

## Supporting Information

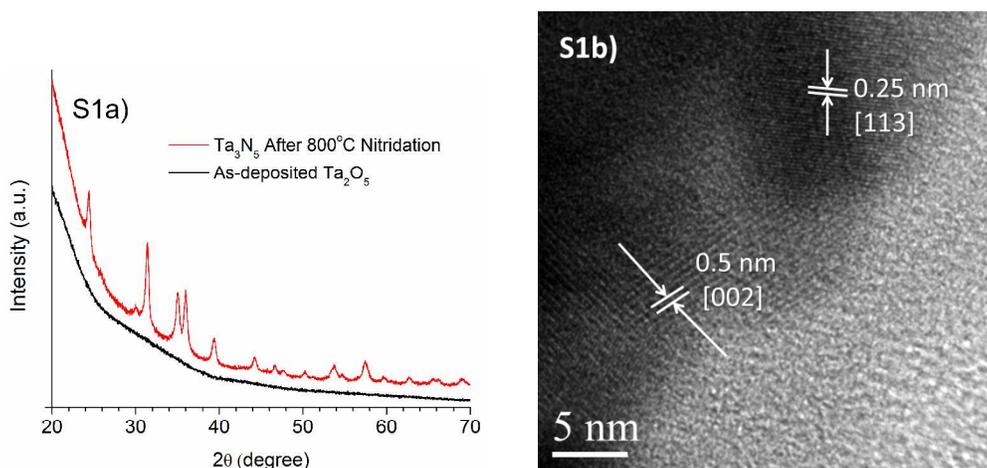
### Nanostructured Ta<sub>3</sub>N<sub>5</sub> Films as Visible-Light Active Photoanodes for Water Oxidation

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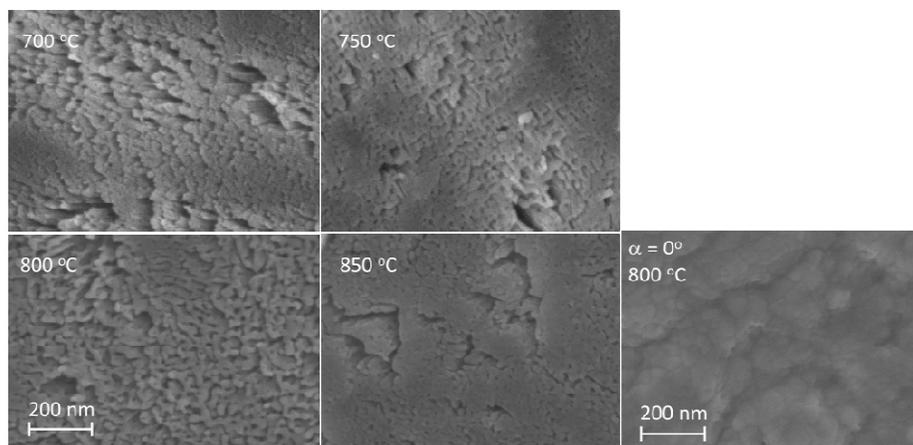
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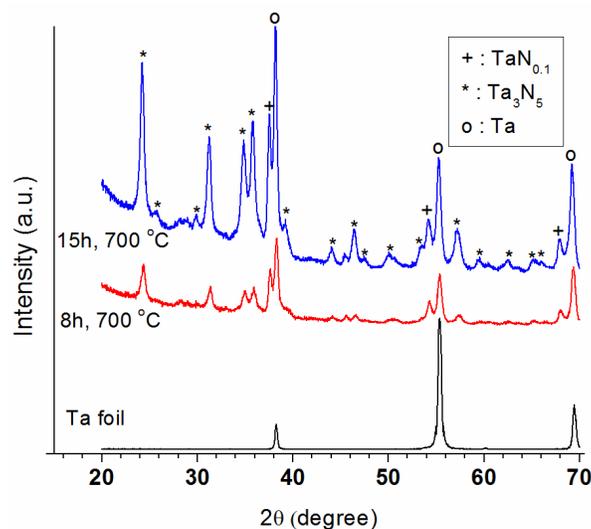
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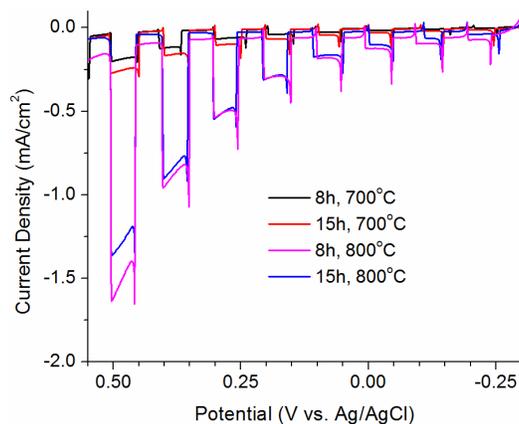
**Figure S1.** a) XRD patterns of as-deposited Ta<sub>2</sub>O<sub>5</sub> on a quartz substrate and the corresponding Ta<sub>3</sub>N<sub>5</sub> films obtained after nitriding for 8 h at 800 °C in a NH<sub>3</sub> gas flow of 100 mL/min. The 100 nm-thick Ta<sub>2</sub>O<sub>5</sub> film was grown by RBD at 70° incidence. All the peaks of the film after nitridation are assigned to that of orthorhombic Ta<sub>3</sub>N<sub>5</sub> phase (PDF #01-072-0813). b) A high resolution transmission electron microscopy (HRTEM) image of a Ta<sub>2</sub>O<sub>5</sub> film after nitridation confirming the formation of crystallized Ta<sub>3</sub>N<sub>5</sub>.



**Figure S2.** Typical morphology of  $\text{Ta}_3\text{N}_5$  films nitrided at various temperatures. All  $\text{Ta}_2\text{O}_5$  films were nitrided for 8 h in an  $\text{NH}_3$  gas flow of 100 mL/min. The scale bar applies to all four images. The dense film (bottom) prepared at normal incidence ( $\alpha = 0^\circ$ ) was added to compare with the similar thick one ( $\alpha = 70^\circ$ ) at 800 °C.

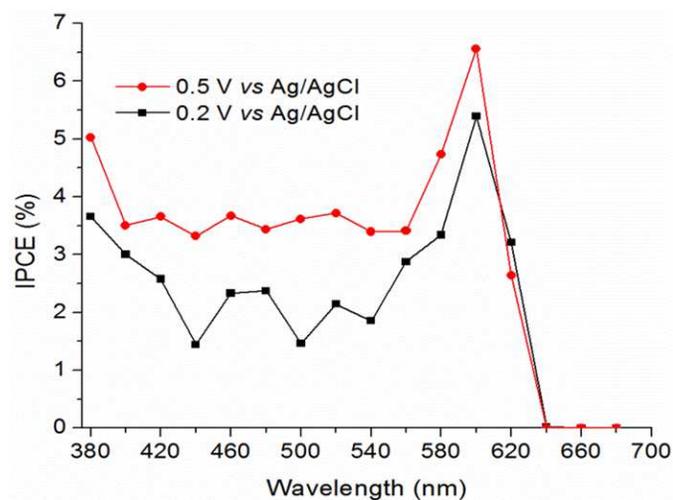


**Figure S3.** XRD patterns (the curves are offset) of  $\text{Ta}_3\text{N}_5$  films nitrided for 8 h and 15 h at 700 °C in a  $\text{NH}_3$  gas flow of 100 mL/min. There are no new peaks associated with lengthening the nitridation duration although the peaks increase in height.



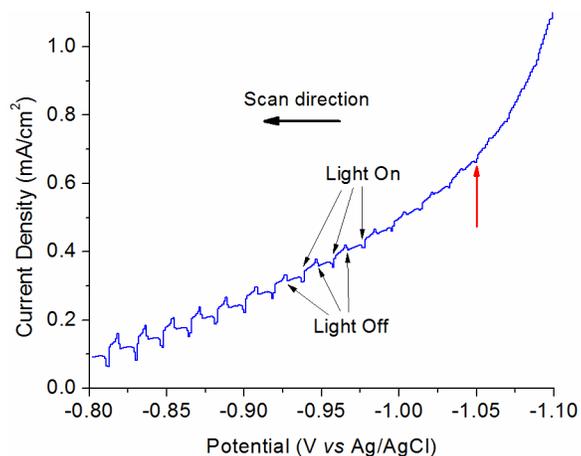
**Figure S4.** PEC comparison of Ta<sub>3</sub>N<sub>5</sub> films nitrified for 8 h and 15 h at 700 °C and 800 °C in a NH<sub>3</sub> gas flow of 100 mL/min. The light source is a ~ 73 mW/cm<sup>2</sup> white-light intensity Xenon lamp.

Ta<sub>3</sub>N<sub>5</sub> films nitrified for a longer duration (15 h instead of 8 h) were prepared at 700 °C and 800 °C, but no new peaks in the XRD patterns were observed compared with the Ta<sub>3</sub>N<sub>5</sub> film that was nitrified for 8 h (Figure S3). Although there was an increase of PEC performance of the film nitrified at 700 °C with 15 h duration, there was no such similar improvement in the case for 800 °C (Figure S4).

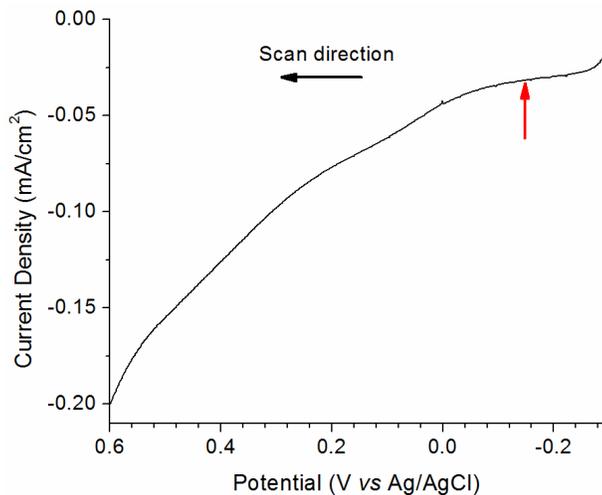


**Figure S5.** The steady-state IPCE spectra for Ta<sub>3</sub>N<sub>5</sub> films taken in 1M KOH solution at various applied potentials.

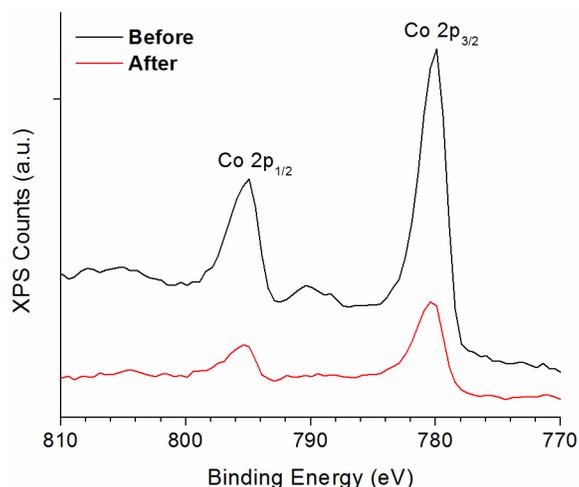
The IPCE values measured from the steady state photocurrent at each wavelength are smaller than one would expect given the photocurrents shown in Figure 2b (main text) at the same potential. Also, the IPCE data is noisy which is likely due to the low intensity of the monochromatic light and relatively large dark current. One interesting aspect of the IPCE spectra is that the IPCE reaches a peak at 600 nm, which is very close to the onset threshold and we don't understand this trend. This behavior is similar to WO<sub>3</sub> films<sup>1</sup> and promising compared to α-Fe<sub>2</sub>O<sub>3</sub>,<sup>2</sup> the IPCE of which drops off long before the onset threshold.



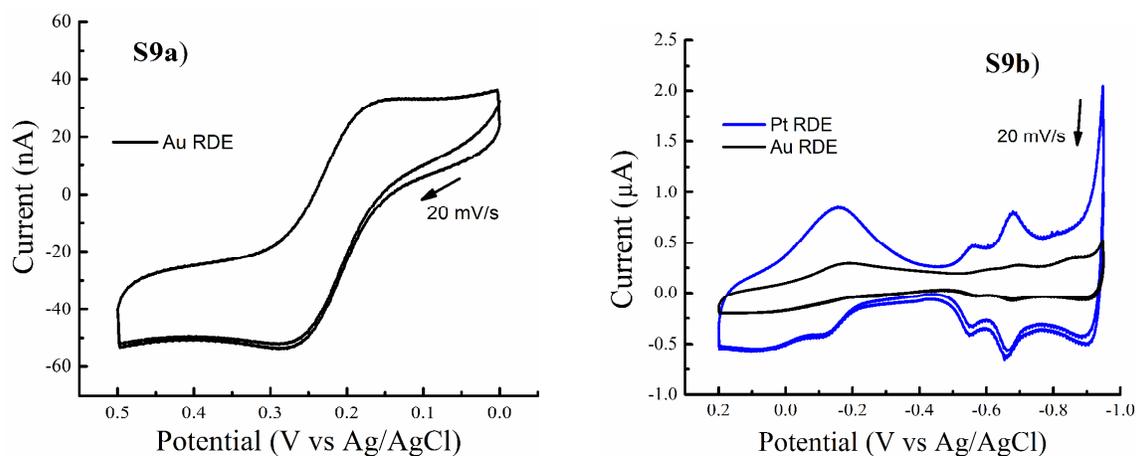
**Figure S6.** Light chopping experiment near -1.0 V vs Ag/AgCl in 1M KOH solution to estimate the onset potential of a dense Ta<sub>3</sub>N<sub>5</sub> film as mentioned in Figure 5 (main text). The red arrow indicates the estimated position of the flat band potential ( $E_{fb} \sim -1.05$  V vs Ag/AgCl), the first anodic current in response to light irradiation.



**Figure S7.** A typical dark scan (no light illumination) of a 100 nm-thick Ta<sub>3</sub>N<sub>5</sub> film nitrided at 800°C in 1M KOH solution. The red arrow indicates the potential where the Ta<sub>3</sub>N<sub>5</sub> film starts to be oxidized which is well before the thermodynamic onset potential for the oxidation of water ( $\sim +0.23$  V vs Ag/AgCl at pH 13.6).



**Figure S8.** XPS spectra (the curves are offset) of the Co 2p region on the cobalt treated Ta<sub>3</sub>N<sub>5</sub> film before and after 30 min full-spectrum illumination ( $\sim 73 \text{ mW/cm}^2$ ) in 1M KOH at +0.5 V vs Ag/AgCl. The binding energy of 796 eV for Co2p<sub>1/2</sub> implies oxidation state of Co<sup>2+</sup>.<sup>3,4</sup>



**Figure S9.** a) Cyclic voltammogram (CV) of a Au ring in 1 mM Ferrocenemethanol and 0.1 KCl solution. b) CV of Au ring and Pt plated Au ring in 0.1 M NaOH solution. Pt was deposited on a Au ring by repeated CVs from 0.2 V to -0.7 V for three scans in 10 mM H<sub>2</sub>PtCl<sub>6</sub> and 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution at a scan rate of 20 mV/s.

## REFERENCES

- (1) Santato, C.; Ulmann, M.; Augustynski, J. *J. Phys. Chem. B* **2001**, *105*, 936-940.
- (2) Hahn, N. T.; Ye, H.; Flaherty, D. W.; Bard, A. J.; Mullins, C. B. *ACS Nano* **2010**, *4*, 1977-1986.
- (3) Foelske, A.; Strehblow, H.-H. *Surf. Interface Anal.* **2002**, *34*, 125-129.
- (4) Foelske, A.; Strehblow, H.-H. *Surf. Interface Anal.* **2000**, *29*, 548-555.