

Supplementary Information

Ta₂O₅ Nanowires: A Novel Synthetic Method and Their Solar Energy Utilization

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Experimental details

Preparation

All the chemicals were purchased commercially and used without further purification. In a typical synthesis of Ta₂O₅ nanowires, 1.0 g of Ta₂O₅ powders (analytically pure, Sinopharm) were dissolved in 10 mL of hydrofluoric acid solution (HF 40%), and kept in oil bath at 110 °C for 2 h. The obtained Ta-fluoro complex solution was cooled to room temperature and the pH value of the solution was tuned to about 9.0 by adding 20 mL of ammonia (analytically pure, 30%). Consequently, the white precipitate was obtained (marked as Am-Ta₂O₅), and was further washed thoroughly with deionized water to

remove NH_4^+ and F^- ions. Then the precipitate was redissolved in 30 mL of the solution containing hydrogen peroxide (analytically pure, 25 – 28%) and ammonia (5:1 by volume) under continuously stirring to get a precursor. For safety reason, the precursor was heated at 60 °C for 1 h to promote decomposition of H_2O_2 , and then was transferred into a Teflon-lined autoclave (50 mL capacity) keeping at 240 °C for 24 h. The resultant precipitate was washed thoroughly with deionized water and ethanol. Finally, the as-prepared product was freeze-dried overnight prior to being characterized.

Nitrogen doped Ta_2O_5 products were prepared by annealing Ta_2O_5 nanowires under NH_3 flow at 700, 750 and 800 °C for 3 h. Commercially purchased Ta_2O_5 powders were also annealed under NH_3 flow for reference.

Characterization

The crystal structure and phase identification of the samples were performed by X-ray diffraction (XRD Bruker D8 ADVANCE) with a monochromatized source of Cu $\text{K}\alpha_1$ radiation ($\lambda = 0.15405$ nm) at 1.6 kW (40 KV, 40 mA). A JEOL JSM-6700F scanning electron microscope (SEM) was used to investigate the morphologies of the samples. For field-emission transmission electron microscopy (TEM) observation, the samples were redispersed in ethanol by ultrasonic treatment and dropped on carbon-copper grids. TEM as well as high-resolution transmission electron microscopy (HRTEM) images were collected by using a JEOL JEM 2100F microscope working at 200 kV. The nitrogen sorption measurements were performed using Micromeritics Tristar 3000 at 77 K, and the specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method. The optical absorption characteristics of the powders were determined via UV-Vis diffuse reflectance spectrum (DRS) on a spectrophotometer (Hitachi U4100) equipped with an integrating sphere accessory.

Photocatalytic tests

The photocatalytic hydrogen generation tests were conducted in a gas-closed circulation system. 100 mg of photocatalyst was dispersed in a solution containing 160 mL of deionized water and 40 mL of methanol as sacrificial reducing agent in a Pyrex cell with a quartz window on the top. The light source was a 500 W Xe lamp covered with a water-cooled quartz jacket. The amount of evolved H_2 was determined with on-line gas chromatography equipped with a thermal conductivity detector (TCD). Nitrogen was purged through the cell before the photocatalytic reaction to remove oxygen.

The photocatalytic contaminant degradation was investigated by monitoring the degradation kinetics of a model pollutant methyl orange (MO) under UV light. A 500 W high pressure mercury lamp was used as the light source, and a refrigerating water circuit was used to keep the reaction temperature at room temperature. The experiments were performed as follows: 250 mg of photocatalyst was added into

a MO solution (250 mL, 10 mg L⁻¹). Before illumination, the suspension was magnetically stirred for 1 h in the dark to reach the adsorption-desorption equilibrium between the MO and the photocatalyst. Then the stirred suspension was exposed to UV irradiation. The concentration of the MO was monitored by tracking the absorbance at 464 nm over time using a Hitachi U-3010 UV-vis spectrophotometer.

DSC Assemblage and Performance Measurement

The Ta₂O₅ pastes were prepared applying a similar method given in the literature [*Thin Solid Films* **2008**, 516, 4613]. The fluorine-doped SnO₂ conducting glass (FTO, Pilkington, 2.2 mm thickness, 15 Ω/□) used as current collector was first cleaned, and the paste was coated on the FTO glass by screen-printing (0.25 cm²), dried at 100 °C for 15 min and then heated at 500 °C for 30 min. After cooling to 80 °C, the electrodes were immersed into dye solution (0.3 mM, N719 dissolved in ethanol, Dyesol) and kept at room temperature for 20-24 hours to assure completely dye uptake. The counter Pt-electrode was obtained by coating with a drop of H₂PtCl₆ solution (5 mM isopropanol solution) on the FTO glass and heated at 400 °C for 10 min. The dye-covered Ta₂O₅ electrode and Pt-counter electrode were assembled into a sandwich type cell. The electrolyte solution was composed of 0.1 M LiI, 0.05 M I₂, 0.3 M 1,2-dimethyl-3-propylimidazolium iodide, and 0.5 M tert-butylpyridine in 3-methoxypropionitrile. Photocurrent density–voltage characteristics (*J–V* curves) were measured on Keithley Model 2440 source meter under AM 1.5 illumination. A 1000W Oriel solar simulator was used as a light source and the power of the light was calibrated to one sun light intensity by using a NREL-calibrated Si cell (Oriel 91150).

Figures

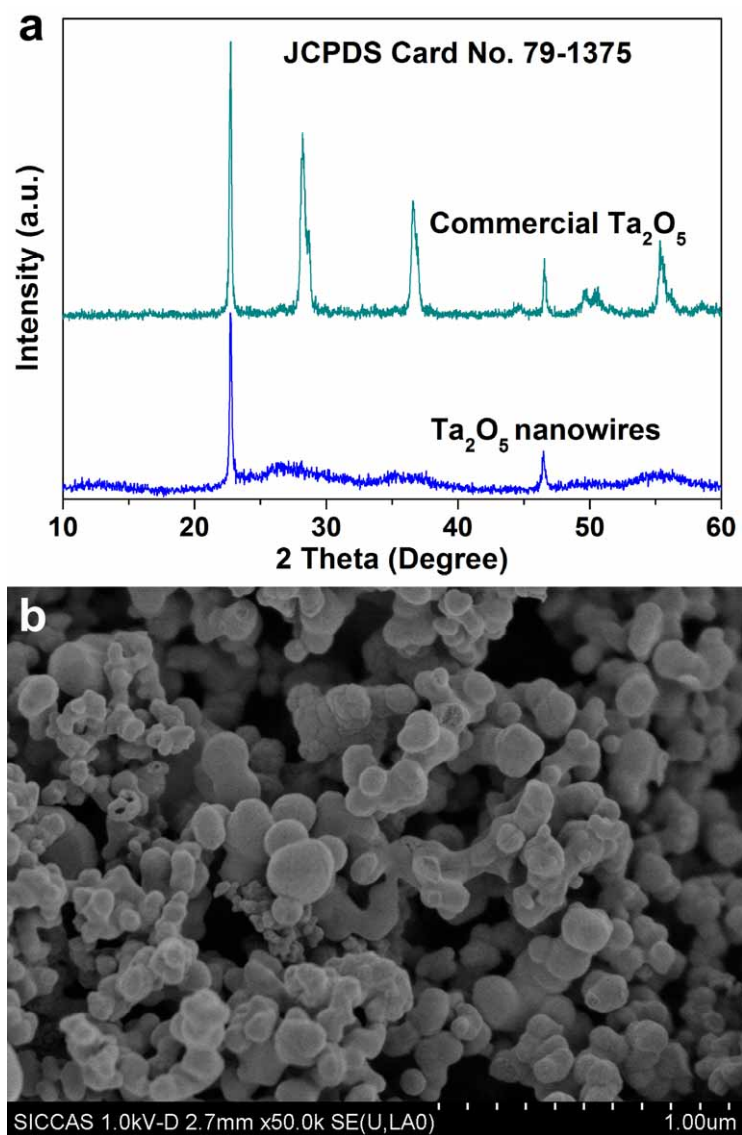


Fig. S1 a) XRD patterns of Ta₂O₅ nanowires and commercial Ta₂O₅, (b) SEM image of commercial Ta₂O₅.

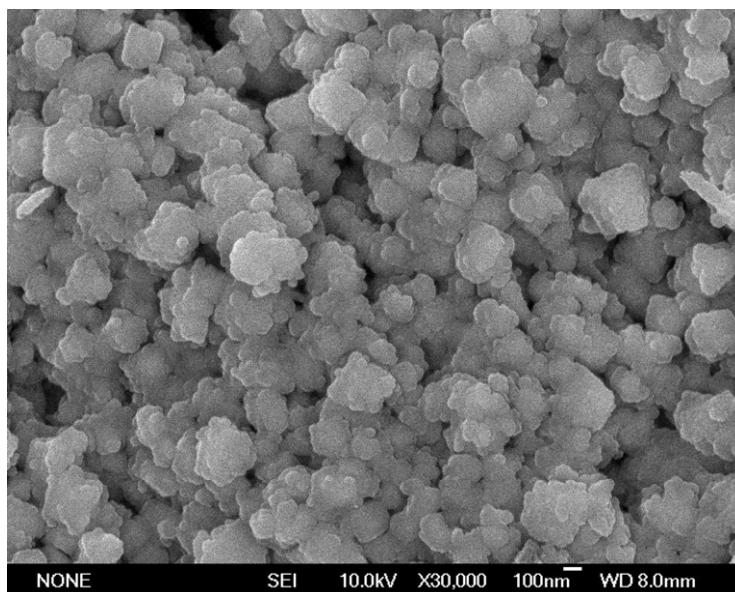


Fig. S2 SEM image of Ta₂O₅ particles prepared by adding HF to the precursor.

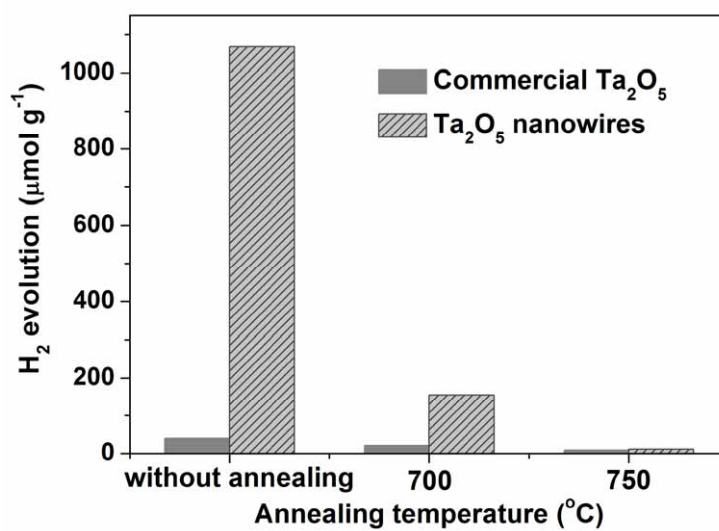


Fig. S3 Photocatalytic H₂ evolution rates of N-doped Ta₂O₅ nanowires and commercial Ta₂O₅ annealed at different temperatures.