**, *321*, 1072–1075.
- (46) Kay, A.; Cesar, I.; Gratzel, M. *J. Am. Chem. Soc.* **2006**, *128*, 15714–15721.
- (47) Barroso, M.; Cowan, A. J.; Pendlebury, S. R.; Gratzel, M.; Klug, D. R.; Durrant, J. R. *J. Am. Chem. Soc.* **2011**, *133*, 14868–14871.
- (48) McDonald, K. J.; Choi, K.-S. *Chem. Mater.* **2011**, *23*, 1686–1693.
- (49) Seabold, J. A.; Choi, K.-S. *Chem. Mater.* **2011**, *23*, 1105–1112.
- (50) Ye, H.; Park, H. S.; Bard, A. J. *J. Phys. Chem. C* **2011**, *115*, 12464–12470.
- (51) Cong, Y.; Park, H. S.; Dang, H. X.; Fan, F.-R. F.; Bard, A. J.; Mullins, C. B. *Chem. Mater.* **2012**, *24*, 579–586.
- (52) Liao, M.; Feng, J.; Luo, W.; Wang, Z.; Zhang, J.; Li, Z.; Yu, T.; Zou, Z. *Adv. Funct. Mater.* **2012**, *22*, 3066–3074.
- (53) Bard, A.; Faulkner, L. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; John Wiley & Sons, Inc.: New York, 2001.
- (54) Chen, Z.; Jaramillo, T. F.; Deutsch, T. G.; Kleiman-Shwarstein, A.; Forman, A. J.; Gaillard, N.; Garland, R.; Takanabe, K.; Heske, C.; Sunkara, M.; et al. *J. Mater. Res.* **2010**, *25*, 3–16.
- (55) Cong, Y.; Park, H. S.; Wang, S.; Dang, H. X.; Fan, F.-R. F.; Mullins, C. B.; Bard, A. J. *J. Phys. Chem. C* **2012**, *116*, 14541–14550.
- (56) Banerjee, S.; Mohapatra, S. K.; Misra, M. *Chem. Commun.* **2009**, 7137–7139.
- (57) Chun, W.-J.; Ishikawa, A.; Fujisawa, H.; Takata, T.; Kondo, J. N.; Hara, M.; Kawai, M.; Matsumoto, Y.; Domen, K. *J. Phys. Chem. B* **2003**, *107*, 1798–1803.
- (58) Maeda, K.; Terashima, H.; Kase, K.; Higashi, M.; Tabata, M.; Domen, K. *Bull. Chem. Soc. Jpn.* **2008**, *81*, 927–937.
- (59) Maeda, K.; Domen, K. *MRS Bull.* **2011**, *36*, 25–31.
- (60) Nakamura, R.; Tanaka, T.; Nakato, Y. *J. Phys. Chem. B* **2005**, *109*, 8920–8927.
- (61) Kerrec, O.; Devilliers, D.; Groult, H.; Marcus, P. *Mater. Sci. Eng., B* **1998**, *55*, 134–142.
- (62) Hardee, K. L.; Bard, A. J. *J. Electrochem. Soc.* **1977**, *124*, 215–224.
- (63) Iwanski, P.; Curran, J. S.; Gissler, W.; Memming, R. *J. Electrochem. Soc.* **1981**, *128*, 2128–2133.
- (64) Anderman, M.; Kennedy, J. H. *J. Electrochem. Soc.* **1984**, *131*, 21–26.