

# **CHEMISTRY**

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### Supporting Information

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#### **Ta<sub>3</sub>N<sub>5</sub> Nanowire Bundles as Visible-Light-Responsive Photoanodes**

**Cheng Hao Wu,<sup>[a]</sup> Christopher Hahn,<sup>[a]</sup> Sher Bahadar Khan,<sup>[b]</sup> Abdullah M. Asiri,<sup>[b]</sup>  
Salem M. Bawaked,<sup>[b]</sup> and Peidong Yang\*<sup>[a, b]</sup>**

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## A. Experimental Details:

*Synthesis of Ta<sub>3</sub>N<sub>5</sub> NWBs:* The synthesis includes two steps: 1) a molten salt synthesis of K<sub>6</sub>Ta<sub>10.8</sub>O<sub>30</sub> micro/nanowires and 2) a conversion from K<sub>6</sub>Ta<sub>10.8</sub>O<sub>30</sub> to Ta<sub>3</sub>N<sub>5</sub> NWBs. The molten salt synthesis was modified from literature.<sup>[1]</sup> In a typical experiment, 100mg Ta<sub>2</sub>O<sub>5</sub> (99.99%, metal basis, < 5 micro, Sigma-Aldrich) powder was mixed with 100mg K<sub>2</sub>CO<sub>3</sub> (ACS, >99.0%, Sigma-Aldrich) and 10g KCl (GR ACS, EMD<sup>TM</sup>) in a mortar. The mixture was grinded for at least 20min to ensure that the reagents were well mixed. The powder mixture was then transferred to an alumina crucible with a lid, which was used to prevent quick evaporation of the molten salt, and the crucible was held at 1175°C in an oven for 5 hours. The tantalate micro/nanowires products were then thoroughly washed in hot DI water and hydrochloric acid to remove all the residual salt. The nitridation conversion was performed in a tube furnace with the tantalate micro/nanowires drop-casted onto a quartz substrate. The furnace was heated to 900°C at a ramping rate of about 2°C/min under NH<sub>3</sub> flow (50 sccm) and was kept at the same temperature for 6 hours. After cooling down in the NH<sub>3</sub> environment, red Ta<sub>3</sub>N<sub>5</sub> NWBs were obtained.

*Characterization of Ta<sub>3</sub>N<sub>5</sub> NWBs:* SEM images were taken using a JEOL JSM-6430F field emission scanning electron microscope. XRD analysis was carried out using a Bruker AXS D8 Advance diffractometer. Absorption spectra were collected using a Shimadzu UV-3010 PC UV-VIS-IR Scanning spectrophotometer equipped with a Shimadzu ISR-3100 integrating sphere. TEM images were taken using a Hitachi H-7650 at 120kV. High-resolution TEM images were taken using a JEOL JEM-2100 LaB<sub>6</sub> microscope at 200kV.

*Gas evolution measurement:* A 450W Xenon lamp coupled with a 400nm long-pass filter and a diffuser was used to provide uniform visible light illumination (about 75mW/cm<sup>2</sup>). For a typical experiment, 5mg of Ta<sub>3</sub>N<sub>5</sub> NWBs was dispersed in 3ml saturated La<sub>2</sub>O<sub>3</sub> aqueous solution (pH ≈ 8) in a glass cell. This electrolyte has the optimal pH condition for the oxygen evolution activity of Ta<sub>3</sub>N<sub>5</sub> based on the pH-dependence study by M. Hara et al.<sup>[2]</sup> The glass cell was purged and filled with ultrapure Ar (99.9999%) gas. The Xenon lamp illuminated the bottom part of the cell, which is made of quartz. 5mg silver acetate was added to the mixture as an electron scavenger for the oxygen evolution measurement. The amount of O<sub>2</sub> evolved under illumination was measured by a micro gas chromatograph. After every 4 hours, the cell was pumped down and refilled with ultrapure Ar. Data from three cycles was recorded.

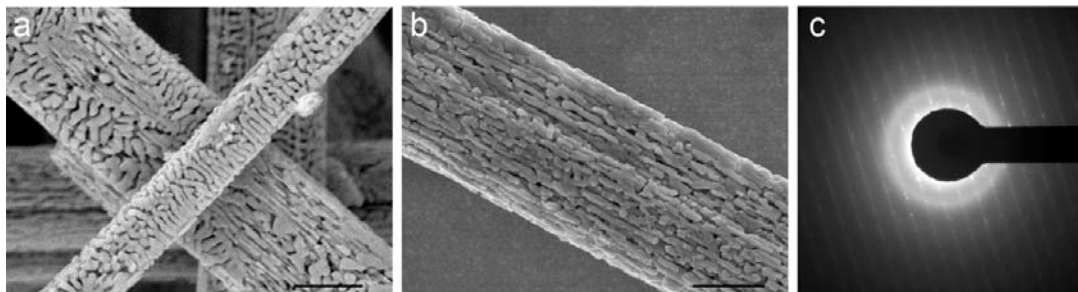
*Fabrication of Ta<sub>3</sub>N<sub>5</sub> NWB electrode:* Ta<sub>3</sub>N<sub>5</sub> NWBs were dispersed in water and drop-casted onto an FTO-coated glass substrate. The electrode was dried in ambient environment and the density of NWBs was about 1 mg/cm<sup>2</sup>. In order to improve the necking between bundles, the NWB electrode was treated as follows: 20μL TaCl<sub>5</sub> methanol solution (10mM) was pipetted onto the electrode, and the electrode was subsequently dried in air. This procedure was then repeated four more times. Finally, the electrode was annealed in NH<sub>3</sub> flow (50sccm) at 500°C for 30min. The Ta<sub>3</sub>N<sub>5</sub> powder electrodes were fabricated by a similar approach.

*IrO<sub>2</sub> catalyst loading:* An IrO<sub>2</sub> colloidal solution was prepared by hydrolysis of Na<sub>2</sub>IrCl<sub>6</sub> in an aqueous basic solution (pH 12) at 343K.<sup>[3]</sup> The Ta<sub>3</sub>N<sub>5</sub> NWB electrode was soaked in the IrO<sub>2</sub> solution for an hour and then annealed in NH<sub>3</sub> flow (50sccm) at 400°C for 30min.

*Photoelectrochemical measurement:* Photocurrent and photovoltage measurements of Ta<sub>3</sub>N<sub>5</sub> NWB electrodes were conducted using a Gamry Reference 600 potentiostat with an Ag/AgCl reference electrode and a Pt counter electrode. A 300W Xenon lamp (Newport, 6528) coupled with an AM 1.5 filter and a diffuser was used to provide uniform illumination

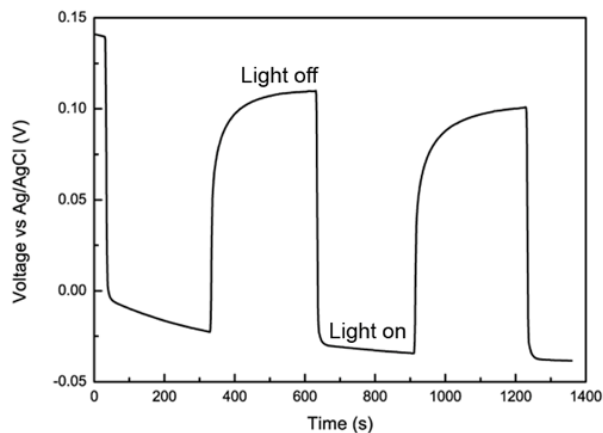
with a power density of  $100\text{mW}/\text{cm}^2$  over the entire electrode. The  $\text{Ta}_3\text{N}_5$  NWB electrode was immersed in  $0.1\text{ M Na}_2\text{SO}_4$  solution ( $\text{pH} \approx 6$ ) and illuminated from the backside through a quartz cuvette.

B. Control experiments with fast, uncontrolled ramp rates:



**Figure S1.** Typical SEM images of  $\text{Ta}_3\text{N}_5$  bundles from control experiments: a) with no ramping control and b) with the ramping rate of  $\sim 15 - \text{C}/\text{min}$ . c) A typical electron diffraction pattern from a bundle of  $\text{Ta}_3\text{N}_5$  nanoparticles/nanorods. Scale bar =  $1\mu\text{m}$  in a) and b).

C. Photovoltage of a  $\text{Ta}_3\text{N}_5$  NWB electrode loaded with  $\text{IrO}_2$  co-catalyst:



**Figure S2.** Open circuit potential change of a  $\text{Ta}_3\text{N}_5$  NWB electrode (loaded with  $\text{IrO}_2$ ).

References:

- [1] C. Lan, J. Gong, Z. Wang, S. Yang, *Mat. Sci. Eng. B-Solid* **2011**, 176, 679–683.
- [2] M. Hara, G. Hitoki, T. Takata, J. Kondo, *Catal. Today* **2003**, 78, 555–560.
- [3] M. Hara, C. Waraksa, T. John, *J. Phys. Chem. A* **2000**, 104, 5275–5280.