Electronic supplementary information for

Efficient Solar Photocatalytic Hydrogen Production by direct Z-Scheme heterojunction

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Experimental section

Materials and reagents

All reagents were analytical grade and used without further purification. Titanous sulfate $Ti(SO_4)_2$, urea, ammonium fluoride (NH_4F), and tantalum oxide (Ta_2O_5) were purchased from Sinopharm Chemical Reagent Co., Ltd. The water used in experiments are deionized water with a resistivity of 18.2 MΩ cm.

Preparation of TiO_2 and Ta_3N_5 nanoparticles

TiO_2 nanoparticles were prepared by hydrothermal method.[1] Firstly, 3.6 g $Ti(SO_4)_2$ was added to 150 mL distilled water under vigorous stirring for 30 min. Then, 0.56 g NH_4F and 1.8 g urea were added to the above solution. After continuing stirring for another 30 min, the mixed solution was subsequently transferred to a 100 mL Teflon-lined stainless steel autoclave. The autoclave was kept at 180 ^oC for 12 hours and then cooled to room temperature naturally. After the reaction, the white precipitate was collected and washed with distilled water and ethanol for three times. The final product was dried in a vacuum oven at 60 ^oC for 10 h.

Ta_3N_5 nanoparticles were synthesized by the nitridation of crystalline tantalum oxide (Ta_2O_5) at high temperatures in the presence of NH_3 gas as nitrogen source. Firstly, 0.1 g Ta_2O_5 powder was placed into a rectangular porcelain boat evenly. Then, the above boat was transferred to a tube furnace and heated at 1223 K for 10 h with the heating rate of 5 K /min and NH_3 flow rate is 350 ml/min. After cooled to room temperature, some bright red particles were obtained.

Preparation of Ta_3N_5/TiO_2 heterojunctions

The Ta_3N_5/TiO_2 composite was prepared according to the previous method *via* a facile hydrothermal method.[1] Typically, 0.3 g of TiO_2 and a certain amount of Ta_3N_5 were dispersed in 50 and 15 mL absolute ethanol with vigorous stirring for 30 min, respectively. Then, the Ta_3N_5 suspension was slowly added dropwise to the above TiO_2 solution under continuous ultra-sonication, followed by magnetic stirring for 6 h. Subsequently, the obtained mixture was transferred to a 100 mL Teflon-lined autoclave, which was sealed and heated at 160 °C for 6 h. After cooled to room temperature naturally, the reddish solid was collected by centrifugation and dried at 60 °C for 4 h under vacuum conditions. Finally, the Ta_3N_5/TiO_2 composites with different Ta_3N_5 molar fractions (1%, 3%, 5%, and 10%) were prepared, which could be denoted as X% Ta_3N_5/TiO_2, based on the molar ratio X of Ta_3N_5 and TiO_2.

Characterization

X-ray diffraction (XRD) measurement was carried out by using the PANalytical X'pert MPD Pro diffractometer, with Cu K_α irradiation (λ = 1.5406 Å). Optical properties were determined by the Hitachi double-beam U-4100 UV–vis-near-IR spectrophotometer (Cary 5000, Agilent, USA) and equipped with an integrating sphere, in which $BaSO_4$ acted as the background. X-ray photo-electron spectroscopy (XPS) was measured with a Kratos spectrometer (AXIS Ultra DLD) equipped with a standard and monochromatic Al Kα line as the excitation source (hν = 1486.6 eV). The C1s peak at 284.8 eV of adventitious carbon was used for calibration. The crystallite morphology was determined by using a JEOL 7800F scanning electron microscopy (SEM) and FEI Tecnai G2 F30 S-Twin transmission electron microscope (TEM) attached with an OXFORD MAX-80 energy-dispersive X-ray detector (EDX). The element distribution and characteristics was analyzed by energy-dispersive spectrometry (EDS), using an energy-dispersive X-ray spectrometer attached to the FE-TEM instrument. Electrochemical test was conducted on a CHI600D electrochemical analyzer (Chenhua Instruments Co.,Shanghai), which was employed to measure the transient photocurrent response, electrochemical impedance spectra (EIS), the polarization curve, and Mott-Schottky (MS) plot. Steady-state photo-luminescence (PL) properties were characterized at room temperature, using a time-resolved PTIQM-4 fluorescence spectrophotometer at an excitation wavelength of 370 nm.

Photocatalytic test

The photocatalyst activity test was carried out on a gas-closed system with a side irradiation Pyrex cell. The light source was the Xe-300BF Xenon lamp with 300 W from the Perfect Light. Before the irradiation, 50 mg catalyst and calculated amount of H_2PtCl_6 aqueous solution (1.0 wt%) was dissolved into the 80 ml triethanolamine (20 wt%) and deionized water solution. With ultrasonic treatment for 15 minutes, this homogeneous solution was transferred to the quartz glass reactor. The area of unilateral plane is circular plate with an area of 2 cm in diameteris. After being evacuated by Ar gas for over 15 min, the photocatalysts were irradiated by different wavelength light (λ ≥ 420 nm, λ ≤ 420 nm or full spectrum) through a cutoff filter. The reaction temperature was controlled by the ongoing cooling water system around the battle. In this study, the amount of hydrogen production was determined by drainage method. All the sample test are taken place in the same condition and operation. Apparent quantum efficiency (AQE) was measured using Y-nm band-pass filters (Y=330, 350, 380, 420, 450, 480, 500, 540, 600 nm) and an irradiation meter and were defined by the following equation: [2]

$$AQE\ (\%) = 2N_{H_2}/N_P \qquad (1)$$

Here, N_{H_2} is the number of evolved H_2 molecules; N_P stands for the number of incident photons.

Hydroxyl radical analysis

The hydroxyl radicals (·OH) in hydrogen reaction was detected by the electron paramagnetic resonance (EPR) and photo-luminescence (PL) two methods. [3,4] EPR of radicals trapped by 5, 5-dimethyl-1- pyrroline N-oxide (DMPO) was recorded on a Brucker EPR A200 spectrometer with the largest magnetic field intensity can reach 14500G. The samples containing 0.1 mg/mL 5% Ta_3N_5/TiO_2 (Anatase) and 0.05 M DMPO were vacuumed following by ventilated with argon for 3 times. After that, the samples were introduced into home-made quartz tube inside the microwave cavity and illuminated with a 300 W Xe lamp, where the distance between the sample and the lamp was fixed to 1.0 m. PL of radicals trapped by terephthalic acid was tested by the followed process: 50 mg photocatalysts were involved into 100 mL mixture solution containing 20 mM NaOH and 6 mM terephthalic acid, followed by stirring in dark for 30 min to ensure the adsorption/desorption equilibrium. After being evacuated with Ar gas for over 20 min to remove dissolved oxygen, the suspension was illuminated by a 300 W Xeon lamp with different time. Within a specific time interval, 4 mL of the suspension was extracted from reactor via injection syringe with a long needle and then centrifuged for fluorescence spectroscopy measurements.

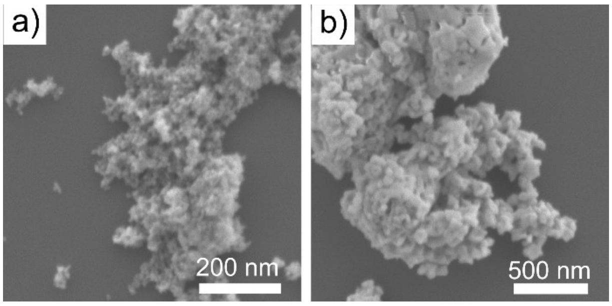

Figure S1. SEM images of (a) TiO_2 and (b) Ta_3N_5.

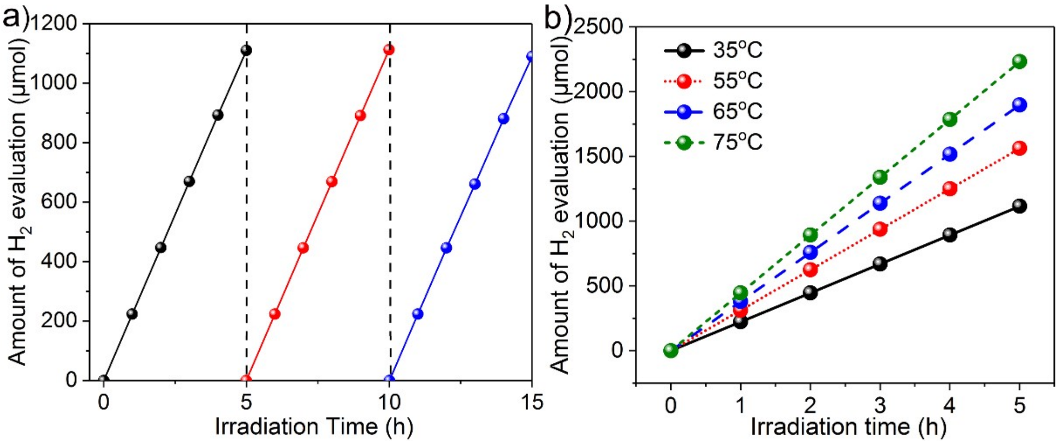

Figure S2. Time-course photocatalytic hydrogen production at (a) 35 °C and (b) different temperatures over 5% Ta_3N_5/TiO_2 heterojunction.

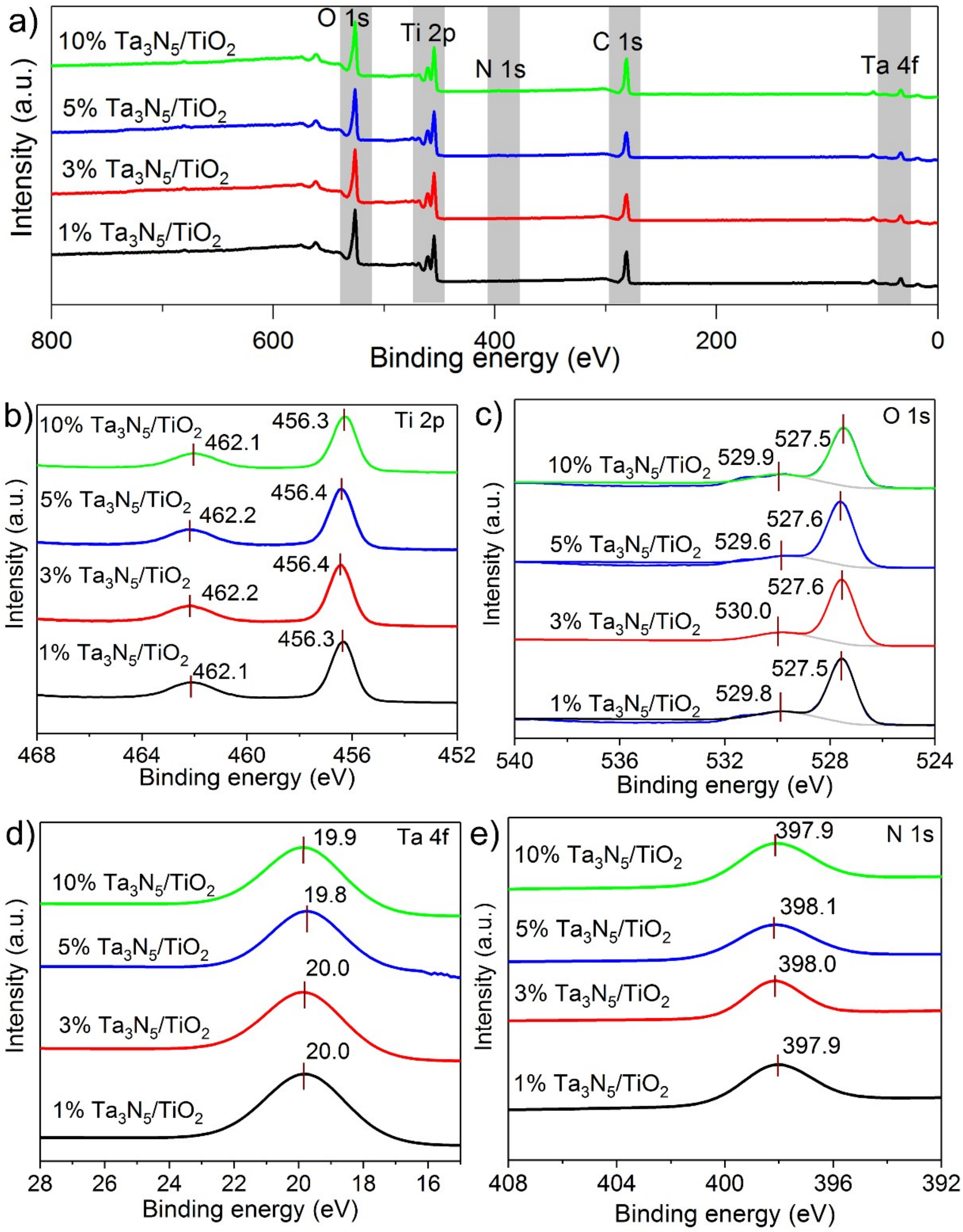

Figure S3. (a) XPS survey spectra Ta_3N_5/TiO_2 composites and (b-e) the corresponding high-solution XPS scans of (b) Ti, (c) O, (d) Ta, (e) N in the composites.

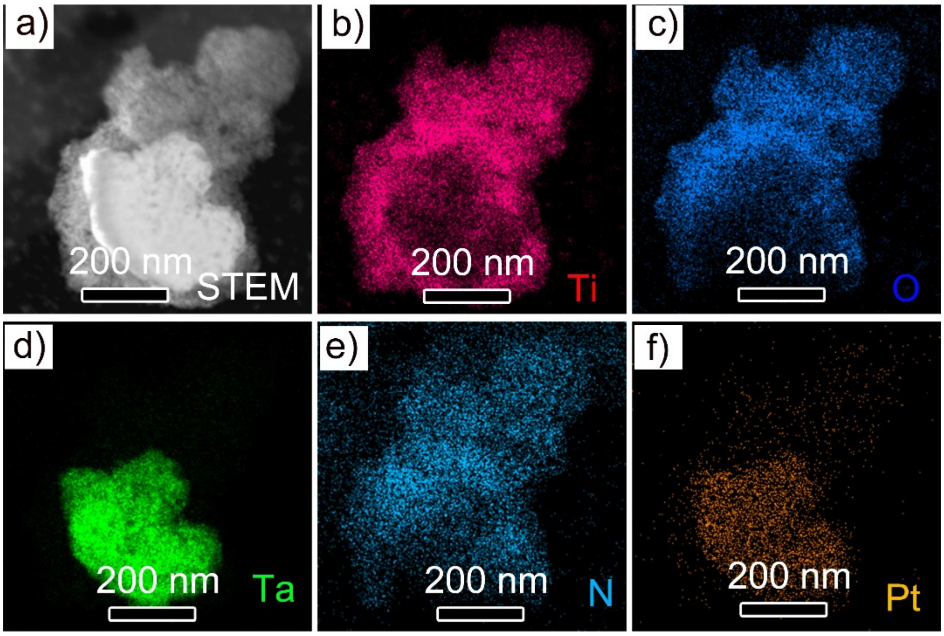

Figure S4. STEM and corresponding elemental mapping images of 5% Ta_3N_5/TiO_2 heterojunction under full spectral irradiation.

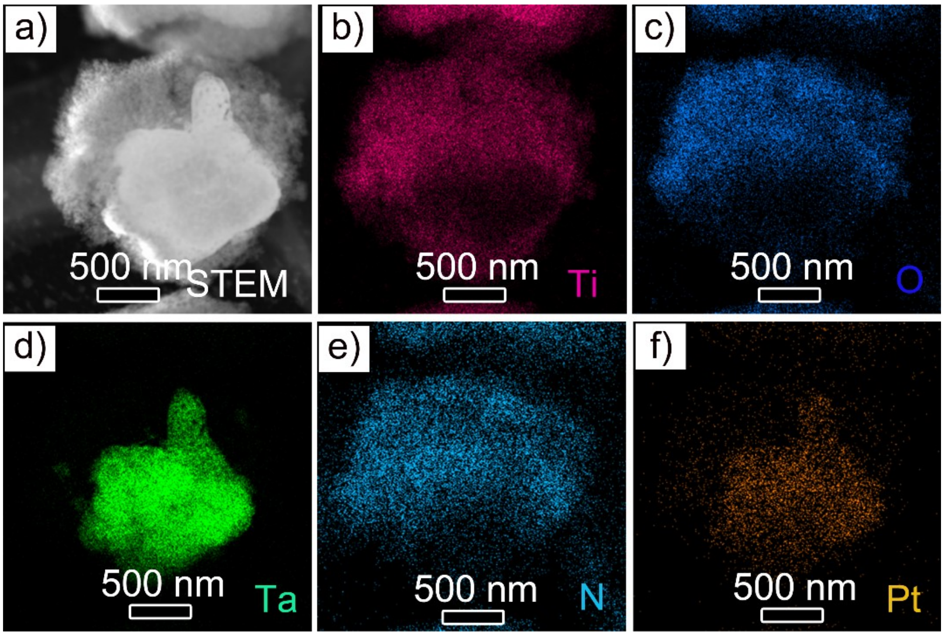

Figure S5. STEM and corresponding elemental mapping images of 5% Ta_3N_5/TiO_2 heterojunction under UV light irradiation.

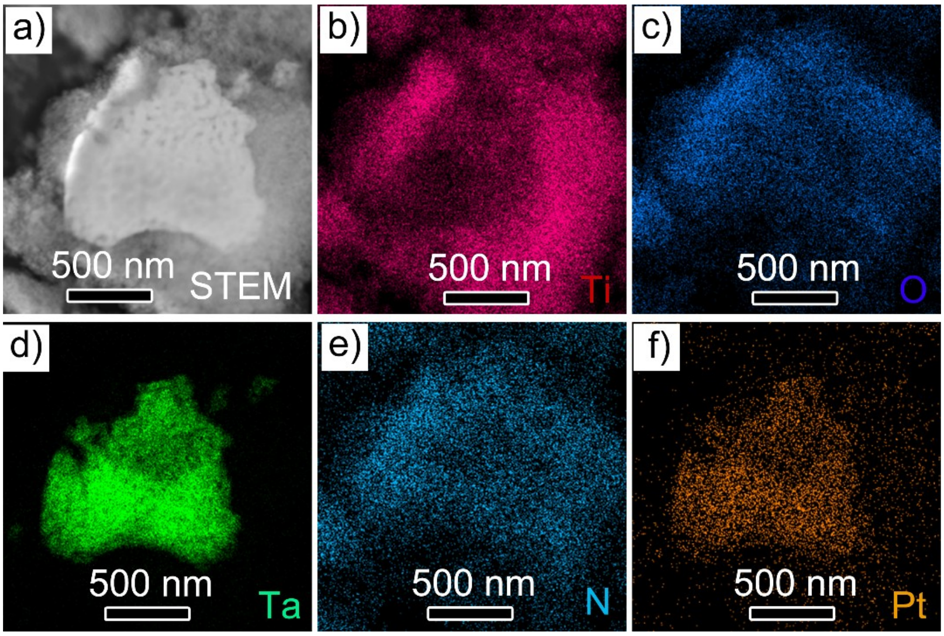

Figure S6. STEM and corresponding elemental mapping images of 5% Ta_3N_5/TiO_2 heterojunction under visible light irradiation.

References

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