Supporting Information

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Ta₃N₅ Nanowire Bundles as Visible-Light-Responsive Photoanodes

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A. Experimental Details:

**Synthesis of Ta₃N₅ NWBs:** The synthesis includes two steps: 1) a molten salt synthesis of K₆Ta₁₀.₈O₃₀ micro/nanowires and 2) a conversion from K₆Ta₁₀.₈O₃₀ to Ta₃N₅ NWBs. The molten salt synthesis was modified from literature. In a typical experiment, 100mg Ta₂O₅ (99.99%, metal basis, < 5 micro, Sigma-Aldrich) powder was mixed with 100mg K₂CO₃ (ACS, >99.0%, Sigma-Aldrich) and 10g KCl (GR ACS, EMD) 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 NH₃ flow (50 sccm) and was kept at the same temperature for 6 hours. After cooling down in the NH₃ environment, red Ta₃N₅ NWBs were obtained.

**Characterization of Ta₃N₅ 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 LaB₆ 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/cm²). For a typical experiment, 5mg of Ta₃N₅ NWBs was dispersed in 3ml saturated La₂O₃ aqueous solution (pH ≈ 8) in a glass cell. This electrolyte has the optimal pH condition for the oxygen evolution activity of Ta₃N₅ based on the pH-dependence study by M. Hara et al. 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 O₂ 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 Ta₃N₅ NWB electrode:** Ta₃N₅ 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/cm². In order to improve the necking between bundles, the NWB electrode was treated as follows: 20μL TaCl₅ 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 NH₃ flow (50sccm) at 500°C for 30min. The Ta₃N₅ powder electrodes were fabricated by a similar approach.

**IrO₂ catalyst loading:** An IrO₂ colloidal solution was prepared by hydrolysis of Na₂IrCl₆ in an aqueous basic solution (pH 12) at 343K. The Ta₃N₅ NWB electrode was soaked in the IrO₂ solution for an hour and then annealed in NH₃ flow (50sccm) at 400°C for 30min.

**Photoelectrochemical measurement:** Photocurrent and photovoltage measurements of Ta₃N₅ 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 100mW/cm² over the entire electrode. The Ta₃N₅ NWB electrode was immersed in 0.1 M Na₂SO₄ solution (pH ≈ 6) and illuminated from the backside through a quartz cuvette.

B. Control experiments with fast, uncontrolled ramp rates:

Figure S1. Typical SEM images of Ta₃N₅ bundles from control experiments: a) with no ramping control and b) with the ramping rate of ~15 °C/min. c) A typical electron diffraction pattern from a bundle of Ta₃N₅ nanoparticles/nanorods. Scale bar = 1μm in a) and b).

C. Photovoltage of a Ta₃N₅ NWB electrode loaded with IrO₂ co-catalyst:

Figure S2. Open circuit potential change of a Ta₃N₅ NWB electrode (loaded with IrO₂).

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