

Supporting Information

Interfacial Ti≡N Bonding of g-C₃N₄/TiH_{1.92} Type-II Heterojunctions Photocatalyst Significantly Enhanced Photocatalytic Hydrogen Evolution from Water Splitting†

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Experimental Section

Materials

The primary reagents used in this study, including urea (≥ 99%), ethanol (EtOH ≥ 99.7%) and triethanolamine (TEOA), were purchased from Sinopharm Chemical Reagent Co., LTD. Titanium hydride (99%) and N-methyl pyrrolidone (NMP 99%) were purchased from Aladdin reagent CO., Ltd. All chemicals were analytical grades and used without further purification. Moreover, deionized water was used during the material synthesis while conducting experiments purified by the Direct-Q 3UV water purification system (Milipore Corp., France).

Synthesis of Exfoliated TiH_{1.92} Nanoparticles

200 mg of commercial TiH₂ powder was put into 30 ml of N-methyl pyrrolidone (NMP). This mixture was treated with ultrasonication for 2 hours (ultrasonic Homogenizer, temperature: ~15 °C, power: ~100 W). TiH_{1.92} nanoparticles obtained after ultrasonication treatment were further purified by centrifugation (5 mins, 12 k speed/min) and washed with anhydrous ethanol and distilled water for several times.

Synthesis of g-C₃N₄/TiH_{1.92} Photocatalyst

In a typical synthetic procedure, graphitic carbon nitride (g-C₃N₄) was fabricated by pyrolyzing, urea (20g) at 550 °C for 4 hours. g-C₃N₄ and exfoliated TiH_{1.92} NPs with different weight-ratios of exfoliated TiH_{1.92} of 1 wt%, 2 wt%, 3 wt%, 4 wt% and 5 wt%. were added into 20 ml ethanol absolute. After that, the mixed suspension was dispersed ultrasonically (Kunshan ultrasonic instruments Co., Ltd) for 20 minutes and dried by keeping it in a water bath at 80 °C for 1 hour under continuous vigorous stirring. When all the solvent was evaporated, the resultant dried solid was cooled down at room temperature. The obtained precursors were calcined to obtain g-C₃N₄/TiH_{1.92} composites in the tube furnace at 350 °C (Ningbo Scieitz Biotechnology Co., Ltd) for 1 hour at a ramp rate of 5 °C/min under an Ar-gas flow (Argon gas purity: 99.99%). Samples of C₃N₄/TiH_{1.92} with different TiH_{1.92} weight ratios of 1 wt%, 2 wt%, 3 wt%, 4 wt%

and 5 wt% were named as CN/TiH_x-1, CN/TiH_x-2, CN/TiH_x-3, CN/TiH_x-4 and CN/TiH_x-5, ($x = 1.92$), respectively.

Photocatalytic Experiments

The photocatalytic water-splitting experiments were conducted in a sealed pyrex top-irradiation reaction vessel linked with a closed glass circulation system. Typically, 50 mg of catalyst was dispersed in 100 ml solution (90 ml water and 10 ml triethanolamine as a sacrificial agent). Then, 1 wt% Pt was deposited over the surface of catalysts via in-situ photodeposition method using H₂PtCl₆·6H₂O. Prior to irradiation with 300 W xenon-lamp, the sealed reaction system was evacuated for approximately 30 minutes to degassed completely to ensure anaerobic conditions. After that, the system was irradiated under visible light using an appropriate cut-off filter to control the wavelength of incident light ($\lambda \geq 420$ nm). During the whole reaction, the temperature of the solution was maintained at 10 °C by the circulation of cooling ethylene glycol. An online gas chromatography (GC1120, Shanghai Sunny Hengping Limited, HTCD, N₂ carrier gas) was equipped to the reaction system to detect the produced gas after the photocatalytic reaction. After the photocatalytic reaction, the catalyst was separated from the reaction solution for further use and characterization.

Characterization

X-ray diffraction (XRD) patterns were obtained by Rigaku X-ray diffractometer (MXPAHF, Japan) with Cu K α irradiation ($\lambda = 1.541$ Å), with 40 kV operating voltage and 200 mA current. XRD data were collected at a diffraction angle of 10-80° with a scanning speed of 10°/min. The Fourier transform infrared (FT-IR) spectra were recorded by using Nicolet Nexux spectrometer with KBr pellets. Transmission electron microscopy (TEM) images were measured on HITACHI H-7650 transmission electron microscope operated at 100 kV. HAADF-STEM images were carried out on JEOL-2010, (Japan) at accelerating voltage of 200 kV. UV-vis diffuse reflectance spectra of different photocatalysts were taken at a UV-vis spectrophotometer (Shimadzu, Model 2501 PC), and BaSO₄ (spectrum pure) was used as reference material. The time-resolved photoluminescence spectra were recorded at Laser Strob time-resolved spectrofluorometer (Photon Technology International (Canada) Inc.) with an USHIO xenon lamp source and a 914-photomultiplier detection system, a GL-302 high-resolution dye laser (lifetimes from 100 ps to 50 ms, excited by a nitrogen laser). While the spectroscopy measurement wavelength range was: 250-1700 nm; fluorescence lifetime measurement 100 ps to 10 ms (wavelength: 240-1700 nm), sample cryogenic system minimum temperature 10 K. Thermogravimetric analysis (TGA) was performed by NETZSCH TG 209F1 Libra analyzer. The steady-state photoluminescence (PL) spectra were obtained at room temperature excited by using a fluorescence spectrophotometer (JY Fluorolog-3-Tau) with an incident light of 370 nm. X-ray photoelectron spectroscopy (XPS) was carried out by using a Perkin-Elmer RBD upgraded PHI-5000C ESCA system.

Table S1. Comparison of photocatalytic hydrogen evolution rate with previous literature.

Material	Synthetic Method	Co-Catalyst	H ₂ Production ($\mu\text{mol h}^{-1} \text{g}^{-1}$)	Ref.
g-C ₃ N ₄ -TiO ₂	Photodeposition, Hydrothermal	TEOA/3 wt% Pt	1042	1
O-g-C ₃ N ₄ -TiO ₂	Photo-deposition, Hydrothermal	TEOA/3 wt% Pt	566	2
g-C ₃ N ₄ -TiO ₂	Heat treatment, Electro- spinning	TEOA/1 wt% Au, Ag or Pt	294	3
g-C ₃ N ₄ -NPBIm	Hydrothermal	TEOA/1 wt% Pt	939.4	4
g-C ₃ N ₄ -CoO	Hydrothermal	TEOA/3 wt% Pt	651	5
g-C ₃ N ₄ -CoFe ₂ O ₃	Hydrothermal	TEOA/1wt% Pt	186.1	6
g-C ₃ N ₄ -TiH _{1.92}	Hydrothermal	TEOA/1 wt% Pt	1511	This work

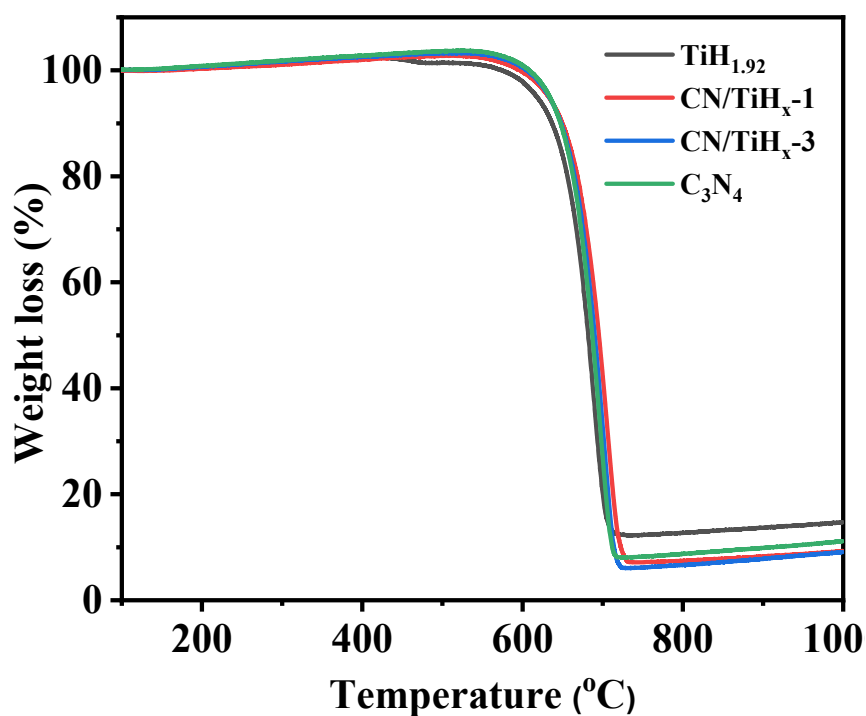


Fig. S1 Thermogravimetric analysis of TiH_{1.92}, g-C₃N₄ and CN/TiH_x samples.

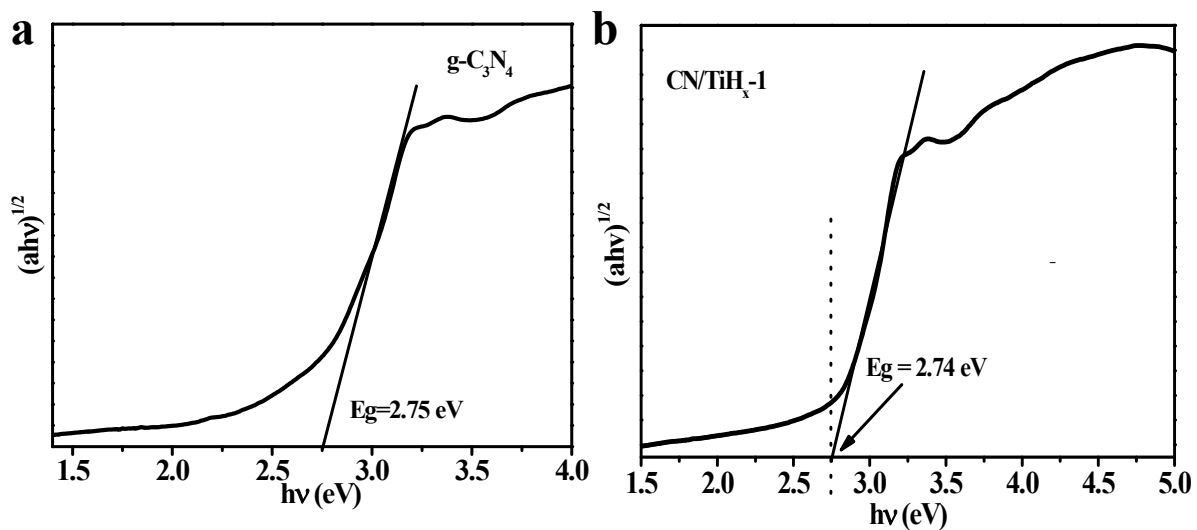


Fig. S2. Band gaps of $g\text{-C}_3\text{N}_4$ (a) and $\text{CN/TiH}_x\text{-1}$ (b).

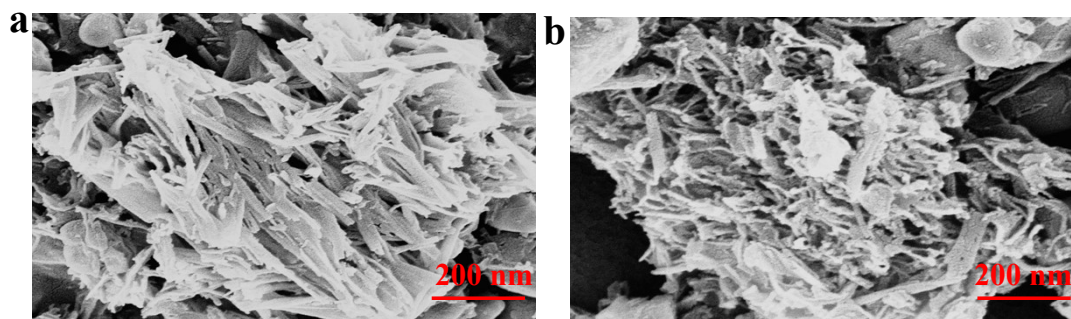


Fig. S3. SEM images of $g\text{-C}_3\text{N}_4$ (a) and $\text{CN/TiH}_x\text{-1}$ (b).

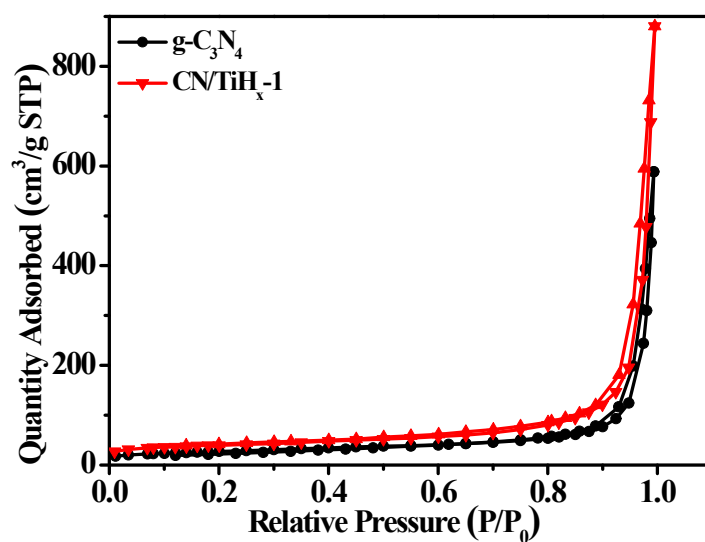


Fig. S4. Nitrogen adsorption-desorption isotherm of $g\text{-C}_3\text{N}_4$ and CN/TiH_x .

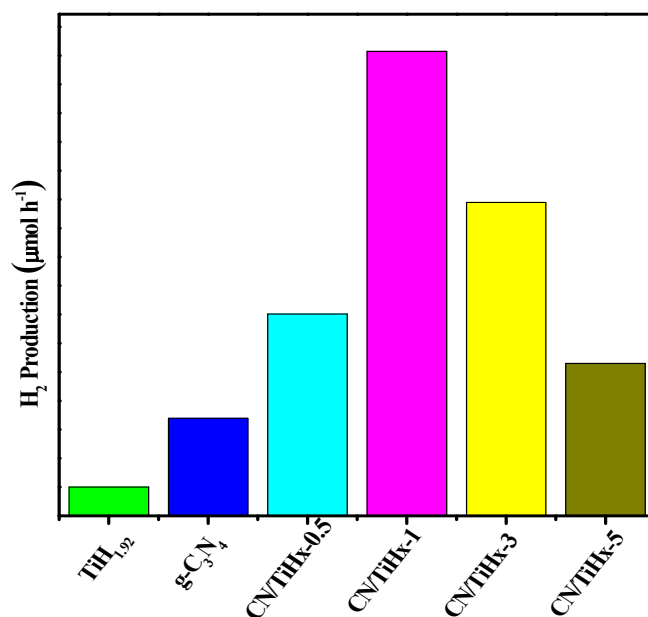


Fig. S5. Hydrogen evolution rates of TiH_{1.92}, C₃N₄ and CN/TiH_x samples.

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